Special Symposium in Honour of Professor Bernard Kirtman

Organizers

Benoit Champagne
Facultes Universitaire Notre-Dame de la Paix, Rue de Bruxelles, 5000 Namur, Belgium
benoit.champagne@fundp.ac.be

Feng Long Gu
Dept. Materials Science, Kyushu University, Kasuga, Fukuoka 816-8580
Japan
gu@cube.kyushu-u.ac.jp

Josep M. Luis
Department of Chemistry, University of Girona, 17071 Girona, Catalonia
Spain
josepm.luis@udg.es

Michael Springborg
Department of Chemistry, University of Saarland, 66123 Saarbruecken
Germany
m.springborg@mx.uni-saarland.de
Special Symposium in Honour of Professor Bernard Kirtman

This symposium is organized in honour of Bernie KIRTMAN, a scientist who has contributed substantially to several domains of theoretical chemistry, encompassing perturbation theory, ro-vibrational Hamiltonians, nonlinear optics of oligomers and other pi-conjugated systems, surface modelling, vibrational hyperpolarizabilities, band structure calculations, and search of better exchange-correlation functionals for treating extended systems in electric fields. The work of Bernie Kirtman has had strong impact on the previous ICCMSE conferences and has been presented at most of those conferences, either by Bernie Kirtman in person or by some of his many collaborators. This symposium will therefore address these different, though intertwined, topics by inviting his collaborators as well as other key scientists in the field.

General information on the Symposium is also available in http://www.uni-saarland.de/fak8/springborg/iccmse_09.html.

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m.springborg@mx.uni-saarland.de
Preface

During a number of years, Bernie Kirtman has been an inspiring and friendly scientific collaborator and friend. Many scientists, including the four listed below, have enjoyed the scientific interactions with Bernie. Although Bernie has been working on a larger variety of scientific questions within computational / theoretical chemistry, very many of his works are devoted to related scientific issues: structural, vibrational, and electronic responses; large systems; conjugated molecules and polymers; density-functional theory. Therefore, we, the four organizers of this symposium, felt that it was relevant, interesting, and adequate to try to organize a scientific symposium centered around those issues and, simultaneously, with earlier and present collaborators of Bernie forming a major (but not exclusive) part of the attendees. Besides making it possible to honor the scientific achievements of Bernie, interesting scientific presentations and discussions would result.

Bernie has several times attended the International Conference on Computational Methods in Sciences and Engineering (ICCMSE). This series of conferences, organized by Theodore Simos and George Maroulis, offers a very pleasant frame, both with respect to science and with respect to the surroundings, for holding a symposium with the aim outlined above. Therefore, it was decided to make use of the offer of Theodore Simos and George Maroulis to organize a symposium to the honor of Bernie Kirtman at the ICCMSE 2009. Also the time of the year (September / October) and the place (the island of Rhodes, Greece) would help making the symposium a pleasant event.

Despite all the efforts we, the scientific colleagues of Bernie, have made over the years to influence the life of Bernie, nobody has been as important as Tybie, the wife of Bernie, who always has made it possible that Bernie’s scientific devotion was fruitful. A significant part of our appreciation of the efforts of Bernie goes, therefore, also to her.

In this booklet we have collected the programme of the symposium as well as a list of its attendees. Subsequently, a shorter review of the work of Bernie is presented and, finally, the (shorter or longer) abstracts for most of the talks are given, in the order of their presentation at the symposium.

September 2009,
Benoît Champagne
Feng Long Gu
Josep M. Luis
Michael Springborg
## Tuesday 29 September 2009

### Kirtman’s symposium, SESSION: 1

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**CHAIR:** Celso de MELO, *(ROOM 1)*

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Elena Bogdan
Edith Botek
Roberto Cammi
Frédéric Castet
Benoît Champagne
Ove Christiansen
Yi Dong
Roberto Dovesi
Mauro Ferrero
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L’Oeuvre Of Bernie Kirtman

Benoît Champagne*, Feng Long Gu†, Josep M. Luis** and Michael Springborg‡

*Laboratoire de Chimie Théorique, FUNDP, B-5000 Namur, Belgium
†Center for Computational Quantum Chemistry, South China Normal University, Guangzhou, 510631 P. R. China and Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
**Institut de Química Computacional and Departament de Química, Universitat de Girona, E-17071 Girona, Catalonia, Spain
‡Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, Germany

Abstract. Some of the contributions of Bernie Kirtman to the field of quantum chemistry are briefly reviewed. In particular, Bernie Kirtman’s contributions to the calculation of linear and non-linear responses of conjugated systems to electromagnetic fields are discussed. This includes the question whether such systems at best are treated as being long but finite or as infinite and periodic. The role of the coupling of the electronic responses to structural / vibrational responses is emphasized.

Keywords: response functions, extended systems, electromagnetic fields

PACS: 31.15.-p, 31.15.ap, 31.15.xp, 33.15.Kr

I. INTRODUCTION

The four authors of this paper have organized a symposium at the ICCMSE 2009 conference to the honor of Bernie Kirtman. Each of us has for a longer or shorter period enjoyed a collaboration with Bernie Kirtman during the last 1 – 2 decades. This contribution is a personal presentation of the scientific results of our collaborations as well as of related works by Bernie but is, nevertheless, in some sense a summary of a small part of the scientific work of Bernie Kirtman.

Bernie Kirtman has, however, been scientifically active in many other areas, and it is not possible to give just a fair account of all his contributions to quantum chemistry. The subjects we have chosen to summarize are, accordingly, based first of all on personal interests and our own interactions with Bernie Kirtman and not at all an attempt to give a representative account of all contributions of Bernie Kirtman.

II. CONJUGATED MOLECULES AND POLYMERS – FINITE VERSUS PERIODIC STRUCTURES

II A. Polarizability and Second hyperpolarizability of Conjugated Oligomers

About 30 years ago, Bernie Kirtman started to investigate the properties of organic polymers, with an eye on those systems that become conductor upon doping. In particular, with Celso De Melo he devised density matrix methods for localized electronic interactions to extend the range of applicability as may be necessary to deal with solitons and polarons [1, 2].

When looking for efficient methods to determine the polymer properties, he rapidly assessed the pros and cons of the two main approaches, 1) the direct calculation for an infinite chain taking advantage of translational symmetry and 2) the finite chain approach where the properties are calculated as a function of chain length. For the latter, in 1983 [3], using ab initio Hartree-Fock, he investigated the convergence of the equilibrium geometries, energies per C2H2 unit, isomerization energies, ionization potentials, band gaps, and band widths as a function of polyacetylene (PA) chain length. Besides providing estimates for the polymer properties, this paper highlighted that the convergence behavior can be very different for different structural and electronic properties, and also different from the convergence of lattice summations in polymer band structure calculations.
His subsequent work on this topic was coping with the linear and nonlinear optical properties of finite polyacetylene chains, demonstrating the strong chain length dependence of these properties, mainly the nonlinear one [4]. Fig. 1 illustrates such a behavior, that has been addressed in several subsequent studies.

Fits and extrapolations of the linear and nonlinear responses per unit cell have then been proposed to better estimate the PA properties. Moreover, as another common denominator to many of Bernie’s works, the systems properties have been addressed at several levels of approximation, looking therefore for consistency between the results as well as for the best of several worlds (approximations). It appeared that this investigation on the polarizability ($\alpha$) and second hyperpolarizability ($\gamma$) of PA chains was going to call for many other ones, tackling different aspects ranging from the chemical nature of the unit cell and the level of approximation (empirical versus \textit{ab initio}, Hartree-Fock versus correlated) to the nature of the response (electronic versus vibrational). Thus, with Muhammad Hasan, Bernie worked on the linear and nonlinear responses of polydiacetylene and polybutatriene chains [5, 6]. In particular, the crucial basis set issue for calculating $\alpha$ and $\gamma$ was raised and different strategies of extrapolation have been used, i.e. 1) considering the fit of the property or of its logarithm, and 2) assessing the order of the $1/N$ power series expansion.

In 1992, they published a study on both the electronic and vibrational polarizabilities and hyperpolarizabilities of polysilane chains [7], $\sigma$-conjugated systems known to display properties usually associated with $\pi$-conjugated systems. That paper contains lots of information for scientists involved in designing new NLO materials from quantum chemistry calculations. Of course, we will come back in a subsequent Chapter (Sec. IV) on the methods for calculating the vibrational contributions to the (hyper)polarizabilities but let’s point out that in this 1992 investigation, it was already shown that the vibrational contributions – both static and dynamic – can be substantial with respect to the electronic one. Polysilane chains turned out also to be suitable systems to investigate basis set effects and to conclude that the 6-31G basis set yields accurate longitudinal (hyper)polarizability values if the chains are long enough whereas no computational advantage was found in using effective core potentials. Though generally not easy, nor straightforward, comparisons with experiment were also performed, indicating a reasonable agreement.

The same year appeared his first review on the topic: ‘Nonlinear Optical Properties of Conjugated Polymers from \textit{Ab Initio} Finite Oligomer Calculations’ [8] where Bernie not only summarized his most recent works but also described in details the effects of polarization in long chains: the application of an external electric field along the direction of a polyacetylene chain leads to $i$) a transfer of charge between the end segments, which are fixed in length (5–10 units) and to $ii$) a long quasi neutral central region where the unit cells are similarly polarized. He then proposed that advantage should be taken from this situation, for example by combining the local space approximation (LSA) to bond/connect the three parts of the systems with crystal orbital calculations to deal with the periodic central region,
The length of the arrows, which have been translated for visualization purposes, is proportional to the amplitude of the motion.

Asymptotic limits for DFT calculations dealt with buckminsterfullerene [17] and showed that the \( \alpha \) calculations of vibrational response is dominated by intense vibrational contributions to the second hyperpolarizability even at optical frequencies and, like for PA chains, the largest contribution to the Raman degenerate four-wave mixing.

FIGURE 2. Schematic drawing of the unit cell vibration in \( \text{C}_{22}\text{H}_{24} \) that makes the largest contribution to the Raman \( [\alpha^2]^{0,0} \) term. The length of the arrows, which have been translated for visualization purposes, is proportional to the amplitude of the motion. From [14].

These methods (extrapolation and electron correlation) were also applied on other systems including polyyne and polypyrrole [11, 12]. The nonresonant frequency-dispersion effects were then studied by applying the time-dependent Hartree-Fock (TDHF) scheme to PA chains [13]. The \( \gamma(\omega_\sigma; \omega_1, \omega_2, \omega_3)/\gamma(0) \) ratios, which in the low frequency limit follows \( 1 + A\omega_\sigma^2 \) with \( A \) a constant independent of the NLO process and \( \omega_\sigma^2 = \omega_1^2 + \omega_2^2 + \omega_3^2 \), have been calculated for different processes and different frequencies. Then, completing the first turn of investigations as foreseen in 1992, the vibrational contributions to the polarizability and hyperpolarizabilities of oligomers were characterized in 1996, by focusing on the role of collective vibrational modes, including the effective conjugate coordinate (ECC) mode, the transverse as well as the longitudinal acoustic/accordeon modes [14]. In particular, the in-phase vibration that makes the largest contribution to the Raman \( [\alpha^2]^{0,0} \) term has been highlighted and shown to be a mixture of carbon skeleton motion resembling the skeleton motion of the effective conjugate coordinate (ECC) and of hydrogen wagging motion (Fig. 2). However, the Raman vibrational hyperpolarizability contribution is mostly due to the ECC component.

Most of these achievements were then integrated in a second review article ‘Calculation of Nonlinear Optical Properties of Conjugated Polymers’ [15]. Moreover, using the supermolecule approach, effects of interchain interactions on the polarizability and second hyperpolarizability of short PA oligomers were shown to lead to substantial decrease of \( \gamma_\mathrm{L}/N \). Finally, focusing on his goal of providing a comprehensive treatment of NLO activity in polymers, he pointed out additional directions of investigation, including the use of density functional theory methods to include electron correlation effects as well as the assessment of structural defects and impurities.

In addition to intensive developments of efficient methods to estimate the vibrational hyperpolarizabilities (Section IV), the end of the 90’s was marked by studies addressing the relationships between the electronic and vibrational hyperpolarizabilities in \( \pi^- \) and \( \sigma^- \)-conjugated oligomers. One of these, carried out with Perpète and Champagne, shows that, using the double harmonic approximation, polydiacetylene and polybutatriene chains exhibit substantial vibrational contributions to the second hyperpolarizability even at optical frequencies and, like for PA chains, the vibrational response is dominated by intense \( k = 0 \) Raman modes [16]. Another study based on combining HF and DFT calculations dealt with buckminsterfullerene [17] and showed that the \( \gamma'/\gamma'' \) ratio can be as large as 1.26 for degenerate four-wave mixing.

Several works were also devoted to the solid state effects, considering at \textit{ab initio} levels small aggregates (of prototype PA oligomers) and going towards large clusters by using interactions schemes. So, at the CPHF/6-31G level, it was found that solid state interactions in PA lead to a large decrease in the static vibrational second hyperpolarizability per chain and that, for the high-frequency intrachain vibrational modes, this decrease closely parallels that of the static
electronic counterpart [18]. Then, in collaboration with C. Dykstra, an electrostatic interaction scheme was set up and benchmarked by extensive ab initio calculations to investigate the bulk behavior of PA fibers [19]. It was shown (i) how sizeable medium effects on $\alpha$ and $\gamma$ can arise, (ii) that classical electrostatics can accurately reproduce a full quantum treatment, and (iii) that for a large bundle of hexatriene molecules the medium effects will lead to as much as a 95% reduction in $\gamma$ and a 50% reduction in $\alpha$.

An important strategy to enhance the hyperpolarizabilities consists in creating structural and electronic defects by doping $\pi$-conjugated systems. Bernie has addressed these effects for PA chains. First, the effect of charging on the longitudinal second hyperpolarizability of chains containing up to nearly 70 carbon atoms has been investigated ab initio by characterizing chains with and without an explicit alkali atom (Li, Na, K) as dopant [20]. Whereas charging dramatically enhances the static electronic and vibrational hyperpolarizabilities of an isolated chain at intermediate chain lengths, the presence of an alkali atom counterion substantially reduces this effect. As the size of the alkali atom increases most properties, including the hyperpolarizabilities, approach those of the isolated chain (Fig. 3). Detailed analysis shows that the behavior of the electronic hyperpolarizability is most simply explained in terms of a reduced electrostatic pinning potential due to increased distance between chain and counterion. At all chain lengths the electronic $\gamma$ of PA is enhanced by alkali-doping. For chains containing 50 carbon atoms ($N_C = 50$), the increase due to K-doping is about $9 \times 10^7$ a.u., which more than doubles the value for an undoped chain of similar length. The normalized quantity, the second hyperpolarizability per C atom, $\gamma/N_C$, exhibits a maximum for the isolated soliton (at about $N_C = 61$) that is over four times that of the infinite undoped (and unbent) chain. When the alkali dopant is taken into account this maximum diminishes considerably and shifts to larger $N_C$ than we have considered. In comparison with the maximum for the undoped species (at $N_C = \infty$) there is a small enhancement of $\gamma/N_C$ for K-doping, but none for either Li- or Na-doping at the coupled-perturbed Hartree-Fock (CPHF) / 6-31G level of theory. On the other hand, intermediate length isolated chains bearing a charged soliton show order of magnitude increases in $\gamma$ for the degenerate four wave mixing (DFWM) and, especially, electric field-induced second harmonic generation (dc-SHG) processes compared to undoped PA. As in the case of the electronic counterpart this enhancement persists, but is significantly reduced when the dopant atom is included. Vibrational anharmonicity, which contributes only to the dc-Kerr effect at our level of treatment, is much more important in the doped than undoped species. This contribution was later extended by considering the impact of the doping level on the electronic second hyperpolarizability of alkali-doped PA chains [21]. Enhancement factors approaching two orders of magnitude, with respect to the undoped chain, were found for K at the largest concentrations that can be sustained with dissociation. Since most of these calculations have been performed at the HF/6-31G level, additional MP2 calculations as well as calculations using larger basis sets (6-31G*, 6-311G*, 6-31+G, and 6-31+G*) were carried out to show that the HF structure-property relationships are retained.

These results exemplified, owing to their numerous aspects, how challenging is the optimization of the materials for NLO applications and how theoretical calculations and analysis can help in this design. Some of these aspects have

![Figure 3](https://example.com/figure3.png)

**FIGURE 3.** Evolution with chain length of the longitudinal static electronic second hyperpolarizability (in a.u.) per carbon atom of neutral, charged (positive or negative), and doped polyacetylene chains. From [20].
II B. First Hyperpolarizability in \( \pi \)-Conjugated Systems: Push-Pull Compounds versus Asymmetric Unit Cell Oligomers

An alternative class of conjugated systems displaying large first hyperpolarizabilities are oligomers built from asymmetric unit cells, like polymethineimine [PMI, (CH=N)\(_N\)]. In 1996, using the CPHF approach, Bernie and co-workers investigated the chain length dependence of the static longitudinal first hyperpolarizability per unit cell (\( \beta/N \)) of PMI [24]. It was shown that (i) the first hyperpolarizability per unit length is of the same order of magnitude as in traditional push-pull \( \pi \)-conjugated systems and (ii) that the \( \beta/N \) curve exhibits a characteristic ‘dromedary back’ shape, which results from the interplay between backbone and chain end asymmetries. This study was extended by combining the unit cell asymmetry with substitution by donor/acceptor (D/A) end groups and by investigating conformation effects [25].

Following an initial comment on the relationship between the electronic and vibrational first hyperpolarizability [26], a two-state valence-bond charge-transfer (VB-CT) model for D/A \( \pi \)-conjugated systems has been analyzed to yield several parameter-independent relations between the electronic and vibrational hyperpolarizabilities [27]. Then, using \textit{ab initio} computational tests sampling a broad range of D/A strengths showed that these relations are not satisfied and therefore that little confidence can be given to the VB-CT model to estimate the ratios between the electronic and vibrational hyperpolarizabilities.

Further insight into the relationship between the electronic and vibrational first hyperpolarizability was grasped from a CPHF/6-31G investigation of D/A \( \pi \)-conjugated systems with linkers of specific nature, length, and charge [28]. In three situations, the electronic and vibrational components exhibit different behaviors: when the conjugation is broken by an \( sp^3 \) defect, when changing the nature of the aromatic rings in stilbene-like linkers, and upon doping \( \alpha, \omega \)-nitro-amino all-trans polyyene and forming polaron-like defects.

These investigations then led to examine whether a single electric field can be used to simulate the entire set of electrical properties of a given D/A \( \pi \)-conjugated system, i.e., whether a field can be used to simulate the effects of a D/A pair [29]. This was achieved by calculating the electrical properties \( \mu, \alpha, \beta, \text{ and } \gamma \) for a representative set of D/A polyenes by both \textit{ab initio} methods and electric field simulation starting with the corresponding unsubstituted polyenes. Both vibrational and electronic contributions were considered. It turned out that, (i) for each property, the field simulation yields a particular combination of vibrational and electronic terms, (ii) when these two terms are plotted vs. \( F_s \) (the simulating field) the resulting curves are similar in shape, and (iii) the curve for \( \alpha, \beta, \text{ and } \gamma \) has the general shape determined by the derivative of the next lower-order property. However, although one particular \( F_s \) can approximately reproduce the \textit{ab initio} \( \mu \) and \( \beta \) (both electronic and vibrational) for a given D/A polyene, the same field does not reproduce either \( \alpha \) or \( \gamma \). In fact, it was found that there is in general no field that will do so. This led to conclude that the field simulation approach can only be used to provide a unified description of the odd-order properties (i.e., \( \mu \) and \( \beta \)) and that field non-uniformity and/or specific bonding interactions are important to reproduce the complete D/A effect.

Subsequent papers have been dealing with improving the quality of the calculations and with going towards semi-quantitative predictions like in a MP2 study on the electronic and vibrational first hyperpolarizability of push-pull polyenes [30] (see also Sec. IV).

The two most recent contributions in this field of designing molecules with large first hyperpolarizabilities are related to commenting and assessing propositions due to Mark Kuzyk [31, 32], who raised theoretical questions about fundamental limits on the electronic hyperpolarizabilities by using Thomas-Kuhn sum rule constraints. In one paper, it was shown that applying these sum rules on a two-state model constitutes an overconstrained situation. In the other paper, the alternative dipolar-free SOS expression for the first hyperpolarizability (diagonal tensor components) was examined for typical push-pull \( \pi \)-conjugated systems using the \textit{ab initio} configuration interaction schemes to approximate the excited state properties. Since the traditional and dipolar-free quantities are each evaluated approximately the two SOS expressions yield different values for \( \beta \) and it was found that (i) they evolve symmetrically as the number of excited states is increased so that their average is nearly constant, (ii) in the static limit, the two values agree better with one another when their average is close to the ‘exact’ correlated result, and (iii) frequency-dispersion can affect the agreement between the alternative expressions. On the basis of (i) and (ii) it appears best for typical push-pull \( \pi \)-conjugated systems to estimate the static \( \beta \), and the error in the value so obtained, by averaging the Kuzyk and traditional results.
III. LOCAL-SPACE AND ELONGATION METHODS

One of the most important contributions of Bernie Kirtman to polymer science is to build band structures either by periodic boundary condition (PBC) calculations or finite cluster calculations. In this part, a method to build an accurate band structure for polymers from oligomer calculations is presented, which is a product of collaboration of Bernie Kirtman with Yuriko Aoki, Anna Pomogaeva, and Feng Long Gu. This method is to extend the treatment of Cui et al. [33] for assigning a value for the wave vector to each molecular orbital (MO). The main improvement of the Cui-Kertez method is the development of reciprocal space projection technique. As important new ingredients the proposed methodology involves the systematic elimination of strongly localized states and treatment of band crossing. Finally, an interpolation/extrapolation technique is used to continue the bands across the entire Brillouin zone. This method is cooperated to the elongation method [34, 35, 36, 37] for an accurate quantum-chemical treatment of very large oligomers.

As applications, test calculations at HF and DFT levels with different basis sets for H2O chains and some π-conjugated polymers illustrate our procedure and verify that it can very precisely reproduce the band structures obtained from PBC calculations. Other applications, including series of complex quasi-one-dimensional compounds with large unit cell have been also carried out.

The important merit of this method is its simplicity. Little additional computations do it require to get a physically meaningful picture and it does not depend on a way of one-electron states (energies) calculations. The proposed method has advantages over PBC calculations for periodic systems with big unit cells or for using large basis set, especially within an linear-combination-of-atomic-orbitals (LCAO) framework. Thus, it increases the attractiveness of the finite oligomer method for a variety of applications. Especially it is important for studying systems with any local defects where conventional PBC calculations are still problematic.

III A. Methods for Constructing Band Structures from oligomers

For an open chain of \( M \) identical, equidistant atoms with one AO, \( \chi_j \), per atom eigenfunctions and energies at the Hückel approach are:

\[
\phi_m(\text{chain}) = \sum_{j=1}^{M} \sin\left(\frac{\pi m (M+1)}{M+1}\right) \chi_j \\
\epsilon_m(\text{chain}) = \alpha + 2\beta \cos\left(\frac{\pi m}{M+1}\right), \quad m = 1, 2, \ldots, M,
\]

while for a ring of \( N \) equivalent atoms:

\[
\phi_m(\text{ring}) = \sum_{j=0}^{N-1} \exp\left(2\pi i \frac{m}{N} j\right) \chi_j \\
\epsilon_m(\text{ring}) = \alpha + 2\beta \cos\left(\frac{2m}{N}\right), \quad m = 0, 1, \ldots, N-1.
\]

Here \( \alpha \) is the Coulomb integral, and \( \beta \) is the resonance integral. Since a ring is periodic, these MOs satisfy Bloch theorem, thus, a wave vector (number) is associated with each state of the ring system,

\[
k_m = \frac{2\pi m}{Na}, \quad m = 0, 1, \ldots, N-1,
\]

where \( a \) is the lattice spacing. By comparing Eqs. (1) and (2), we see that the open chain states are included amongst the states of the ring system with

\[
N = 2(M+1).
\]

Hence, it is possible to associate every state of the open chain with a \( k \)-value in the first Brillouin zone (BZ):

\[
k_q = \frac{q \pi}{M+1 \ a}, \quad q = 1, 2, \ldots, M, \quad 0 < k < \frac{\pi}{a}.
\]
Beyond the simplest Hückel approximation, with more than one AO per unit

\[ \phi_{\text{in}}(\text{chain}) = \sum_{j=1}^{M} \sum_{r} C_{rj} \chi_{rj}^{j}, \tag{6} \]

where \( C_{rj} \) is the LCAO-MO coefficient corresponding to the \( j \)th repeat unit and the \( r \)th AO in that unit, Cui et al. suggested that the appropriate \( k_q \) could be found from the value of \( q \) which maximizes

\[ X_q = \sum_{r} \sum_{j=1}^{M} C_{rj} \sin \left( \frac{\pi q j}{M+1} \right), \quad q = 1, 2, \ldots, M. \tag{7} \]

By maximizing \( X_q \) one matches the nodal structure of the infinite chain MO as closely as possible.

Using this methodology, the authors were able to build schematically band structures for series of short oligomers at semi-empirical level.

Unfortunately, as it will be shown later, the simple procedure described above does not always work satisfactorily. Using this methodology, the authors were able to build schematically band structures for series of short oligomers at semi-empirical level.

For the infinite chain with cyclic boundary conditions the LCAO-COs of interest may be written as:

\[ \psi_{mq} = \sum_{r'} b_{q,n}^{r'}(q) \sum_{j'} \exp \left( \frac{2\pi i j' q}{N} \right) \chi_{r'j'} \tag{8} \]

in which \( q = 1, 2, \ldots, N \) and \( n \) is the band index. These eigenfunctions occur in degenerate pairs that are complex conjugates of one another. In order to make a match with real oligomer MOs it is desirable to form the two linear combinations

\[ \psi_{m1} = \sum_{r'} \tilde{b}^{1,n}_{q,r'}(q) \sum_{j'} \sin \left( \frac{2\pi j' q}{N} \right) \chi_{r'j'} \]
\[ \psi_{m2} = \sum_{r'} \tilde{b}^{2,n}_{q,r'}(q) \sum_{j'} \cos \left( \frac{2\pi j' q}{N} \right) \chi_{r'j'}. \tag{9} \]

Using the relationship between number of units of an oligomer (\( M \)) and those of a ring (\( N \)) given by Eq. (9), and taking into account the non-orthogonality of the AOs, we are led to define the quantities for matching purposes.

\[ X_{mq}^{r} = \sum_{r'} \tilde{b}^{1,n}_{q,r'}(q) \sum_{j} C_{rj} \sum_{j'} \sin \left( \frac{\pi j q}{M+1} \right) \langle \chi_{rj} | \chi_{r'j'} \rangle \]
\[ Y_{mq}^{r} = \sum_{r'} \tilde{b}^{2,n}_{q,r'}(q) \sum_{j} C_{rj} \sum_{j'} \cos \left( \frac{\pi j q}{M+1} \right) \langle \chi_{rj} | \chi_{r'j'} \rangle \tag{10} \]

Coefficients \( C_{rj} \) and AO overlap matrix are obtained from oligomer calculations. The next step is to select approximate LCAO-CO coefficients for Eq. (8) in a manner that depends only on oligomer calculations. Thus, we ignore the dependence of the LCAO-CO coefficients upon \( q \). For purpose of simplicity let us assume a primitive model of LCAO-CO (8) where expansion coefficients over unit cell are taken to be independent of \( r' \) and \( n \) as well. Thus, in the simplest case let us set in (10) \( \tilde{b}^{1} = \tilde{b}^{2} = 1 \). Later the reliability of the assumption will be discussed.

Finally, in order to give equal weight to \( X_{mq}^{r} \) and \( Y_{mq}^{r} \), for a particular MO, \( q \) as the value which maximizes

\[ R_q = \sum_{r} \left[ (X_{mq}^{r})^2 + (Y_{mq}^{r})^2 \right]^{1/2} \tag{11} \]

is chosen to define \( k \)-value.

Thus, for every MO of an oligomer, the procedure formally allows assigning wave vector. The number of available \( k \)-values in BZ for each band depends on length of the oligomer, however, no MO could be associated with \( \Gamma \) point or edges of BZ.
The efficiency of the methodology is shown in Fig. 4. The smooth curve renders the oxygen lone pair $\pi$ band (the highest valence band) of infinite water chain calculated with PBC by means of PLH software [38] at the HF level with STO-3G basis set. Discrete marks are orbital energies of 31 units oligomer calculations. Open circles show results of $X_q$ $k$-assignment procedure suggested by Cue et al., open squares are a result of replacement sin by cos($Y_q$), and crosses mark $k$-values determined by $R_q$.

Clearly, the method based on $R_q$ successfully reproduces the polymer band structure whereas the $X_q$ method suggested by Cui et al. does not. Furthermore, the situation is not improved by replacing $X_q$ with $Y_q$ for some subset of the MOs.

**III B. Test Calculations**

**III B A. $H_2O$ chain**

The total set of water polymer's bands calculated at HF/STO-3G level is presented in Fig. 5, a core band is omitted for simplicity. All oligomer calculations were performed using GAMESS software. For H2O chain, both O–H bonds were taken to be 0.96 Å in length and the H–O–H angle to be 104.5°. As schematically shown in Fig. 5, the translational axis were chosen to lie along the H-bonded sequence O–H···O–H··· with the distance between O atoms equal to 2.72 Å.

Circles in Fig. 5 present band structure obtained from calculations of the finite oligomer of 31 units of length. For the purpose of comparison the same geometry was used to carry out HF/STO-3G calculations with PBC using PLH software [38]. This figure shows essentially perfect agreement with the corresponding polymer calculation. The fundamental gap is $E_g = 24.56$ eV, which is in error by about 0.02 eV compared to the PBC value. The same perfect agreement was achieved with PBC calculations performed with CRYSTAL06 software.
III B. Poly-para-phenylene and Polyacetylene

For GAMESS HF/STO-3G band structure calculations on PPP the following geometry was utilized: C–C bond length equal to 1.41 Å within phenyl rings and 1.54 Å between rings; C–H bond length 1.09 Å, all bond angles 120°, and translational vector 4.36 Å. For PA the geometry was: C–C bond length 1.454 Å, C=C bond length 1.33 Å, C–H bond length 1.08 Å, C–C=C bond angle 124°, C=C–H bond angle 116.7°, and translational vector 2.46 Å. The same geometry was used to carry out HF/STO-3G calculations with PBC using PLH software.

As seen from Fig. 6, the band structures of PPP and PA obtained from 31 unit oligomer calculations are indistinguishable from the polymer calculations at the scale shown. The two highest valence bands and two lowest conduction bands of PPP are π-electron states. Since the π-system of PPP is completely delocalized, these states are well-described by Hückel MOs and a good band structure can be obtained using an oligomer with just a few units. The fundamental energy gap (at the Γ point) is 9.76 eV; it differs from the PBC value by only $10^{-5}$ eV.

For PA the uppermost valence π- and σ-bands cross at $k = 0.202\pi/a$ while for PLH the crossing is at $k = 0.200\pi/a$. The fundamental gap ($\pi \rightarrow \pi^*$) is located at $k = \pi/a$. Within the HF/STO-3G approximation $E_g = 8.23$ eV is much too large, as expected, but the difference with the PBC value is only 0.01 eV. There is also a crossing of two σ conduction bands at $k = 0.687\pi/a$ as compared to $k = 0.691\pi/a$ according to our PLH calculations. The energy difference between the two treatments is only 0.00055 eV. Fig. 6 also shows an avoided crossing between two σ valence bands. At the closest point the energy gap is 2.014 eV, which differs from the PLH value of 1.988 eV by about 0.025 eV. The infinite polymer bands exhibit near degeneracies at $k = 0$ and $k = \pi/a$ which are reproduced very well by the finite oligomer calculations.

In order to investigate the reliability of our method for a somewhat more difficult case, band structures for polydiacetylene oligomers in the acetylenic (PDA) form are built. The results are shown in Table 1 where our PDA oligomer results for the various HF and B3LYP calculations are compared with those obtained for the periodic polymer...
FIGURE 6. Band structures of PPP (a) and PA (b) extracted from GAMESS HF/STO-3G calculations of 31 unit oligomers (crosses) as compared to those calculated with PBC using the PLH program (solid lines).

TABLE 1. The ionization potential (IP), electron affinity (EA), and bandgap ($E_g = IP – EA$) obtained for PDA from 31 unit oligomer calculations and from POLYMER calculations on the infinite periodic chain by the HF and B3LYP methods with different basis sets.

<table>
<thead>
<tr>
<th>Method</th>
<th>IP (eV) polymer</th>
<th>IP (eV) oligomer</th>
<th>$E_g$ (eV) polymer</th>
<th>$E_g$ (eV) oligomer</th>
<th>EA (eV) polymer</th>
<th>EA (eV) oligomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/STO-3G</td>
<td>5.92</td>
<td>5.92</td>
<td>9.87</td>
<td>9.87</td>
<td>-3.95</td>
<td>-3.95</td>
</tr>
<tr>
<td>HF/3-21G</td>
<td>7.36</td>
<td>7.36</td>
<td>7.78</td>
<td>7.78</td>
<td>-0.42</td>
<td>-0.43</td>
</tr>
<tr>
<td>HF/6-31G</td>
<td>7.18</td>
<td>7.17</td>
<td>7.68</td>
<td>7.67</td>
<td>-0.50</td>
<td>-0.50</td>
</tr>
<tr>
<td>B3LYP/STO-3G</td>
<td>3.39</td>
<td>3.39</td>
<td>2.53</td>
<td>2.53</td>
<td>0.86</td>
<td>0.85</td>
</tr>
<tr>
<td>B3LYP/3-21G</td>
<td>4.99</td>
<td>4.98</td>
<td>1.78</td>
<td>1.79</td>
<td>3.20</td>
<td>3.19</td>
</tr>
<tr>
<td>B3LYP/6-31G</td>
<td>4.84</td>
<td>4.83</td>
<td>1.72</td>
<td>1.72</td>
<td>3.12</td>
<td>3.11</td>
</tr>
</tbody>
</table>

by Tobita et al. [39] using the POLYMER program [40] (and the same geometry in either case). Table 1 includes a comparison for the ionization potential (IP) and electron affinity (EA), as well as the bandgap ($E_g = IP – EA$). The difference between the PBC results and the extrapolated oligomer properties is always less than 0.01 eV. The same is true at $k = \pi / a$ (not shown), although in that case the symmetry of the lowest unoccupied band depends upon the basis set.
III. C. Concluding Remarks

A method is proposed to build an accurate band structure for polymers from oligomer calculations, based on the treatment of Cui et al. for assigning a value for the wave vector to each MO. The band assignment procedure allows not only to distinguish energy bands of a periodic system but also to reduce problems due to the occurrence of so-called doublings and holes. The method is cooperated with the elongation method which it can efficiently treat very large oligomers and, thereby, obtain band structures and other properties more accurately than from conventional molecular cluster calculations. The method was tested for H₂O chains and some π-conjugated polymers like trans-polyacetylene and poly(para-phenylene), polyethylene and polydiacetylenes. It was found that a reliable band structure could be built from quantum-chemical calculations of an oligomer of about 15–20 units of length. For oligomers of 30 units of length the difference of band structure near the edges of Brillouin zone with one obtained by PBC calculations is about 0.01–0.02 eV. Results obtained using DFT, as well as HF approximations, and different basis sets, serve to confirm the robustness of the method.

IV. VIBRATIONAL CONTRIBUTION TO LINEAR AND NONLINEAR OPTICAL PROPERTIES

In this section we review some of the developments that have been made by Bernie Kirtman over the last twenty years with regard to the calculation of vibrational contribution to linear and nonlinear optical properties (NLOP). The vibrational contribution to NLOP, which arises from vibronic coupling, can often be as important as the pure electronic contribution or even more important [41]. Two major intertwining approaches have been developed. The older approach is from the viewpoint of ordinary sum-over-states perturbation theory (SOS-PT) and the other approach is from what may be called the nuclear relaxation/curvature point of view.

In the usual SOS-PT expressions [42] for the (hyper)polarizabilities the electronic property arise from the SOS terms which intermediate vibronic states |K, k⟩ refers to an excited electronic state (K ≠ 0). Hence, all terms containing one intermediate states with K = 0 are part of what is known as the pure vibrational contribution. Resonant, or near-resonant processes occur when in the denominators of the SOS-PT excitation vibronic frequency is equal or very close to optical frequency. Otherwise, the process is non-resonant.

The first simplification of the SOS-PT formulas, with negligible consequences [43], is the clamped nucleus approximation, that replaces in the denominators the difference of vibronic energies by the electronic counterpart at a fixed nuclear geometry. In the Bishop and Kirtman (BK) perturbation treatment [44, 45, 46] two basic additional assumptions are made. Under ordinary non-resonant conditions, when |K⟩ is an intermediate excited electronic state, one may ignore the optical frequency term in the corresponding energy denominator. Then, the pure vibrational (hyper)polarizabilities may be expressed compactly in terms of so-called square bracket quantities [e.g. β⁺(−ωα; ω₁, ω₂) = |µα| + |µ1|]. A complete set of square bracket formulas is given in Table I of Ref. [46]. The second approximation consists in assuming that the instantaneous electrical properties and potential energy may be expanded as a power series in the normal coordinate displacements. The total BK (hyper)polarizability is the sum of the pure clamped nucleus electronic term (evaluated at the electronic ground state equilibrium geometry) plus the pure vibrational contribution plus the zero-point vibrational averaging correction.

The zeroth-order approximation in the BK perturbation treatment of pure vibrational NLO is the double harmonic model, which includes just the terms in the property expression that are linear in the normal coordinates and quadratic in the potential energy. Quadratic terms in the property expansions are considered to be first-order in electrical anharmonicity, cubic terms are taken to be second-order, etc. Similarly, cubic terms in the vibrational potential are considered to be first-order in mechanical anharmonicity, quartic terms are second-order, and so forth. Here we note that compact expressions, complete through second total order in electrical plus mechanical anharmonicity, have been presented [46].

In assessing the importance of vibrational NLOP respect to their electronic counterparts it is necessary to distinguish between processes that involve at least one d.c. field and those that do not. The vibrational contribution is negligible for the latter category (e.g. second harmonic generation). However, the vibrational contributions can be even larger than the electronic NLOP for the former category (e.g. the electro-optic Kerr effect) [47].

The second approach to calculate the vibrational NLOP is based on determining the change in the equilibrium geometry induced by a static external field [48, 49, 50, 51]. Even though there is an exact correspondence between the BK perturbation treatment and the nuclear relaxation approach the latter has spawned valuable new concepts and
related computational procedures. From the viewpoint of this alternative procedure it is natural to divide the total vibrational (hyper)polarizability into nuclear relaxation ($P_{nr}$) and curvature ($P_{c}$) contributions. $P_{nr}$ and $P_{c}$ arise from the change in the electronic and zero-point vibrational averaging corrections caused by the field-induced relaxation of the equilibrium geometry, respectively. $P_{c}$ can be divided into two terms: the zero-point vibrational averaging (zpva) contribution, $P_{zpva}$, and the remainder $P_{c-zpva}$.

Under the influence of a uniform static electric field, the electronic energy of a chemical system can be expressed as a double power series expansion in the normal coordinates and the electric field [41]. Imposing the minimum condition on the electronic energy expansion leads to analytical expressions for the field-dependent equilibrium geometry in terms of field-free normal coordinate displacements. Then, substitution of these displacements back into electronic energy expansion gives directly the nuclear relaxation contribution. The $P_{c}$ are derived in the same fashion as $P_{nr}$ except that one substitutes back into the double power series expansion for zero-point energy instead of the electronic potential energy [48]. There is a straightforward correspondence between the BK perturbation theory formulas and those obtained from the nuclear relaxation/curvature approach. $P_{nr}$ contains the lowest-order BK term of each square bracket type in the expression for pure vibrational contributions, whereas $P_{c}$ contains the remaining BK terms [49].

Under the infinite optical frequency approximation, which corresponds to the limit $\omega \to \infty$, the expression for the dynamic $P_{nr}$ and $P_{c-zpva}$ also can be obtained from the nuclear relaxation/curvature point of view. For typical laser optical frequencies test calculations [51] confirm that the infinite optical frequency approximation is highly accurate. The $\omega \to \infty$ limit of $P_{nr}$ [e.g. $\beta^{nr}(-\omega, 0)_{\omega \to \infty}$] may be obtained by means of the same procedure as for the static (hyper)polarizabilities, but expanding the static $\alpha^{nr}$ and $\beta^{nr}$ as a double power series instead of the electronic energy [49, 50]. The infinite optical frequency cut-off $P_{c-zpva}$ can be obtained by expanding the static $\alpha^{zpva}$ and $\beta^{zpva}$ as a double power series [48].

The bottleneck in calculating $P_{nr}$ and $P_{c-zpva}$ from analytical expressions is due to the required evaluation of high-order derivatives with respect to the normal modes [52]. One might assume that high-order anharmonic terms will make a negligible contribution to vibrational NLO. However, the results we have obtained for typical $\pi$-conjugated NLO molecules show that this may not be the case [52]. This problem can be circumvented by using Finite Field (FF) methods with the nuclear relaxation/curvature approach, which is the major advantage of the latter. The FF calculations involve carrying out a geometry optimization for the molecule in the presence of a static electric field and the calculations of $P_{c}$ and $P_{zpva}$ at such field dependent equilibrium geometries. In the calculation of the field-dependent equilibrium geometry the field-free Eckart conditions must be enforced in order to prevent molecular reorientation during geometry optimization [53]. Since the Eckart conditions are mass-dependent $P_{nr}$ will exhibit an isotope effect.

In order to calculate $P_{zpva}$, or $P_{nr}$ and $P_{c-zpva}$ at arbitrary frequencies for medium size and larger molecules, the BK analytical expressions are currently the only feasible alternative. But the bottleneck of the evaluation of vibrational BK hyperpolarizabilities is the large number of $n$th-order derivatives with respect to normal modes that must be computed. This number is on the order of $(3N - 6)^n$ with $N$ being the number of normal modes. This difficulty may be overcome by introducing a set of static field-induced vibrational coordinates (FICs) which radically reduce the number of $n$th-order derivatives to be evaluated [51, 53, 54, 55]. For instance, for the nuclear relaxation contribution to the static longitudinal $\beta$ or the longitudinal dc-P effect, the perturbation theory expressions containing sums over $3N - 6$ normal coordinates can be reduced to formulas that involve only a single FIC. The FICs are just the displacement coordinates derived from the change in the equilibrium geometry induced by a static applied field. Although the original definition of the FICs was based on static fields, the idea has been extended to the construction of frequency-dependent FICs so that one can account for the frequency dispersion of the vibrational NLO properties as well [51]. The FICs may be determined either analytically or by an FF method.

In the finite field approach the FICs are generated simply by evaluating numerical derivatives of the change in equilibrium geometry induced by a finite field with respect to the magnitude of that field [53]. The analytical definition of the the static first-, second- and higher-order FICs are based on the expansion of the field-free normal coordinate displacement induced by a uniform static electric field as a power series in the field. The definition of the analytical frequency-dependent FICs are based on the relationship between the static and dynamic BK vibrational NLO expressions [51]. For each diagonal component of nuclear relaxation (hyper)polarizability tensor only one or two FICs are required [51, 54]. For the zpva contributions the FICs can be used to reduce the computational cost of the terms that contains first derivatives of the diagonal elements of the Hessian with respect to the set of normal modes. But unfortunately, the zpva terms that contains the second derivatives of the property respect to the normal modes can not be simplified using FICs [55]. The analytical formulas for $P_{c-zpva}$ can also be simplified using FICs. However, the order of the derivatives involved is so high that their evaluation is feasible only for small molecules. For that reason these vibrational contributions are usually evaluated through the FF [48]. The fact that the number of FICs does not
depend upon the size of the molecule leads to important computational advantages. For instance, the calculation of the longitudinal component of the static $\chi^\text{nr}$ for $1,1$-diammino-6,6-diphosphinohexa-1,3,5-triene with normal coordinates requires to compute the Hessian matrix 3660 times, whereas using FICs only 6 Hessian calculations are required [52].

By using FICs in the FF procedures it was possible to investigate the initial convergence of the perturbation series for some typical $\pi$-conjugated NLO molecules [47, 52]. Based on the nuclear relaxation/curvature approach it is natural to monitor the convergence by looking at two separate perturbation sequences [55]. The first one (A) is $P^\text{e}$, $[\text{zpva}]$1, $[\text{zpva}]^\text{nr}$, ... and the second one (B) is given by $P^\text{nr}$, $P^\text{e}([z\text{pva}])^\text{nr}$, $P^\text{e}([z\text{pva}])^\text{nr}$, ... All terms in each sequences are listed in increasing order of perturbation theory. It is usually found, or assumed, that the perturbation series is, at least initially, convergent. For typical $\pi$-conjugated NLO molecules, $[\text{zpva}]^\text{nr}$ is small in comparison with $P^\text{e}$. However, the same is not always true for the first two terms of sequence (B) [52]. For weakly bound systems, such as HF dimer [56], calculations reveal that the series diverges immediately. But even in less obvious cases, like some of the $\pi$-conjugated NLO molecules referred to above, problematic behavior can occur [52].

In the diverging cases, instead of relying on the perturbation expansion, the vibrational Schrödinger equation should be solved using a variational approach. Recently a variational method based on analytical response theory, applied initially to linear polarizabilities, has been proposed by Ove Christiansen, et al. [57, 58]. For large molecules or very accurate $ab$ initio treatments, this method is limited in applicability by the major computational effort needed to calculate the potential energy and electrical property surfaces. This problem can be ameliorated by utilizing the finite field-nuclear relaxation (FF-NR) approach [48, 49, 50, 59] which relies on determining the zpva contribution using a variational approach. If the field-dependent variational vibrational wavefunctions was exact, all anharmonic effects beyond lowest-order included in the nuclear relaxation contribution would be taken into account. The starting point in the calculations of the vibrational vibrational wavefunction is the vibrational SCF method, in which each normal mode vibrates in the average field generated by all the other modes. The remaining correlation corrections due to mode-mode anharmonicity can, then, be added on by the vibrational analogue of Möller-Plesset perturbation theory, configuration interaction, or coupled cluster techniques. In order to calculate the curvature NLOP for anharmonic systems, an accurate numerical description of the potential energy surface is also required, which makes the calculations feasible only for small molecules.

For very anharmonic chemical systems, typically, only a limited number of internal coordinates will play a significant role in determining vibrational NLO properties, especially when these properties are large [47, 51, 52, 55, 61]. Then, one may consider calculating the NLO properties by separating off these motions from all others, and treating the remainder in a simpler fashion. Based on an FF-NR approach, it has been developed a method wherein the key motions are decoupled from all other vibrations in first-order [60]. The umbrella motion in ammonia was used as an example and the quasi-degeneracy of the ground vibrational state was explicitly taken into account with an approach based on generalized Van Vleck perturbation theory (GVV-PT) [62, 63]. Vibrational wavefunctions for the inversion motion, which are required for the FF-NR treatment, are obtained by numerical solution of the 1D Schrödinger equations including a proper expression for the kinetic energy operator evaluated numerically. Thus, this approach completely reduces the calculation of vibrational nonlinear optical properties to an effective one-dimensional (1D) problem. Furthermore, this new method overcomes convergence problems associated with a conventional single well treatment.

The basis set and electron correlation requirement for the calculation of the (hyper)polarizabilities depends, of course, on the desired accuracy, the property, and the nature of the system. For NLO $\pi$-conjugated organic molecules longitudinal (hyper)polarizabilities the atomic basis necessary to achieve a given accuracy is smaller than for the properties of more compact molecules) [47, 47]. However, the basis set requirements increase with the order of the property and the level of correlation treatment. For the vibrational (hyper)polarizabilites of these type of NLO molecules in almost all instances the $6−31+G(d)$ basis give good results [47].

The effect of electron correlation on the (hyper)polarizabilities can change the value of the property up to an order of magnitude [47, 52, 64]. They originate indirectly from the change in geometry and directly from the change in the electronic charge distribution. In $\pi$-conjugated organic molecules a large geometry effect can occur because the properties are very sensitive to the bond length alternation. MP2 method adequately reproduces the effect of correlation on the relative magnitude of the electronic and vibrational contributions to each property and, in addition, gives a reasonable prediction for the individual terms. However, higher level methods are necessary to obtain quantitative estimates for the latter. DFT is a interesting option to introduce the effects of the correlations, although is t is now well-established [65, 66, 67] that there is a fundamental problem with DFT electrical property calculations done on extended chains using conventional functionals (see Sec. V).

Bernard Kirtman also has investigated the role of molecular vibrations in resonant L&NLO properties. These
properties govern the intensity of light absorption (or emission) accompanying the transition between two vibronic energy levels. His interest was focus on one- and two-photon absorption (OPA and TPA). The OPA intensities are determined by the imaginary part of the linear polarizability whereas the TPA intensities are governed by the imaginary part of $\gamma (\omega, -\omega, 0)$. In the former case the intensity will be significant only when the incident photon frequency ($\omega$) coincides, or nearly coincides, with the energy difference between the ground state and the excited state $\Lambda$. For TPA the energy difference must nearly coincide with $2\omega$ in order to have simultaneous absorption of two photons. Expressions for vibrational OPA and TPA [68] may be derived starting from the same SOS vibronic (hyper)polarizability formula used by BK for non-resonant processes. At or near a resonance there will be one term in the SOS expressions for OPA (TPA) for which the excitation energy in the denominators will be very similar to $\omega (2\omega)$, whereas all other terms are considered to be negligible [68]. After eliminating the non-resonant terms the derivations of the perturbation theory expression proceed as in the BK treatment of non-resonant NLO, and the electrical properties and the potential energy surface may be expanded as a Taylor series in the normal coordinates.

The final perturbation theory TPA expression [68] require the calculation of Franck-Condon (FC) integrals. Hence, the calculation of FC integrals is the key step in the procedure. There are several methodologies to evaluate FC integrals at the harmonic level. However, methods for including anharmonicity are either limited in practice to triatomic molecules or assume separability of the normal modes. Recently, a simple new method was developed by Bernard Kirtman and coworkers for calculating accurate FC factors including non-diagonal anharmonic coupling and Duschinsky rotations [69]. The formulation of this new methodology is based on taking the difference of the Schrödinger equations for nuclear motion in the ground and excited electronic states, and the Hermitian property of the vibrational Hamiltonian. The effect of anharmonicity can be accounted for by perturbation theory [69, 70, 71] or using a variational approach [72]. One of the most critical step in this new procedure is the truncation of the vibrational basis set for the excited electronic state. This basis set must contain all functions necessary to obtain accurate FC factors, but must also be small enough for the calculations to be efficient. The algorithm used involves an iterative build-up of the basis set by increasing the range of vibrational quantum numbers while, simultaneously, removing unnecessary functions [71].

V. DENSITY FUNCTIONAL THEORY AND ITS CATASTROPHE WHEN APPLIED TO LINEAR AND NONLINEAR OPTICAL PROPERTIES

As discussed in Section II, electron correlation effects play a key role in estimating the polarizabilities and hyperpolarizabilities. In the middle of the 90's density functional theory (DFT) — in combination with conventional gradient-corrected and hybrid exchange-correlation (XC) functionals — was already recognized as a very powerful technique to estimate structural and electronic properties as well as reaction mechanisms. In addition, several reports had already demonstrated that DFT shows some potential to describe linear and nonlinear optical properties (See for instance [73, 74, 75, 76, 77]).

Looking for an accurate and fast method to describe rather large oligomers, Bernie initiated a project on using DFT for NLO calculations in large $\pi$-conjugated systems. First, several DFT schemes were employed in order to describe the longitudinal polarizability and second hyperpolarizability of polyacetylene chains, including a broad range of XC functionals with and without asymptotic corrections [65]. It was concluded that these conventional XC functionals fails in several ways: 1) the correlation effect on the polarizability is either too small or goes in the wrong direction, 2) the second hyperpolarizability is significantly overestimated, 3) the chain length dependence is excessive, and 4) the bond length alternation effects are either underestimated or even qualitatively incorrect. It was also pointed out that these overestimations of $\alpha$ and $\gamma$ are not related to the asymptotic behavior of the potential but are related to the short-sightedness of the XC potentials which are relatively insensitive to the polarization charge induced by the external electric field at the chain ends.

In a subsequent study dealing with push-pull $\pi$-conjugated systems [67], it was shown that the DFT failures observed for $\alpha$ and $\gamma$ of polyacetylene chains are not only reproduced but are also extended to the evaluation of $\mu$ and $\beta$. In particular, an almost catastrophic behavior with respect to increasing chain length is found for $\beta$ (Fig. 7). Again, an incomplete screening of the external electric field is responsible for the large discrepancies with respect to accurate values. These results further show that current XC functionals incorrectly describe the polarization of conjugated systems when the polarization is due either to donor/acceptor substitution or to an external field or both. These facts puzzled a large number of DFT aficionados.

This incorrect behavior was shown to find its origin in the Kohn-Sham DFT, of which the exchange potentials do not
FIGURE 7. Evolution of the longitudinal first hyperpolarizability per unit cell, $\beta_L(N)/N$, of NH$_2$-(CH=CH)$_N$-NO$_2$ as a function of the number, $N$, of CH=CH units for different methods. Left) MP2/6-31G geometry and 6-31G properties; Right) bottom : AM1 geometry with STO-3G properties (RHF values multiplied by a factor of 10). From [67].

FIGURE 8. Constituent parts of the KLI potential of (H$_2$)$_9$ in an electric field with a 6-311++G** basis. The H atoms are at alternating distances of 2 and 3 au (central pair at ±1.0 au). It demonstrates that the SIC-free X-only KLI functional displays in the response part of the exchange functional a linear term counteracting the applied electric field. From [66].

exhibit the correct $-1/r$ long-range asymptotic behavior (using hybrid DFT, only fractions of this correct behavior are accounted for) while it does not provide an exact cancellation of self-interaction terms. These drawbacks have been further traced back to an incorrect electric field dependence of the response part of the exchange potential in local and gradient-corrected density approximations, which lacks a linear term counteracting the applied electric field [66]. On the other hand, using an exact X-only functional, this ultra non-local component of the response part is reproduced (Fig. 8), showing directions of improvements for new XC functionals.
One of these approaches consists in using the optimized effective potential (OEP) for exact exchange (EXX) developed by Yang and co-workers [78, 79], where the unknown part of the effective potential is expressed as a linear combination of Gaussian functions. The performance of this method, which includes ultranonlocal exchange effects through a local potential, was addressed for calculating the dipole moment and static (hyper)polarizabilities of the prototypical D/A \( \pi \)-conjugated systems, NO\(_2\) – (CH\(=\)CH)\(_n\) – NH\(_2\) [80]. Doing so, a good agreement with the HF values was found for \( \mu \), \( \alpha \), \( \beta \), and \( \gamma \) and, in particular, the OEP-EXX results reproduce the expected chain length dependence of the first hyperpolarizability per monomer unit. Nevertheless, there remains a significant correlation error while these results already show the need to develop better basis sets for representing the EXX potential. These OEP-EXX studies were then extended to the evaluation of the polarizability and second hyperpolarizability of polydiacetylene (PDA) and polybutatriene (PBT) chains, using various conventional gaussian basis sets for the exchange potential [81]. Comparing these results to reference CPHF calculations and to \textit{ab initio} correlated values, it turned out that (i) small conventional basis sets do not, in general, adequately represent the exchange so that \( \alpha \) and \( \gamma \) are either underestimated or overestimated while the chain length dependence of their values per unit cell is incorrect (Fig. 9); (ii) the performance of a given X-basis set depends on the MO basis and is generally improved when using a larger MO basis; (iii) these effects are exaggerated for \( \gamma \) compared to \( \alpha \); and (iv) in the limit of a complete X-basis set, the results suggest that the OEP-EXX values may approach the CPHF data. Moreover, using standard AO basis sets for the X-basis leads to a degradation in quality when the system’s length increases, which is consistent with the fact that the number of functions in the X-basis becomes a smaller fraction of the number required to reproduce exactly the finite-basis-set HF energies with OEP. These observations also led to the conclusion that owing to its sensitivity to details of the X potential, electric field responses pose very stringent tests for the quality of functionals and potentials.

Another way of improving the conventional DFT schemes is by means of the partitioning technique, introduced by Savin and co-workers [82], where the electron repulsion operator is divided into short- and long-range parts using the standard error function,

\[
\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}},
\]

where \( \mu \) is a parameter that determines their ratio. The X functional is, then, obtained by using the long-range part in the HF exchange expression, while the short-range part modifies a conventional DFT exchange potential. Among the different available versions, the long-range correction (LC) scheme of Hirao and co-workers (\( \mu = 0.33 \), BLYP) [83] was applied to determine the polarizabilities and second hyperpolarizabilities of polydiacetylene and polybutatriene oligomers [84]. In comparison with coupled-cluster calculations including single and double excitations as well as a perturbative treatment of triple excitations, the results indicate that (i) the tendency of conventional functionals to result in a catastrophic overshoot for these properties is alleviated but not fully eliminated, (ii) for \( \alpha \), both LC-BLYP and CPHF overshoot the reference CCSD(T) value, and (iii) for \( \gamma \), LC-BLYP overshoots the reference while CPHF undershoots it (Fig. 10). It is important to highlight the fact that Møller-Plesset second-order perturbation theory method (MP2) yields improved values for \( \alpha \) but not for \( \gamma \). Thus, no clear-cut preference for LC-BLYP over Hartree-
VI. THE VECTOR-POTENTIAL APPROACH

As discussed in Sec. II, of central interest to Bernie Kirtman has been the determination of properties of large systems, whereby very many of his studies have focused on conjugated polymers. These systems are regular, extended ones, meaning that they contain a large number of periodically repeated, identical building blocks (unit cells) and that at most near the ends deviations from this regularity occur. Since his interest has concentrated on those that are extended in only one dimension (i.e., quasi-one-dimensional chain compounds), we shall do so here, too. The approach we shall discuss in this section can, however, be extended to higher dimensions. Thus, we shall consider some property, $Z$, that depends on the number of building blocks, $N$, so that for $N \to \infty$, $Z(N)$ is proportional to $N$. From finite-chain calculations we may determine the thermodynamic limit through, e.g.,

$$\bar{Z} = \lim_{N \to \infty} \frac{Z(N)}{N} = \lim_{N \to \infty} \frac{1}{\Delta N} \left[ Z(N) - Z(N - \Delta N) \right].$$

(13)

In some cases this limit is first reached for values of $N$ that are so large that it may be useful instead to consider infinite, periodic systems directly. Then, for many properties $Z$ the values of $\bar{Z}$ can be extracted fairly simply from conventional band-structure calculations on (in our case) infinite, periodic chains. This is, however, not the case for $Z$ being the linear or non-linear response to electromagnetic fields, whereby we here shall concentrate on the responses to electrostatic (DC) fields. In that case, $Z$ corresponds to the static polarizabilities and hyperpolarizabilities.

In the general case, the presence of a (time-dependent or -independent) electromagnetic field is described through both a scalar potential $V(\vec{r})$ and a vector potential $\vec{A}(\vec{r})$. These are, however, not unique so that by changing $V(\vec{r})$ and $\vec{A}(\vec{r})$ simultaneously (i.e., varying the gauge) the effects of the field on the system of interest remain unchanged. In the special case of the external field being an electrostatic one this leads to the special situation that one may choose either $V(\vec{r}) = 0$ or $\vec{A}(\vec{r}) = \vec{0}$ (also other choices are possible that here, however, are irrelevant).

In a collaboration with Feng Long Gu and the late David Bishop, Bernie Kirtman considered the case of an infinite, periodic chain exposed to an electrostatic field [85, 86]. In their so called vector-potential approach they set $V(\vec{r}) = 0$. They considered the complicated case that the field was parallel to the chain axis, whereas field components perpendicular to this axis can be trivially treated. They could show that the presence of the DC field did not destroy the translational symmetry so that any electronic orbital could be written as

$$\psi_j(k,\vec{r}) = e^{ikz}u_j(k,\vec{r}),$$

(14)
with $j$ being a band index and $u_j(\vec{r})$ a function that has the lattice periodicity. Moreover, by expanding the wavefunctions in Eq. (14) in Bloch waves from atom-centered basis functions,

$$
\Psi_j(k, \vec{r}) = \sum_p C_{pj}(k) \chi_p(k, \vec{r}),
$$

$$
\chi_p(k, \vec{r}) = \frac{1}{\sqrt{K}} \sum_l e^{ikl} \chi_{lp}(\vec{r})
$$

with $\chi_{lp}$ being the $p$th basis function of the $l$th unit, they could show that the unknown coefficients $C_{pj}(k)$ satisfy the equations

$$
\left\{ \frac{\mathcal{F}(k) - E_{DC}}{E_{DC}} \cdot \left[ M(k) + iS(k) \frac{\partial}{\partial k} \right] \right\} C_j(k) = \varepsilon_j(k) \cdot S(k) \cdot C_j(k)
$$

where $E_{DC}$ is the strength of the electrostatic field. Moreover, $C_j(k)$ is the (field-dependent) $j$th column of the matrix $\equiv(k)$, and

$$
S_{qp}(k) = \sum_l e^{ikl} \langle \chi_0| \chi_p \rangle,
$$

$$
M_{qp}(k) = \sum_l e^{ikl} \langle \chi_0| z - l a| \chi_p \rangle = \sum_l e^{-ikl} \langle \chi_0| z| \chi_{lp} \rangle,
$$

$$
F_{qp}(k) = \sum_l e^{ikl} \langle \chi_0| \mathcal{F}| \chi_{lp} \rangle
$$

are the overlap, unit cell dipole, and Fock or Kohn-Sham matrix elements, respectively. They assumed that the many-particle wavefunction could be written as a single determinant, i.e., that either the Hartree-Fock approximation is valid or that the density-functional formalism in the formulation of Kohn and Sham is used.

The direct effects of the DC field are contained in the second term on the left-hand side of Eq. (16), although indirect effects occur, too, since the matrix elements of $\mathcal{F}(k)$ depend on the coefficients $C_j(k)$.

Starting with Eq. (16) one may now follow two different approaches. In one, the effects of the DC field are treated perturbatively, although it is taken into account that the coefficients $C_j(k)$ depend on the presence of the field. This leads to the so called coupled-perturbed Hartree-Fock (CPHF) or coupled-perturbed Kohn-Sham (CPKS) approaches. In the original work, this was the approach taken by Bernie Kirtman and coworkers [85, 86].

However, one problem remains. Eq. (16) is solved for each $k$ point separately, meaning that the coefficients $C_j(k)$ may contain phase factors that depend on $j$ and $k$ and that may vary essentially randomly as a function of $k$. Therefore, the derivatives of the coefficients $C_j(k)$ with respect to $k$ (that are required in Eq. (16)) may be numerically ill-behaved. Bernie Kirtman and coworkers suggested writing

$$
\frac{\partial}{\partial k} C_j(k) = \equiv(k) \cdot C_j(k),
$$

and derived equations from which the elements of $\equiv(k)$ largely could be determined. The approach is, however, not easy to use and parts of $\equiv(k)$ remain unknown, whereby a later development (see below) may be a useful alternative.

Eq. (16) offers also a possibility of calculating the responses of the extended systems to the DC field directly. This was the approach that has been followed by Bernie Kirtman, Michael Springborg, Yi Dong, and Violina Tevekeliyska. In their first work [87] they established the connection with the scalar-potential approach. For a finite system and using that gauge, $\tilde{A}(\vec{r}) = 0$ whereas the scalar potential becomes $\tilde{E}_{DC} \cdot \vec{r}$. In the presence of the electrostatic field the total energy is given as

$$
\varepsilon_{tot} = \langle \Psi| \hat{H}_{tot}| \Psi \rangle = \langle \Psi| \hat{H}_{tot,0}| \Psi \rangle + \tilde{E}_{DC} \cdot \vec{\mu}_{tot}.
$$

Here, $\hat{H}_{tot}$ and $\hat{H}_{tot,0}$ is the total Hamilton operator of the electrons and the nuclei of our system with and without the external field, respectively. Moreover,

$$
\vec{\mu}_{tot} = \int \rho_{tot}(\vec{r}) d\vec{r} \equiv \vec{\mu}_n - \vec{\mu}_e
$$

is the dipole moment of the system that has been split into a nuclear and an electronic part.

For the macroscopic system the dipole moment per unit cell becomes the polarization,

$$
\lim_{N \to \infty} [\vec{\mu} / N] = \vec{P} = \vec{R}_n - \vec{P}_e,
$$

where $\vec{P}_e$ is the electric field of the external field.
where the polarization $\vec{P}$ has been split into one contribution from the nuclei and one from the electrons. Together with Michael Springborg and Yi Dong, Bernie Kirtman could show that when the macroscopic system is treated as being infinite and periodic, the definition of $\vec{P}$ becomes non-trivial. Several approximate forms were possible that all become identical in the limit of an infinite number of $k$ points, $K$, in the $k$ space sampling. Of those were expressions that earlier have been proposed within the so called modern theory of polarization [88, 89, 90, 91], including

$$P_e = P_{KSV} = \frac{2i}{K} \sum_{k=1}^{K} \sum_{j=1}^{B} \langle u_j(k) \rangle \frac{\partial}{\partial k} u_j(k).$$  \hspace{1cm} (22)

Here, $B$ is the number of doubly occupied bands and we assume that there is a gap between occupied and empty orbitals. Subsequently, Bernie Kirtman and Michael Springborg together with their coworkers demonstrated [92, 93, 94, 95, 96] that with this expression for the dipole moment per unit cell in Eq. (19), expanding the electronic orbitals according to Eq. (15), and applying the variational principle result in the secular equation Eq. (16), i.e., the same as obtained with the vector-potential approach.

One importance consequence of this work is that it offers an expression for the total energy in the presence of the electrostatic field. From this, Bernie Kirtman and Michael Springborg derived closed, analytical expressions for the derivatives with respect to structural parameters, making automatic structure optimization possible [95].

Bernie Kirtman and Michael Springborg offered an alternative way of treating the $k$ derivatives in Eq. (16), i.e., the terms $\frac{\partial}{\partial k} C(k)$ [94]. At first, since Eq. (16), as it stands, is not a standard matrix eigenvalue problem (due to the $k$ derivatives), they transformed it into a such by using that

$$\mathbf{1} = \mathbf{C}^\dagger(k) \cdot \mathbf{S}(k) \cdot \mathbf{C}(k) \hspace{1cm} (23)$$

so that

$$\mathbf{S}(k) \frac{\partial}{\partial k} \mathbf{C}(k) = \left[ \mathbf{S}(k) \left( \frac{\partial}{\partial k} \mathbf{C}(k) \right) \mathbf{C}^\dagger(k) \mathbf{S}(k) \right] \mathbf{C}(k). \hspace{1cm} (24)$$

Then, just as the $E$ matrix, the expression in the square brackets can be treated self-consistently.

Second, in order to treat the numerical problems related to the essentially random $k$ and band ($j$) dependent phase factors of $C(k)$ they proposed a numerical smoothing procedure. This is based on adding extra phase factors to the orbital expansion coefficients,

$$C_{qj}(k) \rightarrow C_{qj}(k) e^{\phi_j(k)}. \hspace{1cm} (25)$$

In a multi-step procedure, the phases are optimized by minimizing (for each band, $j$, separately)

$$Q_j = \sum_i \sum_q \left| C_{qj}(k+\Delta k) e^{i\phi_j(k+\Delta k)} - C_{qj}(k) e^{i\phi_j(k)} \right|^2 + \lambda \sum_i \sum_q \left| C_{qj}(k+2\Delta k) e^{i\phi_j(k+2\Delta k)} - C_{qj}(k) e^{i\phi_j(k)} \right|^2 \hspace{1cm} (26)$$

under the constraint

$$\phi_j(-\frac{\pi}{a}) = \phi_j(\frac{\pi}{a}) \hspace{1cm} (27)$$

and with $\phi_j(0)$ fixed. $\lambda = 0.1$ was found to be a good choice.

Subsequently, the derivatives of the orbital expansion coefficients with respect to $k$ are calculated numerically using

$$\frac{\partial C_{qj}(k)}{\partial k} \simeq \frac{1}{\Delta k} \sum_{n=1}^{N_k} w_{n,q} \left[ C_{qj}(k + n \cdot \Delta k) - C_{qj}(k - n \cdot \Delta k) \right] \hspace{1cm} (28)$$

with

$$C_{qj}(k + 2\pi/a) = C_{qj}(k). \hspace{1cm} (29)$$

The coefficients $\{w_{n,q}\}$ are taken from Dvornikov [97].

This approach allows for treating an infinite, periodic system exposed to an electrostatic field self-consistently and, what is important, both electronic and structural responses are included. So far, the approach has been tested and applied only for model systems, but it is currently being implemented into ab initio program packages.

The vector-potential approach that Bernie Kirtman, together with several collaborators, has been developing over the years has turned out to also provide interesting information about finite systems, see, e.g., [98]. Bernie Kirtman
and colleagues have also analyzed the possibility to obtain information of the (electronic and structural) responses of extended, periodic systems to DC fields by exposing the infinite, periodic system to a field with a different shape (i.e., a piece-wise linear potential) [99]. They found that this, in principle, was possible, although not all responses were accessible and, moreover, the computational requirements were significantly larger than those required for treating a long, finite system exposed to the true external potential and orders of magnitude slower than the vector-potential approach.

VII. CONCLUSIONS

In this contribution we have summarized some of the results of our collaborations with Bernie Kirtman. The results are first of all of methodological and fundamental nature, emphasizing that part of the work of Bernie Kirtman that has been devoted to the development, improvement, and understanding of new theoretical methods. To demonstrate that Bernie Kirtman also has been strongly active in applying quantum chemical methods to determine specific properties of specific materials has been given only second priority in this presentation. We emphasize that this is solely due to the personal interests and interactions of the present authors with Bernie Kirtman and does not reflect any attempt of ranking the contributions of Bernie Kirtman.

Very many results have been obtained by Bernie Kirtman and we, as many others, are happy to learn from Bernie Kirtman and to use his results. There are, however, still many open issues that require his active participation (see, for instance, [96] for the case of the vector-potential approach) and we, therefore, look forward to continue the collaboration with him.

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A Quantum Chemical Approach To The Molecular Conductance Problem

Augusto César L. Moreira and Celso P. de Melo

Departamento de Física - Universidade Federal de Pernambuco
50.670-901 Recife – PE - Brazil

Abstract. We will present two alternative methods to deal with the molecular conductance problem by taking into account crucial aspects that determine the electronic flow of charge throughout the entire system, such as the internal structure of the molecule and the size of the electrodes that effectively participate of the localized interaction. In the first, when a weak coupling exists between the electrodes and the molecule, we divide the overall electron transfer between the two electrodes in three sequential steps: a) tunneling from (to) left electrode to (from) the molecule, b) an intra-molecular transition and c) tunneling from (to) right electrode to (from) the molecule, and describe the metal-molecule junction within the Wentzel-Kramers-Brillouin (WKB) approximation. In the second approach, for the case of strongly coupled sub-systems, we adapted Kirtman & de Melo’s Local Space Approximation (LSA) to the description of the molecular conductance problem. We then start with three isolated (i.e., non-interacting) subsystems: $C_1$ (left electrode), $M$ (molecule) and $C_2$ (right electrode), each one of them described by their first order density matrix, $R^{C_1}$, $R^M$ and $R^{C_2}$, respectively. The LSA preserves the idempotency of the self-consistent density matrix ($R^{(n)}$) in the entire system while restricting the self-consistent problem to the dimensions of the local space. Our for the current and for the corresponding conductance curve are in general good qualitative agreement with the available experimental data and the oscillating fine structure observed in the experimental curves can be associated to specific intramolecular interactions.

In the last decade, molecular electronics (molelectronics) has experienced a renewed interest [1-2] not only as a contending post-silicon technology, but also due to significant advances in the art in fabricating organic devices by sandwiching organic molecules between metallic electrodes [3]. Although these molecular structures prepared by techniques such as Scanning Tunneling Microscopy (STM), Mechanically-Controlled Break Junctions (MCBJ) and Junctions with Self-Assembled Sandwiched Organic Layers [4] are still a far cry from real operating devices, some general results revealing the intrinsic role played by the sandwiched molecules can now be summarized: long molecules have lower conductance than shorter molecules of the same kind, conjugated molecules have higher conductance than non-conjugated molecules, and molecules with structural asymmetry exhibit asymmetric current-voltage characteristics.

From the theoretical point of view, the calculation of molecular conductance falls in the general class of “embedding” problems, which are very difficult to handle. In this class of systems, the local characteristics of a molecule chunk connected to a larger “electronic bath” must dominate the overall response of the entire electronic manifold. In this manner, since the surrounding bath (the metallic electrodes in the molelectronics case) provide active long range charge flow pathways, finite-sized molecular approaches fail to convey all the physical information about the system. On the other hand, advances in the realistic description of the large embedding medium are hampered by the need to include the local electronic interactions in the molecular chunk, which break any relevant symmetries existing in the external region. Such is the case of many solid-state derived theoretical models for understanding electrical transport through very small structures (molecules for example), such as the Landauer-Buttiker model (conductance from transmission), and non equilibrium Green’s function and scattering approaches [5-6], which have to assume a ballistic regime or a resonant condition to the charge transfer through the molecule. Also, hybrid formalisms that mix quantum chemistry approaches (such as Huckel, DFT or HF) with the above cited solid–state models [7-8] have to rely in the artificial hypothesis of charge conservation in the molecular region when dealing with its coupling to the external electrodes.

From a molecular point of view, the main limitation of such methods resides in the fact that they tend to treat the local system of interest (a molecule for example) as a “structureless” black box that acts passively during the charge
transport process, offering channels for the electronic flow but no actual participation of their internal features in the process. A second limitation, which we intend to deal in its proper time, is concerned with size restrictions of the electronic reservoirs that interact with the local region.

In this work we propose two alternative methods to take into account these two crucial aspects of the molecular conductance problem: the internal structure of the molecule of interest and the size of the electrodes that is relevant for the resulting interaction. We will initially consider that in a regime of weak coupling between the electrodes and the molecule, the overall electron transfer between the two electrodes can be divided in three sequential steps: a) tunneling from (to) left electrode to (from) the molecule, b) an intra-molecular transition and c) tunneling from (to) right electrode to (from) the molecule. Processes involving the electrodes are described within the Wentzel-Kramers-Brillouin (WKB) approximation [9]. In all steps, the energy and the wave function of the corresponding molecular structure (i.e., neutral, anionic or cationic states) are considered as functions of the intensity of the external electric field. All relevant parameters are taken using Gaussian package [10] at the DFT level. At the end of the detailed balance description of all charge transfer processes we are able to discriminate between the (“resistive”) pathways leading to effective electronic flow between the electrodes and those (“capacitive”) contributions where the main resulting effect is the molecular polarization of the electrodes. For this weak coupling regime, our theoretical results for the current across a molecule of benzenedithiol (BDT) and for the corresponding conductance curve are in general good qualitative agreement with the available experimental data (Fig. 1). Even the oscillating fine structure observed in the experimental curves is present in our theoretical results: moreover, a specific intramolecular interaction can be associated to each one of the existing “wiggles”.

As a second approach, for the case of strongly coupled sub-systems, we adapted Kirtman & de Melo’s Local Space Approximation (LSA) [13] to the description of the molecular conductance problem. We then start with three isolated (i.e., non-interacting) subsystems: \( C_1 \) (left electrode), \( M \) (molecule) and \( C_2 \) (right electrode), each one of them described by their first order density matrix, \( R^L \), \( R^M \) and \( R^R \), respectively. Once the interaction between the
sub-systems is switched on, our goal is to determine \( (R^{(n)})_L \), the projection into the local space of the self-consistent density matrix \( (R^{(n)}) \) of the entire system after \( n \) iterations. The local space is defined as the set of orbitals belonging to either the molecule or to the atoms in each electrode that play the most relevant role in the electronic interaction among the three sub-systems. (Eventually, after an initial guess, the most convenient size of the local space will be determined as a compromise between the quality of the converged results and computational time.) The fundamental property of any bona fide first-order density matrix \( R \) is that it must be idempotent, i.e., \( R^2 = R \). As long as the idempotency condition and the relation \( \text{tr}(R) = N \), where \( N \) is the total number of electrons in the entire combined system, are preserved along the successive self-consistent iterations, one can be assured that a realistic description of the electronic flow throughout the interacting sub-systems is maintained. The local space approximation preserves the two above conditions while restricting the self-consistent problem to the dimensions of the local space. We will present preliminary results of the LSA treatment applied to the calculation of the conductance of symmetric (benzene) and asymmetric (nitrobenzene and aniline) molecules connected to two metallic electrodes (each one represented by a small cluster of atoms of gold) by thiol (SH) groups. The main features of the current and conductance curves as a function of the intensity of the applied electric field are correctly reproduced.

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The Aplicability Of The HSAB Principle

Miquel Torrent-Sucarrat

Departament de Química Biológica i Modelització Molecular. IQAC – CSIC.
c/ Jordi Girona 18, E-08034 Barcelona, Spain.

Abstract. In a very recent article (Chem. Eur. J. 14, 8652-8660 (2008)), the present author has shown that the picture of the local softness and local hardness is incomplete and that the understanding of these reactivity indices must be “redefined”. In fact, the local softness and hardness contain the “same potential” information and they have to be considered as “local abundance” or “concentration” of their corresponding properties. In this contribution, we will analyze the implications in the applicability of the local version of the HSAB principle.

Keywords: Density Functional Theory - hard/soft acid/base (HSAB) principle - hardness - softness.


INTRODUCTION

Density functional theory based reactivity descriptors provide a powerful framework to explain and predict the reactivity and regioselectivity of molecular systems.1-3 The global hardness and softness and the associated hard/soft acid/base (HSAB) principle4,5 have been used to explain many experimental observed reactivity patterns and these concepts can be found in textbooks of general, inorganic, and organic Chemistry. The global hardness, \( \eta \), given as the second derivative of the Energy, \( E \), with respect to the number of electrons, \( N \), at constant external potential, \( \nu(r) \), represents the resistance of a chemical species to change its electronic configuration, see Eq. (1). The global softness, \( S \), is simply the multiplicative inverse of the global hardness.

\[
\eta = S^{-1} = \left( \frac{\partial^2 E}{\partial N^2} \right)_{\nu(r)} .
\]  

The two most popular operational equations of the global hardness and softness are obtained applying the finite difference approximation

\[
\eta = S^{-1} \equiv I - A
\]  

and introducing Koopmans’ theorem

\[
\eta = S^{-1} \equiv \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} .
\]

Here \( I \) and \( A \) are the first vertical ionization potential and electron affinity of the reference \( N \)-electron system in most cases a neutral molecule, respectively, and \( \varepsilon_{\text{HOMO}} \) and \( \varepsilon_{\text{LUMO}} \) are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. These indices are considered as global descriptors, which describe the characteristic of a molecule as a whole. To explain the
preferential site for a chemical reaction, a local HSAB principle was proposed and the local counterparts of softness and hardness were introduced: local softness, \( s(\vec{r}) \), and hardness, \( \eta(\vec{r}) \).

\[
s(\vec{r}) = \left( \frac{\partial \rho(\vec{r})}{\partial \mu} \right)_{V(\vec{r})} = \left( \frac{\partial \rho(\vec{r})}{\partial N} \right)_{V(\vec{r})} = f(\vec{r})S \quad \text{and} \quad \eta(\vec{r}) = \int \frac{\delta^2 F[\rho(\vec{r})]}{\delta \rho(\vec{r}) \delta \rho(\vec{r})} f'(\vec{r}')d\vec{r}' = \int \eta(r, r')f'(r')d\vec{r}' = f(\vec{r})H,
\]

where \( f(\vec{r}) \) is the Fukui function, a normalized function, which measures the propensity of a reagent to accept (or donate) electrons from (to) another chemical system, and \( \eta(\vec{r}, \vec{r}') \) is the hardness kernel, the second functional derivative of the universal Hohenberg-Kohn functional, \( F[\rho(\vec{r})] \), with respect to the density.

In contrast to the global HSAB principle, the quantitative representation of the local HSAB principle has not been an easy task. In 1968 Klopman proposed that the soft-soft interactions are frontier-controlled and predominantly covalent in nature. Then the preferred site of the molecule to react in a soft-soft interaction is the region with the maximum value of \( s(\vec{r}) \). On the contrary, the conditions for the charge-controlled and ionic in nature hard-hard interactions are not so clear in the literature and even contradictory results are obtained. Li and Evans propose that hard systems show preferential reactivity at the site where \( s(\vec{r}) \) is a minimum. However, Chattaraj and collaborators argue that hard-hard interactions are predominantly ionic in nature and charge-controlled and that for these reactions the preferred site is the one with maximum net charge, in certain cases coinciding with the site with the minimum value of the Fukui function.

In a very recent article, the present author shows that the largest values of the \( s(\vec{r}) \) and \( \eta(\vec{r}) \) do not necessarily correspond to the softest and hardest regions of the molecule, respectively. Moreover, it was displayed that the only acceptable interpretation for the local softness and local hardness is that these functions are pointwise measures of the “local abundance” or “concentration” of the corresponding global quantities. In this framework, \( s(\vec{r}) \) and \( \eta(\vec{r}) \) contain the same potential “information” and they become more general, because they can be applied both to hard and soft systems. In a soft system \( s(\vec{r}) \) and \( \eta(\vec{r}) \) both describe the soft site of the molecule, while in a hard system \( s(\vec{r}) \) and \( \eta(\vec{r}) \) both describe the hard site of the molecule. In this contribution, we analyze the implications of this new point of view in the applicability of these well-know descriptors and the repercussions in the local version of the HSAB principle.

**COMPUTATIONAL DETAILS**

All calculations were carried with 6-31+G(d) basis sets at the B3LYP level using the Gaussian03 package. The local softness and hardness can be evaluated through Eqs. (4) and (5), but some approximations have to be applied. As we have done in previous articles, the hardness kernel has been approximated using the second order derivative of the Coulombic-Thomas-Fermi-1/9th Weizsäcker-Dirac-Wigner functional with respect to the density, while the density of the HOMO orbital has been used to approximate the Fukui function. Finally, the global softness has been calculated with Eq. (3).

**RESULTS AND DISCUSSION**

Melin et al. studied the protonation reaction of hydroxylamine (NH$_2$OH) and thiohydroxylamine (NH$_2$SH) systems using different condensed Fukui functions and charges. Experimental results show that in these two amines the nitrogen is the most susceptible site to be protonated. According to the rule of Li and Evans that the hard reactions tend to occur at the site with smallest Fukui functions, i.e. the smallest local softnesses, the protonation of NH$_2$OH and NH$_2$SH must to be in the oxygen and nitrogen atoms, respectively, see Figures 1a and 1c. For this
reason Melin et al. proposed that a better description of the preferred site of protonation reaction is obtained with the charges than the Fukui functions.

![Figure 1](image-url)  
**FIGURE 1.** Three-dimensional contour plots at B3LYP/6-31+G(d) level of a) $s(r)$ (0.01 a.u.) and b) $\eta(r)$ (0.5 a.u.) for the hydroxylamine molecule and c) $s(\bar{r})$ (0.01 a.u.) and d) $\eta(\bar{r})$ (0.5 a.u.) for the thiohydroxylamine molecule.

The $s(r)$ and $\eta(r)$ are pointwise measures of the local abundance of $S$ and $\eta$, respectively. Thus, the only information that one can obtain from Figure 1 is that the global hardness and softness of NH$_2$OH is mainly due to the nitrogen atom, while the sulfur is the responsible for $\eta$ and $S$ of NH$_2$SH. In fact, the operational equations of the global hardness and softness, see Eqs. (2) and (3), can be more or less considered as molecular orbital control, because they involve first vertical ionization potential and electron affinity and the energies of the HOMO and LUMO. Then, it is clear that $s(r)$ and $\eta(r)$ can only predict orbital control reactions and they can not be used to predict the protonation site of these amines. Moreover, we can affirm that $s(r)$ and $\eta(r)$ can not describe any charge control process; because they have not been designed to explain these reactions.

It is worth noting that these results complement the idea that $s(r)$ and $\eta(r)$ contain the same potential information and as we have already seen they have important implications in the HSAB principle, which can be summarized in the three following conclusions:

a) The HSAB principle can be considered to be applicable mainly to molecular orbital control interactions and they can be described by $\eta$ and $S$ and the corresponding concentration descriptors, $\eta(\bar{r})$ and $s(r)$, respectively.

b) The HSAB interactions will occur at the maxima of the Fukui function, indistinctly if they are soft-soft or hard-hard interactions.
c) If a reaction is a charge controlled, it cannot be described by $\eta$, $S$, $\eta(r)$, and $s(r)$ as descriptors and it cannot be discussed on the basis of the HSAB principle.

The fact that $\eta$ and $S$ are traced back to a molecular orbital picture and the request that $\eta$ fits into the HSAB principle has an important effect on the applicability of this principle, because it eliminates the role of electrostatic interactions. Another possible solution of this problem is to consider that the hard-hard charge controlled reactions are also included in the HSAB principle. However the definition of global hardness, see Eq. (1), in this situation is incomplete and should to be redefined, because it doesn’t include the electrostatic effect. In fact, this solution is analogous to consider a linear combination of different reactivity descriptors, whose weights will change in function if we are describing a soft-soft or a hard-hard interaction, to describe the regioselectivity of the systems. Both solutions of the problem are correct and it is difficult to say, which one is the best.

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Band Structure of Polymer Extracted from Oligomer Calculations by Elongation Method and Its Applications to Nanosystems

Anna Pomogaeva,1 Michael Springborg,2 Bernard Kirtman,3 Feng Long Gu,4 and Yuriko Aoki 5

1Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Science, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
2Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, German
3Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106-9510, U.S.A.
4Center for Computational Quantum Chemistry, South China Normal University, Guangzhou, 510631 China
5Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University, 6-1 Kasuga-Park, Kasuga, Fukuoka 816-8580, Japan; Japan Science and Technology Agency, CREST, 4-1-8 Hon-chou, Kawaguchi, Saitama 332-0012, Japan

Abstract. A method developed for building band structure of polymer from elongation oligomer calculations has been applied for studying electronic structures of nanoscaled periodic systems. Band structures of single-walled (4,4) carbon and boron nitrogen nanotubes have been built at different levels of approximations. This method also has been applied for band structure construction of molecular systems where periodicity is disturbed by presence of local defects.

Keywords: Band structure, oligomer, nanotubes, local defect
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INTRODUCTION

Nowadays, extended crystalline systems, until recently the field of solid-state physics, have also become more and more important subject of the rapidly growing interest of computational chemistry. Molecular crystals, nanotubes, biopolymers, periodic supramolecular associations are matter of numerical investigations and find many advanced applications. However, the conventional crystal orbital (CO) method which applies Born von Karman periodic boundary conditions (PBC) confronts certain difficulties being applied for studying periodic systems with large unit cell [1]. These include quasi-linear dependencies (especially with large basis sets), which are connected to the slow convergence behavior and proper treatment of long-range coulomb interactions, especially if a unit cell model as a linear combination of atomic orbitals (LCAO) is more preferable for chemical bonding analysis. Furthermore, even though CO method is well suited for treatment of ideal crystal, it is difficult to treat systems with any local distortion or substitution, where extended unit cells are required [2].

From the other hand, if a finite periodic cluster is rather long, molecular type of calculations should reflect its periodic character. For example, the Elongation Method (EM) [3] designed for time-saving accurate quantum-chemical calculations, allows to obtain electronic structure of polymers consisted from hundreds of atoms [4]. Recently developed method [5] of building electronic band structures basing on finite oligomer calculations in the modification tuned for using along with the EM [6], could be applied for studying pure periodic nanoscale systems as well as systems with any local defects of periodicity. The present research proposes the method and its applications for such big quasi-one-dimension systems as different nanotubes. We also present some ideas how to apply this method for studying electronic structure of periodic systems contained local defects.
METHODOLOGY

This method to build band structure is based on extending of treatment of Cui, et al. [7] for assigning a value for the wave vector $k$ to each molecular orbital (MO). The lacks of the original methodology are overcome due to the development of reciprocal space projection technique. In order to identify $k$ from the first Brillouin zone (BZ)

$$k = \frac{q \pi}{M + 1 a}, \quad q = 1, 2, \ldots, M, \quad 0 < k < \frac{\pi}{a},$$  \hspace{1cm} (1)

$q$ is looked for, which maximizes the function

$$R_q = \sum_r \sqrt{(X'_q)^2 + (Y'_q)^2}$$  \hspace{1cm} (2)

where

$$X'_q = \sum_j C_{nj} \sum_{rj} \sin \left( \frac{\pi j q}{M + 1} \right) \langle \chi_j^r \mid \chi_j^{r'} \rangle$$

$$Y'_q = \sum_j C_{nj} \sum_{rj} \cos \left( \frac{\pi j q}{M + 1} \right) \langle \chi_j^r \mid \chi_j^{r'} \rangle$$  \hspace{1cm} (3)

for each calculated MO with $C_{nj}$ LCAO coefficients, where $\chi_j^r$ is the $r$th basis function (AO) of the $j$th unit. The $k$-values assignment allows constructing CO, i.e. Bloch function, from a particular MO. Then, a procedure could be applied that involves matching AO coefficients for relevant pairs of orbitals at two neighboring $k$ values using

$$D_{nn'}(k, k') = \sum_r C_{nr}^{CO*}(k) C_{n'r}^{CO}(k')$$  \hspace{1cm} (4)

where $n$ and $n'$ are the band indices. The band assignment procedure allows not only to distinguish energy bands of a periodic system but also to reduce problems due to the occurrence of so-called doublings and holes.

As important new ingredients the proposed methodology involves the systematic elimination of strongly localized states from wave-vector assignment procedure, which is done by calculating of charge distribution over the chain and treatment of band crossing. Finally, interpolation/extrapolation is used to eliminate weakly localized states and to continue the bands across the entire BZ.

Accommodation of the described procedure for the EM involves some additional steps. The EM does not directly provide conventional MOs but gives a set of localized MOs (LMOs) that are related to the former by a unitary transformation [8]. Thus, to obtain MOs delocalized over the entire chain the back transformations should be done for the very last elongations space [6].

APPLICATIONS

The presented method can provide band structures for polymeric systems with large unit cell using calculations both Hartree-Fock (HF) and Density functional (DFT) methods. It is simple at its base and it requests minimum additional computations to get a physically meaningful picture. In the present research MO calculations were carried out using GAMESS software.
Pure periodic systems: Nanotubes

Being a hot topic in numerical scientific investigations, several decades nanotubes (NTs) are objects of interest of solid-state physicists as well as organic chemists, studied, thereby, from incompatible points of view. In the present research the electronic structures of (4,4) armchair single-walled carbon nanotube (CNT) and boron nitride (BN) NT were studied for 20 units oligomers and one-dimensional band structures were built at different levels of approximation. The interesting point here is that while this CNT is a metallic system with zero band gap, BNNTs are perfect insulators with band gaps around 5.5-6 eV. In Fig. 1 (a) band structure of CNT extracted from conventional oligomer calculations is presented. Our band assignment procedure (Eq. 2) confirms band crossing at the Fermi level. Band structure calculations of BNNT could be done using advantages of the EM. Fig. 1 (b) presents band structures of pure BNNT from elongation oligomer DFT calculations using two different model potentials. In the case of hybrid B3LYP potential our calculated value, 5.96 eV is in good correspondence with experimental values. From the other hand, some previous PBC calculations of small armchair single-walled BNNT have been performed [9] using plane wave basis set and local density approximation (LDA). In fact, replacing B3LYP with LDA functional (Fig. 1(b)) does not alter the band shape (although the band gap is reduced to 4.13 eV). Our results are similar to those recently obtained by Zhang et al. [10] for the (2,2) armchair nanotube using a LDA/plane wave approach.

**FIGURE 1.** Band structure of armchair (4,4) CNT(a) and BNNT(b) extracted from DFT/6-31G calculations of 20 units tubes. Black lines are bands calculated with B3LYP hybrid potential and dashed gray lines are done within LDA approximation.

“Disturbed” band structure.

The most attractive applications for finite cluster approximation are systems where a local defect breaks perfect translation symmetry and prevents from using PBC for such periodic systems. For states of an oligomer weakly disturbed by the presents of local defect, \( k \)-values could be determined by the method presented above and “disturbed” band structure could be extracted. The \( k \)-vector assigned to a one-electron state in this case is actually a quasi-wave vector of a perfectly periodic system, periodicity of which is the closest to our real non-periodic object. Apart from weakly disturbed states, states strongly localized on the defect are presented in electronic structure. No \( k \)-value could be associated with such sates. As a whole, the method proposed here allows us to pick out strongly defect localized states to be analyzed separately and to build a disturbed band structure basing on energy states which keep more or less Bloch character.

In Fig. 2 band structure is presented for trans-polyacetylene (PA) chain with so-called sp\(^3\) defect, where one conventional [CH=CH] unit cell is replaced with one CH\(_2\) unit. Some of the bands (the highest occupied and the lowest unoccupied) are definitely disturbed by the presence of the defect. It looks like they are “broadening” in energy. The other bands are undisturbed and perfectly coincide with the bands of pristine PA. It can be seen that one localized energy level is in the valence region and two levels in the conduction band. Since \( k \)-values are meaningless
for such states, the straight lines mark these states on the band structure diagram. Localized character of these MOs could be seen from the charge distribution shown in the right panel in Fig.2. For comparison the figure shows HOMO and LUMO that are rather delocalized.

In this way, band structure can be built for big realistic systems such as carbon doped BNNTs [6].

**FIGURE 2.** Band structures extracted from HF/STO-3G calculations of oligomers of 27 units of length. Dashed curves are bands of pristine oligomer and circles are of the one contained one sp³ defect in the center. Straight lines mark the energy levels of states localized on the defect. The corresponding localized MOs, HOMO and LUMO for the oligomer with defect are shown.

**CONCLUSIONS**

The method to built band structure from oligomer calculations was successfully applied for metals as well as dielectrics, for pure periodic molecular systems as well as the ones with local defects. The presented method can give advantages over PBC calculations for periodic systems with big unit cells, such as nanotubes or for using large basis set, especially in case of disturbed periodicity. Based on molecular types of calculations the method makes a bridge between different branches of science and pretends to shed some light on important problem of connection between electronic structure of atoms in their isolated atomic state and their state in the condensed matter.

**ACKNOWLEDGMENTS**

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**REFERENCES**

Efficient algorithm for computing orbital energies within elongation method

Oleksandr Loboda*, Feng Long Gu*, Anna V. Pomogaeva*, Marcin Makowski* and Yuriko Aoki†

*Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
†Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan; Japan Science and Technology Agency, CREST, 4-1-8 Hon-chou, Kawaguchi, Saitama 332-0012, Japan

Abstract. We developed a new approach for solving eigenvalue problem for the oligomer chain systems based on localized molecular orbitals (LMO) of the separated fragments within elongation method. The method performed in this work and implemented in elongation scheme yields excellent agreement with the conventional results. It has been demonstrated that the proposed algorithm for computing orbital energies and eigenvectors in elongation method reduces the CPU time usage up to 50%.

Keywords: Fock matrix, eigenvalue problem, elongation method

PACS: 36.20.-r

INTRODUCTION

The elongation method (EM) has been introduced in Ref. [1]. It is proved to be an efficient tool for computing variety of properties of large molecular systems.

The basic idea of EM is to divide the studied system into the subsystems and to treat them separately in a polymer growing manner. At the very beginning of the elongation procedure the conventional HF equation has to be solved for the initial cluster. After SCF is converged the canonical molecular orbitals (CMOs) are transformed in a unitary fashion into set of localized MOs (LMOs) [2].

Localization procedure gives in output two kind of regional LMOs. One of them associates with the frozen region (A) and another with the active region (B). The LMOs from A region are not taken into account in the proceeding elongation steps. In contrast, the LMOs from B region are always used for the interaction with the set of orbitals of attacking cluster (M). The optimized orbitals of B+M region are localized again and new set of LMO orbitals associated with the new A and new B regions is generated. During the elongation process the A region LMOs are kept frozen while the B LMOs along with M AOs of active region are involved in elongation. The graphical sketch of EM is shown in Figure 1.

At every elongation step the SCF equations are solved only in small subspace (B+M) of full variational space, regardless of the total number of atoms in system. The clear advantage of EM is that the eigenvalue problem is solved for active region only. However evaluation of some electronic properties requires the eigenvalue solution for the entire system. Obtaining eigenvectors and eigenvalues for the whole molecular chain would demand time-consuming diagonalization of full Fock matrix.

In the present work we try to minimize the cost of full diagonalization by employing prediagonalized energy matrix based on regional LMOs.

It should be stressed that EM itself does not work directly with CMOs, but proposed in this paper algorithm allows to recover from this condition and to obtain CMOs omitting numerous iterative diagonalization procedures. And it is of great importance to have the CMOs to be able to describe delocalized phenomena, like band structure, low frequency vibrational modes such as lattice vibration, Wannier type excitons etc.
The elongation method with the regional localization scheme as it is implemented in GAMESS program package [3] has been used for \textit{ab initio} treatment with STO-3G basis set. The optimization calculation of structures, used in CPU check, has been done by means of Møller–Plesset perturbation theory with 6-31G(d) basis set. The SCF density convergence criteria has been set up to $10^{-8}$.

**METHODOLOGY**

In order to obtain molecular orbital energies and CMOs of the whole system within EM and to avoid the diagonalization of the full Fock matrix we adopted the following scheme:

$$E(A + B + M) = C_{AO}^{CMO}(A + B + M)F_{AO}^{AO}C_{AO}^{CMO}(A + B + M)$$

where unknown moiety $C_{AO}^{CMO}(A+B+M)$ can be obtained from

$$C_{AO}^{CMO}(A + B + M) = C_{AO}^{LMO}(A + B + M)X(A + B + M)$$

where $C_{AO}^{LMO}(A+B+M)$ is the total LMO matrix which consists of separate LMOs associated with A (frozen region) produced from every elongation step and LMOs of active region from the final step:

$$C_{AO}^{LMO}(A + B + M) = C_{AO}^{LMO}(A)\oplus C_{AO}^{LMO}(A)_{n-1} \oplus C_{AO}^{LMO}(B + M)_n$$

and $X$ is the direct sum of the constituent YYs, where each YY describes unitary transformation from LMO to CMO at every elongation step:

$$YY = C_{AO}^{CMO}SC_{AO}^{LMO}$$

where $S$ is the overlap matrix in AO basis.

**RESULTS AND DISCUSSION**

The obtained energy matrix for linear hydrogen chain ($H_2)_12$ is presented in Table 1.
As one can see this matrix is almost diagonal, though we did not carried out any diagonalization procedures. However there is some admixture of non-zero off-diagonal elements. This stems from the small 'tailing' effect of frozen A region onto active region. As the consequence, the presence of non-zero off-diagonal elements affects the accuracy of diagonal eigenvalues.

The calculated orbital energies from elongation HF and from conventional HF are shown in Table 2

**Table 2. MO energies of (H₂)₁₂ in au.**

<table>
<thead>
<tr>
<th>MO</th>
<th>Elg</th>
<th>Elg*</th>
<th>Conv</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.583972</td>
<td>-0.584593</td>
<td>-0.584592</td>
</tr>
<tr>
<td>2</td>
<td>-0.583610</td>
<td>-0.583675</td>
<td>-0.583675</td>
</tr>
<tr>
<td>3</td>
<td>-0.581893</td>
<td>-0.582471</td>
<td>-0.582469</td>
</tr>
<tr>
<td>4</td>
<td>-0.581843</td>
<td>-0.581231</td>
<td>-0.581230</td>
</tr>
<tr>
<td>5</td>
<td>-0.580459</td>
<td>-0.580199</td>
<td>-0.580199</td>
</tr>
<tr>
<td>6</td>
<td>-0.661925</td>
<td>-0.579655</td>
<td>-0.579655</td>
</tr>
<tr>
<td>7</td>
<td>0.664051</td>
<td>0.658212</td>
<td>0.658211</td>
</tr>
<tr>
<td>8</td>
<td>0.675390</td>
<td>0.663549</td>
<td>0.663549</td>
</tr>
<tr>
<td>9</td>
<td>0.684834</td>
<td>0.671223</td>
<td>0.671226</td>
</tr>
<tr>
<td>10</td>
<td>0.677101</td>
<td>0.679607</td>
<td>0.679611</td>
</tr>
<tr>
<td>11</td>
<td>0.684834</td>
<td>0.687148</td>
<td>0.687148</td>
</tr>
<tr>
<td>12</td>
<td>0.688675</td>
<td>0.692237</td>
<td>0.692235</td>
</tr>
</tbody>
</table>

The largest discrepancy among occupied MO energies is 6*10⁻⁴ and among vacant MO energies even worse 4*10⁻³. To eliminate off-diagonal elements we performed rotation of our energy matrix using Jacobi algorithm. After few rotations the MO energy values improved significantly and the gap between conventional and elongation values decreased in 3 orders of magnitude. The corresponding orbital energies after rotation are tabulated in Table 2. The density matrix derived from elongation eigenvectors matches up to the forth decimal the density matrix of conventional MOs.

Time used for collecting all LMOs, YYs and constructing energy matrix is quite insignificant in comparison to rate-determining rotation step. Therefore we focused on this bottleneck of eigenvalue solution. We performed checking of CPU time usage for diagonalization of our energy matrix and compared it to the CPU time used for diagonalization of Fock matrix in conventional calculation. For this purpose we used stacked uracil pares optimized at MP2 level of theory. The optimized distance between two uracil planes, constituting the elementary unit, was 3Å and the distance between units has been arbitrary chosen to be 6 Å. The results are shown on Figure 2.

It should be noted that both methods have the qualitative agreement in produced orbital energies, but upon the increasing size of the studied system the diagonalization time of energy matrix is two times less than diagonalization of Fock matrix in conventional HF method. This gain in time becomes possible because of preoptimized shape of energy matrix. As it can be seen from the Table 1 the energy matrix is essentially diagonal, so it takes less time to diagonalize such sparse matrix than to do the diagonalization from the scratch as in the case of conventional HF method.

**CONCLUSIONS**

The algorithm for computing MO energies has been designed for Elongation Method. The obtained results yield high accuracy in comparison with the conventional approach. The efficient CPU time usage has been achieved for the diagonalization procedure.
FIGURE 2. The structure of investigated molecular chain. CPU time usage in diagonalization procedure. Each unit corresponds to the one uracil pair.

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A hierarchy for additive models of polarizability

Ajit J. Thakkar

Department of Chemistry, University of New Brunswick, Fredericton, NB E3B 5A3, Canada

Abstract. Simple models for estimating the isotropic dipole polarizability of a molecule as the sum of polarizabilities of molecular subunits are reviewed. As an aid to the classification and understanding of such models, a hierarchy is defined in terms of the information required to perform the estimation.

Keywords: polarizabilities, additivity, connectivity, electronegativity equalization, charge equilibration

PACS: 32.10.Dk, 33.15.Kr

INTRODUCTION

Contemporary chemists take for granted the notion that the properties of molecules can be understood in terms of the properties of molecular subunits such as atoms, bonds, functional groups, and fragments. This key idea was recognized soon after Dalton’s atomic theory took hold. It has been part of the bedrock of chemical thought for more than a hundred and fifty years.

John Dalton recorded his atomic theory in his notebooks and presented it to the Literary and Philosophical Society of Manchester in the autumn of 1803 [1]. He published it a few years later in an article on the absorption of gases by water and other liquids [2] and more comprehensively in his seminal book [3]. Just a few decades later, Hermann Kopp published a series of investigations [4–7] establishing that the molar volumes of organic liquids at their boiling points were close to additive functions of the molar volumes of their constituent elements. It is well worth reading the thorough exposition of Kopp’s work in the Kopp Memorial Lecture presented to the London Chemical Society by Thorpe [8]. Experimental evidence to support nearly additive group contributions to molar refraction was published later in the 19th century by Gladstone and Dale [9], and by Brühl [10–12]. The additivity of molecular properties was considered so well-established that it was used for structure determination in the pre-spectroscopic era.

Molar volumes are proportional to molecular volumes which in turn are closely associated with molecular polarizabilities [13, 14]. Moreover, molar refractions are connected to polarizabilities by the Lorentz-Lorenz relationship [15, 16] which follows from the Clausius-Mossotti equation [17, 18]. Thus, the additivity of molecular polarizabilities was already recognized well before the end of the 19th century. The purpose of this paper is to present a brief survey and hierarchical classification of simple additive models for molecular polarizabilities. I chose this subject for the symposium in Professor Bernard Kirtman’s honor because it is one that has held his interest over the years. I salute Bernie for his many scientific contributions. Atomic units are used throughout. The conversion factor between atomic units and SI units is given by: 1 au of polarizability = 1.64878 × 10^{-41} \, C^2 m^2 J^{-1}.

THE HIERARCHY OF ADDITIVITY MODELS

I restrict discussion to those simple additive models of polarizability that require only the chemical formula or Lewis structure of the molecule whose polarizability is to be predicted. In particular, these models assume that the polarizability does not depend upon the geometry or conformation of the molecule. This means that only the isotropic polarizability, one-third of the trace of the polarizability tensor, can be predicted except in special cases of high symmetry. Models that are capable of predicting the polarizability anisotropy are not considered in this work.

The hierarchy of models shown in Table 1 is presented as an aid to understanding and clarifying the many models in the literature. The lowest level is a ‘bare-atoms model’ in which the molecular polarizability is taken to be the sum of the polarizabilities of its constituent atoms in their free states. This model cannot be
TABLE 1. A hierarchy of simple additive models for molecular polarizabilities.

<table>
<thead>
<tr>
<th>Level</th>
<th>Model type</th>
<th>Requisite information</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Network</td>
<td>Atomic numbers, hybridization, full connectivity matrix</td>
</tr>
<tr>
<td>4</td>
<td>Atoms types, bonds, groups</td>
<td>Atomic numbers, hybridization, functional groups, bonds</td>
</tr>
<tr>
<td>3</td>
<td>Atom types</td>
<td>Atomic numbers, hybridization</td>
</tr>
<tr>
<td>2</td>
<td>Dressed atoms</td>
<td>Atomic numbers</td>
</tr>
<tr>
<td>1</td>
<td>Bare atoms</td>
<td>Atomic numbers</td>
</tr>
</tbody>
</table>

expected to work because if it did there would be no molecular chemistry! Indeed, it leads to polarizabilities that are far too large. For example, the polarizabilities of the hydrogen [19] and carbon [20] atoms are 4.5 and 11.67 au respectively. Taking six times the sum of these leads to 97.0 au, a result which is 40% larger than the polarizability (69.3 au) of C₆H₆ [21].

The second stage of the hierarchy is a ‘dressed-atoms model’ in which an atom in a molecule has an effective polarizability that is transferable across all molecules. A model of this sort dates back to at least the early 20th-century work of Eisenlohr [22] and Silberstein [23] who both found it inadequate. This too is not surprising since any chemist knows that the carbon atom in methane behaves differently from a carbon atom in acetylene.

Nevertheless, a 21st century parameterization of a slightly modified model of this sort was reported by Bosque and Sales [24]. They fit experimental values of the mean polarizability, denoted \( \alpha \), of 340 organic substances with an average error of 2.31%. Their model [24] can be written as

\[
\alpha = C + \sum_k n_k \alpha_k
\]  

(1)

in which \( n_k \) is the number of atoms of element \( k \) in the molecule, \( C = 2.15 \text{ au} \) is a constant, and the \( \alpha_k \) are effective polarizabilities for the ten atoms: C, H, N, O, F, Cl, Br, I, S, and P. For example, their effective polarizabilities for hydrogen and carbon are 1.174 and 10.19 au respectively [24]. Taking six times the sum of these and adding \( C \) leads to 70.3 which is only 1.4% larger than the polarizability (69.3 au) of benzene [21]. However, examination of their Table 1 reveals that the model has an error that exceeds 5% for 38 species, or in other words for more than 11% of the molecules, in their training set. Their maximum error for a molecule in the training set is 11.2%. Zhokhova et al. [25] tested Eq. (1) on a larger database of 613 molecules and found that the standard deviation increased by a factor of almost two (1.86). Moreover, the constant \( C \) is clearly unphysical; Eq. (1) predicts a non-zero polarizability in the limit of no atoms.

A dressed-atoms model can provide significantly more accuracy if it is restricted to a family of related molecules. For example, Doerksen and Thakkar [21] reported a model which can be written in the form of Eq. (1) with the unphysical term removed (\( C = 0 \)). The model was specially parameterized for use with heteroaromatic molecules composed of H, C, N, and O atoms. It has an error of only 1.1% for 33 molecules of this type.

In Silberstein’s words [23], “exceptions to the law of additivity, although helpful to the chemist, (are) the clearest confession of non-additivity.” To put it bluntly, non-additivity must be brought in through the back door to improve the additive models on the first two steps of the hierarchy. Models on the third step of the hierarchy do this by recognizing that the environment of the atom must be taken into account. The atomic environment can be accounted for by introducing different types of atoms of the same element, such as single-, double-, and triple-bonded carbon atoms. Eisenlohr [22, 26] and, later, Vogel [27] worked out additive schemes for molar refraction using this approach. The first model explicitly formulated in terms of atom types characterized by their hybridization was probably that of Miller and Savchik [28]. They wrote the molecular polarizability as \((4/N)\) times the square of a sum of atom hybrid components (ahc) for each atom in a given hybridization state, in which \( N \) is the number of electrons. This was soon followed by the work of Kang and Jhon [29] who wrote the molecular polarizability as a sum of atom hybrid polarizabilities (ahp). Miller’s more recent parameterization [30] achieves average errors of 2.2 and 2.8% respectively for the ahc and ahp models applied to about 400 compounds consisting of C, H, N, O, F, Cl, Br, I, S, and P atoms. Models of the ahp type have also been parameterized using \textit{ab initio} polarizabilities [31–34].

Models on the fourth rung of the hierarchy use information about bonds and functional groups in addition to atom types. Writing the molecular polarizability (refraction) as a sum of bond polarizabilities (refractions)
TABLE 2. Mean absolute percent deviations (MAPD) of predicted polarizabilities relative to experimental data.

<table>
<thead>
<tr>
<th>Model</th>
<th>Level</th>
<th>MAPD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bosque and Sales [24]</td>
<td>2</td>
<td>2.22</td>
</tr>
<tr>
<td>Zhou and Dykstra [33]</td>
<td>3</td>
<td>4.23</td>
</tr>
<tr>
<td>Optimized [45] Ewig et al. [34]</td>
<td>3</td>
<td>2.30</td>
</tr>
<tr>
<td>Stout and Dykstra [31]</td>
<td>3</td>
<td>2.10</td>
</tr>
<tr>
<td>Miller aic [30]</td>
<td>3</td>
<td>1.53</td>
</tr>
<tr>
<td>Miller aph [30]</td>
<td>3</td>
<td>1.51</td>
</tr>
<tr>
<td>Goedhart [42]</td>
<td>4</td>
<td>2.73</td>
</tr>
<tr>
<td>Zhokhova et al. [25]</td>
<td>4</td>
<td>2.50</td>
</tr>
<tr>
<td>17 Hydrogen-capped fragments [44]</td>
<td>4</td>
<td>1.58</td>
</tr>
<tr>
<td>MP2 calculation [46]</td>
<td>ab initio</td>
<td>2.09</td>
</tr>
</tbody>
</table>

* From Ref. [45]

dates back to the early to mid-20th century work of von Steiger [35], Smyth [36, 37], Denbigh [38], Vickery and Denbigh [39], and Vogel et al. [40, 41]. Yet another approach was developed extensively by Vogel [27] who represented different types of bonding with a set of prototypical groups that can be interpreted with atomic hybrids. A more recent example is D. J. Goedhart’s unpublished model in which the additive units are functional groups, and there are unique ‘constitutional’ corrections for steric hindrance. The Goedhart model was parameterized by a fit to about a thousand liquid organic compounds containing 43 different functional groups. Apparently [42] Goedhart presented this work at an international seminar on gel permeation chromatography held in Monaco in October 1969. The only published account of the Goedhart model that I am aware of can be found in a book on polymer properties [42].

Kassimi et al. [43] reported two models that express the polarizability of heteroaromatic molecules as a sum of contributions from connections $n_{ij}$ (bonds regardless of bond order) between atoms of atomic number $i$ and $j$. Zhokhova et al. [25] improved the dressed-atom model of Bosque and Sales [24] by adding terms proportional to the number of double, triple, and aromatic bonds in the molecule. A model that expresses the polarizability as a sum of the polarizabilities of capped fragment molecules [44] has been applied at the ab initio level to obtain polarizabilities of the proteinogenic amino acids. Kassimi and Thakkar [45] compared the quality of the predicted polarizabilities of 20 amino acids for several models on the 2nd, 3rd, and 4th rungs of the hierarchy. A summary of their results is presented in Table 2.

Kopp [4–7] observed that structural isomers had nearly identical molar volumes at their boiling points. All models on the first three rungs predict identical polarizabilities for structural isomers. A model on the fourth rung can predict different polarizabilities for different structural isomers but there are ambiguities about the most accurate way to do this [44]. Network models on the 5th grade of the hierarchy are needed to do this correctly. I am aware of only one such model. No et al. [47] proposed the CDEAP model that incorporates ‘charge dependence of the effective atomic polarizability’. Applications of the CDEAP model sometimes [45, 47] use averaged atomic charges for each type of atomic hybrid but this procedure effectively lowers the model to the 3rd rung. In the full CDEAP model, the atomic charges are obtained from the molecular connectivity using a modified form [48–51] of the ‘partial equalization of orbital electronegativity’ (PEOE) method of Gasteiger and coworkers [52–54]. The iterative PEOE procedure equilibrates charge throughout the molecular network and not just between nearest neighbors. Further development of CDEAP and novel network models is proceeding in my laboratory. The hierarchy presented in Table 1 is also applicable to additive models for other scalar properties. In fact, we are currently using it to construct a set of systematically improving additive models for moments of the electronic momentum density [55, 56].

**ACKNOWLEDGMENTS**

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Exciton Effects in Boron-Nitride (BN) Nanotubes

Kikuo Harigaya

Nanotechnology Research Institute, AIST, Tsukuba 305-8568, Japan

Abstract. Exciton effects are studied in single-wall boron-nitride nanotubes. The Coulomb interaction dependence of the band gap, the optical gap, and the binding energy of excitons are discussed. The optical gap of the (5,0) nanotube is about 6eV at the onsite interaction U=2t with the hopping integral t=1.1eV. The binding energy of the exciton is 0.50eV for these parameters. This energy agrees well with that of other theoretical investigations. We find that the energy gap and the binding energy are almost independent of the geometries of nanotubes. This novel property is in contrast with that of the carbon nanotubes which show metallic and semiconducting properties depending on the chiralities.

Keywords: optical excitations, exciton effects, optical absorption, BN nanotubes

PACS: 71.10.Li, 71.35.-y, 78.67.Ch

INTRODUCTION

Nano-carbon materials and hetero-materials including borons (B) and nitrogens (N) have been attracting much attention both in the fundamental science and in the interests of application to nanotechnology devices [1,2]. Their physical and chemical properties change variously depending on geometries [1-3]. In carbon nanotubes, diameters and chiral arrangements of hexagonal pattern on tubules decide whether they are metallic or not [1,2]. The BN nanotubes are intrinsic semiconductors, which have been predicted theoretically [4]. This property has been experimentally observed in single-wall BN nanotubes, quite recently [5].

In this paper, we study optical absorption spectra of BN nanotubes. We use the single-excitation configuration interaction (single-CI) technique in order to consider exciton effects [6]. In the model [7], we have treated the difference between B and N by the site energies, $E_B > 0$ and $E_N < 0$. The same model should be valid for optical properties. We consider zigzag BN nanotubes with the chirality indices $(n,0)$ for $n=5$. We have changed $n$ from 2 to 5, and have found that main results do not change. The calculations will be done for the real geometries, so thin nanotubes are treated only.

We will report the following properties: (1) The binding energy of excitons is about 0.5 eV a $(U,V)=(2t,1t)$ with $t=1.1$ eV for the $(5,0)$ nanotube. Similar magnitudes have been obtained in the recent band calculations. (2) This binding energy is comparable with that of the carbon nanotube ~0.4 eV. (3) The constant optical gap and exciton binding energy with respect to the chirality index $(n,0)$ are obtained. This property agrees with recent experiments [5].

MODEL AND METHOD

Figure 1 illustrates the geometry of BN plane (left), where N and L are the width and length of the honeycomb structure, respectively. The filled and open circles are B and N atoms, respectively. After rolling up the plane in the y direction, the plane becomes the nanotube as shown in the right figure. The electronic systems are imposed with periodic boundary condition in the y direction. The wavenumber is quantized in the y direction. The x-axis is parallel to the nanotube cylinder.

We treat a half-filled $\pi$-electron system on the BN nanotube using the extended Hubbard Hamiltonian with the on-site U and nearest-neighbor V Coulomb interactions [7]. We adopt the Hartree-Fock approximation to this model [6]. The optical excitation is treated by the single-CI method. Optical absorption spectra are calculated with this formalism.
DENSITY OF STATES AND OPTICAL SPECTRA

The DOS and optical spectra of the (5,0) tube are shown in Fig. 2 as the representative case. The unit of the energy is scaled with $t$. Figs. 2 (a) and (b) show the DOS for the parameters $(U,V) = (0,0)$ and $(2t,1t)$. The site energies $E_B = +t$ and $E_N = -t$ are assumed. The same parameters have been used in [8]. When there is not the Coulomb interactions, intrinsic band gap exists owing to the large site energies. The one-dimensional van-Hove singularities are seen clearly in Fig. 2 (a). When the Coulomb interactions are switched on, the band gap becomes larger due to the one-site correlation after the Hartree-Fock treatment. This property can be seen in Fig. 2 (b).

FIGURE 1. The geometry of the hexagonal BN is shown in left. The quantities $N$ and $L$ are the width and length of the honeycomb lattice structure, respectively. Namely, $L$ is the total number of B and N atoms along the zigzag line in the $y$ direction, and $N$ is the number of the zigzag lines. The filled and open circles are B and N atoms. After rolling up the plane in the $y$ direction, the plane becomes the nanotube (right figure).

FIGURE 2. (a) The density of states for the (5,0) nanotube with the interaction strengths (a) $U=0$ and (b) $U=2t$, shown in the units of $1/t$ of the left axis and in the units of $t$ of the bottom axis. The optical absorption spectra of the (5,0) nanotube are shown with the interaction strengths (c) $U=0$ and (d) $U=2t$. The left axis is in the arbitrary units (a.u.) and the bottom axis is in the units of $t$. 
The optical spectrum for \((U,V) = (0,0)\) is shown in Fig. 2 (c). There is the on-set of the optical absorption at the energy about \(2t\). Some structures from the van-Hove singularities are present also. When the Coulomb interactions are included, the optical spectrum becomes narrow as shown in Fig. 2 (d) for \((U,V) = (2t,1t)\). The main feature shifts to higher energies due to the wider band gap. The narrowness of the feature is due to the one-dimensional exciton effects, which have been reported for conjugated polymers [9] and carbon nanotubes [10]

**BINDING ENERGY OF EXCITON**

The binding energy of the exciton is calculated as the difference between the on-set energy of the optical absorption (optical gap) and the energy gap of the Hartree-Fock ground state. This definition is explained in the literature, for example [9]. The binding energy will be reported as the function of the chirality index \((n,0)\) and the Coulomb interaction \(U\). We fix \(V = U/2\), because of our finding of this empirical relation in the optical properties of \(C_{60}\) [6] and conjugated polymers [9].

Figures 3 shows the Hartree-Fock band gap (circles), the optical gap (triangles), and the binding energy (squares), for the chirality index \((5,0)\). We find almost negligible dependence on the chirality index for \(n=2\) to 5. Therefore, the case \(n=5\) is shown only. This property is due to the large on-site energy, and the intrinsic gap magnitude, \(2\Delta = E_B - E_N\). The effect of the chirality index dependence is the correction of the order of \(\left[(t/\Delta) (a/L)\right]^2\), which is significantly smaller than \(E_B - E_N\). Here, \(L\) is defined in Fig. 1. This main result of this paper agrees well with the recent experiments of the single wall BN nanotubes [5]. These three quantities depend on \(U\) as linear functions. They becomes \(2\Delta\) at \(U=0\).

We also find that the binding energy of excitons is about 0.5 eV at \((U,V)=(2t,1t)\) with \(t=1.1\) eV for the \((5,0)\) nanotube. The optical gap is about 6 eV for these parameters. The similar magnitudes of the binding energy have been obtained in the recent band calculations [11,12]. Therefore, the present parameterization seems reasonable in order to describe the exciton effects of BN nanotubes. When we look at the binding energy of excitons in carbon nanotubes, the magnitude \(\sim 0.4\) eV has been reported in the two-photon absorption experiment [13]. Such quantitative comparison between the two systems seem interesting in view of the difference of the atom species.
In the literatures [14-16], the Bethe-Salpeter equation and ab initio methods have been used to calculate the optical spectra. In these calculations, the unscreened Coulomb interactions among electrons are used rather than using the simple Hartree-Fock type models. The screening has been considered in the course of calculations by the Bethe-Salpeter approach. In the present calculations with model Hamiltonians, the parameters adopted are the effective interactions after screening is considered. These are the difference in the ideas between the Bethe-Salpeter approach and the Hartree-Fock plus CI method.

**SUMMARY**

The binding energy of excitons of the BN nanotubes is considered by the single-CI method. We have found that the magnitude is about 0.5 eV at the parameters \((U,V)=(2t,1t)\) with \(t=1.1\) eV for the \((5,0)\) nanotube. We have noted that the similar values have been obtained in the recent band calculations [11,12]. This binding energy is comparable with that of the carbon nanotube \(\sim 0.4\) eV [13], too. The constant optical gap and exciton binding energy with respect to the chirality index \((n,0)\) have been obtained in agreement with recent experiments.

**REFERENCES**

Generalized Elongation Method: From One-Dimension to Three-Dimension

Yuriko Aoki 1 and Feng Long Gu 2

1Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University, 6-1 Kasuga-Park, Kasuga, Fukuoka 816-8580, Japan; Japan Science and Technology Agency, CREST, 4-1-8 Hon-chou, Kawaguchi, Saitama 332-0012, Japan

2 Center for Computational Quantum Chemistry, South China Normal University, Guangzhou, 510631 China

Abstract. A generalized elongation method for three-dimensional systems has been proposed based on the achievement of the elongation method for one-dimensional systems. The main idea of the generalized elongation has been reported and its application to various complex systems is presented.

Keywords: Elongation method, water cluster

PACS: 36.20.-r

INTRODUCTION

The elongation method [1-4], developed by Imamura and Aoki in the early 1990s, was an attempt to efficiently determine electronic structures of periodic and/or random polymers. The original idea of the elongation method mimics experimental polymerization/copolymerization procedures. Contrast to many other approximation methods for large systems, the elongation is fully variational, that is to say, the elongation energy is approaching the conventional one by no lower than it. It has been already demonstrated that the total energy obtained by the elongation method is in excellent agreement to those by the conventional method. The error of the elongation method is within 10^-5 a.u./atom [5-7], showing its high accuracy compared to other methodologies. The elongation method has been applied to various periodic and/or aperiodic quasi-one-dimensional systems [8-10] for the electric and optical properties.

However, the original implementation of the elongation method was restricted only to quasi-one-dimensional systems. It has been long questioned how to extend to three-dimensional systems. In this presentation, a generalized elongation method will be reported for one to three dimensional systems. Some benchmark test calculations are presented to show the reliability and applicability of the generalized elongation method.

METHODOLOGY

For your better understanding of the idea of the generalized elongation method (G-ELG), we present a schematic show in figure 1. The blue circles represent for frozen units while the red circles for active units. The active region is denoted as a pink circle. As system is elongated, the active region will approach the previously frozen units, this leads to strong interaction between them. The key point is that the G-ELG method automatically recognizes this interaction and first re-activates those frozen units entering this pink circle. By correctly collect frozen and active regions, the elongation SCF is performed, and then the CMOs will be re-localized after the SCF converged, so that the next elongation step will be continued without increasing the...
size of the interactive region. By repeating this procedure, that is collecting frozen and active regions, elongation SCF procedure, any random with any-dimensional system can be generated by the G-ELG method.

RESULTS AND DISCUSSIONS

In order to test the reliability of G-ELG, a model system, one-dimensional water clusters (H\textsubscript{2}O\textsubscript{12} have been designed to perform the calculations by using the G-Elg, Old-Elg and conventional methods, as shown in Fig. 2. The procedures of the elongation method are described as the left side in Fig. 2. It can be seen from Fig. 2, because the strong interaction between the eleventh H\textsubscript{2}O and the second H\textsubscript{2}O, the energy difference calculated by the Old-Elg is abruptly increased when the eleventh water was involved. While for the G-Elg method, the energy difference is negligibly small because the second frozen water has been re-activated and included in the interactive space.

Fig. 2 The total energy difference between Old-Elg (blue line) and G-Elg (red line) for one-dimensional (H\textsubscript{2}O\textsubscript{12} calculated at HF/STO-3G level.

Next, for a two-dimensional system, the water clusters have also been calculated by using the G-Elg method. The difference for the total energy between the conventional and G-Elg calculations is shown in Fig. 3. In order to consider the strong interaction between the frozen region and the attacking monomer, any frozen units in 6 au, 10au, 15au and 20au around the attacking monomer will be re-activated, as shown in Fig. 3. As for different distances, the number of re-activated H\textsubscript{2}O is given in Table 1. One can see from Fig. 3, with the increase of distance, the energy difference between the conventional and G-Elg calculations are decreased.
Therefore, the G-Elg calculation can give the satisfactory results for two-dimensional system.

Fig. 3 The total energy difference between Old-Elg and G-Elg for two-dimensional (H2O)_{100} calculated at HF/STO-3G theoretical level.

Table 1. The number of re-activated H2O in the elongation procedures

<table>
<thead>
<tr>
<th>Distance (a.u.)</th>
<th>Number of re-activated H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>20</td>
<td>18</td>
</tr>
</tbody>
</table>

Finally, for a three-dimensional system, the water cluster (H2O)_{20}. The stability energy (SE) of water cluster (H2O)_{20} have also been calculated by using the G-Elg approach. The optimized geometry was taken from the work of Sathyamurthy et al (as shown in Fig 4). Compared to the result of Sathyamurthy’s, the stability energy calculated by the G-Elg method at HF/6-31G(d,p) level is in very good agreement.

Fig. 4 The stability energy (SE) calculated by conventional and G-Elg methods for three-dimensional water cluster (H2O)_{20} at HF/6-31G(d,p) level

<table>
<thead>
<tr>
<th>SE(kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conv [1]</td>
</tr>
<tr>
<td>-216.28</td>
</tr>
</tbody>
</table>

In this work, we present the effectiveness and efficiency of the G-Elg method for the one-dimensional, two-dimensional, and three-dimensional water cluster models. The reliability is tested and its application of the G-Elg method to other large biological systems of interests, such as protein or DNA will be reported elsewhere.
ACKNOWLEDGMENTS

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REFERENCES

Implementation Of A Vector Potential Method In An Ab Initio Hartree-Fock Code

Violina Tevekeliyska*, Michael Springborg*, Benoît Champagne† and Bernard Kirtman**

*Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, Germany
†Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix (FUNDP), rue de Bruxelles, 61, 5000 Namur, Belgium
**Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, U.S.A.

Abstract.
For extended systems exposed to an external, electrostatic field, the presence of the field leads to an extra term ($\vec{E} \cdot \vec{P}$) to the Hamiltonian, where $\vec{E}$ is the field vector and $\vec{P}$ is the polarization of the system of interest. In order to find out how a polymer chain responds to an external electric perturbation, a field with a charge and a current term for the polarization is added to an ab initio Hartree-Fock Hamiltonian. The polarization expression is taken from an efficient vector potential approach (VPA) [1] for calculating electronic and nuclear responses of infinite periodic systems to finite electric fields and is implemented in the ab initio LCAO-SCF algorithm [3], which computes band structure of regular or helical polymers, taking into account the one-dimensional translational symmetry. A smoothing procedure for numerical differentiation of the orbital coefficients is used in order to calculate self-consistently the charge flow contribution to the polarization.

Keywords: polarization, electrostatic fields, periodic systems
PACS: 71.15.-m, 61.50.Ah, 77.22.Ej

I. INTRODUCTION

The response of materials to external electric fields is of great fundamental and practical interest, since dielectric, piezoelectric and ferroelectric behaviors are dictated by it, for instance. The response will be entirely electronic if the frequency of the field is sufficiently high, elsewise structural (i.e., nuclear) degrees of freedom need to be considered as well.

For a finite system, an external, homogeneous field ($\vec{E}$) can be accounted for by adding the extra term ($\vec{E} \cdot \vec{\mu}$) to the Hamiltonian, where $\vec{E}$ is the field vector and $\vec{\mu}$ is the dipol moment of the system, that is replaced by the polarization, $\vec{P}$ (dipol moment per unit cell), when extended and regular systems are considered. In theoretical studies extended and regular systems are most conveniently modelled as being infinite and periodic. However, the usual scalar potential, that describes the interaction with the external field, breaks the periodicity of the system and is unbounded.

Based on a suggestion made initially by Genkin and Mednis [4], Kirtman and co-workers [5, 6] developed a vector potential approach (VPA), that has the virtue of immediately satisfying the periodicity requirement and of introducing frequency dependence in a straightforward manner while still being applicable to static fields. This method has been successfully used to determine both linear and nonlinear polarizabilities [7, 8, 9] although calculations have been limited to the pure electronic response of quasi-one-dimensional (quasi-1D) systems. Within the VPA, the polarization, $\vec{P}$, is formulated in terms of matrix elements involving $d/dk$. To prove the method a parametrized model Hamiltonian has been constucted. This model contains all essential elements of an ab initio Hartree-Fock (or Kohn Sham) Hamiltonian including band orbitals with phases that may vary randomly from one $k$ point to the next. Although numerical results were obtained for a 1D model system [2], where the spin polarization is neglected, the basic ideas of the VPA are transferable to 2D and 3D systems and to a spin-polarized case.

The present paper shows the implementation of the VPA in a PLH code [3] that has been developed in Namur, Belgium, as a first step towards a full ab initio treatment of periodic systems in external electrostatic fields. With this program package, Hartree-Fock calculations on quasi-one-dimensional systems can be carried through, using a basis set of Gaussians. Some theoretical aspects are outlined in the following section. Detailed information can be found in [1, 2, 3]. In section III present results are introduced.
II. THEORETICAL ASPECTS

Within the vector potential approach, using \( P_{KSV} = P_{KGB} \) (static) [5] and Hartree-Fock approximation, where \( P_{KSV} \) is the polarization expression given by King-Smith and Vanderbilt [12], the orbital coefficients, \( C_{pq}(k) \), may be obtained by solving:

\[
\sum_p \left( F_{qp}(k) - E_{DC} \cdot \left[ M_{qp}(k) + iS_{qp}(k) \frac{\partial}{\partial k} \right] \right) C_{pq}(k) = \epsilon_p(k) \sum_p S_{qp}(k) C_{pq}(k). \tag{1}
\]

Here:

\[
S_{qp}(k) = \sum_l e^{i k l a} S_{qp}^0 = \sum_l e^{i k l a} |\chi_q^l \rangle |\chi_p^l \rangle,
\]

\[
M_{qp}(k) = \sum_l e^{i k l a} M_{qp}^0 = \sum_l e^{i k l a} \langle \chi_q^l | - ia |\chi_p^l \rangle = \sum_l e^{-i k l a} \langle \chi_q^l | |\chi_p^l \rangle,
\]

\[
F_{qp}(k) = \sum_l e^{i k l a} F_{qp}^0 = \sum_l e^{i k l a} \langle \chi_q^l | \hat{F} |\chi_p^l \rangle. \tag{2}
\]

are the overlap, unit cell dipole, and Fock matrix elements, respectively, \( S_{qp}^0 \), \( M_{qp}^0 \), and \( F_{qp}^0 \) are the corresponding direct space matrices between the atomic orbitals \( \chi_q^l \) of the reference cell \((0)\) and \( \chi_p^l \) of the \( l \)-th cell. Due to the \( \partial / \partial k \) term, Eq. (1) is not a standard matrix-eigenvalue problem. Using the normalization condition \( 1 = C^\dagger (k) \cdot \hat{S}(k) \cdot C(k) \), the \( \partial C_{pq}(k) / \partial k \) term can be converted to a desired multiplicative form,

\[
\hat{S}(k) \frac{\partial}{\partial k} C(k) = \left[ \hat{S}(k) \left( \frac{\partial}{\partial k} C(k) \right) \right] C^\dagger(k) \hat{S}(k) C(k). \tag{3}
\]

Then the quantity in the square brackets can be treated self-consistently in the same manner as the Fock matrix, and Eq. (3) takes the form

\[
\left\{ E_j(k) - E_{DC} \cdot \left[ M_j(k) + iS_j(k) \left( \frac{\partial}{\partial k} C_j(k) \right) \cdot \hat{C}(k) \cdot \hat{S}(k) \cdot C_j(k) \right] \right\} \cdot C_j(k) = \epsilon_j(k) \cdot \hat{S}(k) \cdot C_j(k). \tag{4}
\]

However, the numerical differentiation of the coefficients will be problematic, since \( \hat{C}(k) \) contains an arbitrary(random) \( k \)-dependent phase factor. To compensate the randomness, a numerically stable approach, that makes the coefficients a ‘smooth’ function of \( k \), was developed [1, 2]. The smoothing procedure is based on adding extra phase factor, which is chosen so that the change in the coefficients from one \( k \) point to the next is minimized, \( C_{aq}(k) \rightarrow C_{aq}(k)e^{i\phi_j(k)} \). In a multi-step procedure, the phases are optimized, for each band, \( j \), separately, by minimizing:

\[
\mathcal{Q}_j = \sum_k \sum_q |C_{aq}(k + \Delta k)e^{i\phi_j(k + \Delta k)} - C_{aq}(k)e^{i\phi_j(k)}|^2
\]

\[
+ \lambda \sum_k \sum_q |C_{aq}(k + 2\Delta k)e^{i\phi_j(k + 2\Delta k)} - C_{aq}(k)e^{i\phi_j(k)}|^2 \tag{5}
\]

under the constraint

\[
\phi_j \left( -\frac{\pi}{a} \right) = \phi_j \left( \frac{\pi}{a} \right) \tag{6}
\]

and with \( \phi_j(0) \) fixed.

Subsequently the derivatives of the orbital expansion coefficients with respect to \( k \) are calculated numerically using

\[
\frac{\partial C_{aq}(k)}{\partial k} \approx \frac{1}{\Delta k} \sum_{n=1}^{N_k} \omega_n C_{aq}(k + n \cdot \Delta k) - C_{aq}(k - n \cdot \Delta k) \tag{7}
\]

with

\[
C_{aq} \left( k + \frac{2\pi}{a} \right) = C_{aq}(k). \tag{8}
\]
Here, \( N_q \) is the number of points used in the numerical differentiation and the coefficients \( \{ \omega_h, N_q \} \) are taken from Dvornikov [14].

In order to determine the field-dependent geometry, the polarization energy must be included,

\[
E_{\text{pol}} = E \cdot P = E \sum_k \sum_j \left\langle \psi_f^k \left| \frac{\partial}{\partial k} e^{-ikz} \right| \psi_i^k \right\rangle
\]

\[
= E \sum_k \sum_j \sum_{qp} \left[ C_{pq}(k)C_{qj}(k)M_{qp}(k) + iC_{qn}(k) \frac{\partial C_{qj}(k)}{\partial k} S_{qp}(k) \right]
\]

\[
\equiv E \cdot (P_p + P_I)
\]

(9)
in addition to contributions from the field-dependent Fock matrix. The polarization is splitted into a charge term \( (P_p) \), that is closely related to the static charge distribution for the central part of a large, finite chain, and into a current-like term \( (P_I) \).

In order to find out how a polymer chain responds to an external electric field, the expression in the square bracket of Eq. (4) has to be added to an \textit{ab initio} Hartree-Fock Hamiltonian, which is given by [3]:

\[
F_{qp}(k) = \sum_r e^{iklr} F_{qr}^{0l} = \sum_r e^{iklr} \langle \chi_q^0 | \hat{\mathcal{F}} | \chi_p^l \rangle
\]

\[
F_{qr}^{0l} = F_{qr}^{0l} + \sum_{j=-N}^{N} \sum_{r} \sum_{s} P_{sr}^{lj} \sum_{h=-\infty}^{\infty} C_{qp}^{j+1-h} - \frac{1}{2} \sum_{j=-N}^{N} \sum_{r} \sum_{s} P_{sr}^{lj+1-h} G_{qp}^{j+1-h}
\]

\[
+ \frac{1}{2} \sum_{j=-N}^{N} \sum_{r} \sum_{s} P_{sr}^{lj} \sum_{h=-\infty}^{\infty} C_{qp}^{j+1-h} - \frac{1}{2} \sum_{j=-N}^{N} \sum_{r} \sum_{s} P_{sr}^{lj+1-h} G_{qp}^{j+1-h}
\]

(10)

and the total polarization \( P_{tot} \) and its \textbf{charge} \( P_p \) and \textbf{current} \( P_I \) contributions have to be calculated.

The calculation of the Fock matrix in the LCAO \textit{ab initio} program is in itself a difficult problem due to the presence of long-range interactions in the electron-nucleus attraction (the second term on the right-hand side of the second equality) and in the electron-electron repulsion (the third term), i.e., in the Coulomb terms. To give a satisfactory representation of the electrostatic interactions, multiple expansion, that is based on the fact that unit cells with negligible overlap can interact via multipoles rather than via the full Fock operator, are used in the PLH code [3]. As a consequence, in the procedure elaborated by the Namur group the sums over \( h \) in the Coulomb terms are explicitly evaluated for the \( 2M+1 \) cells \( (M \geq 2N) \), that define the medium-range region, while the remainder, covering the \( ]-\infty,-M[ \cup M, \infty[ \) domain, is evaluated by means of multipoles. Another difficulty arises from the fact that by integrating the density matrix from reciprocal to real space by means of the following equation

\[
P_{sr}^{lj} = \frac{a}{\pi} \frac{\hat{\omega}}{\hat{\beta}} \int_{-\beta}^{\beta} dk \sum_{j=1}^{N_q} C_{ij}(k) C_{ij}(k) e^{ikja}
\]

\[
= \frac{2a}{\pi} \frac{\hat{\omega}}{\hat{\beta}} \int_{-\beta}^{\beta} dk \{ \Re \{ P_{sr}(k) \} \cos(kja) - \Im \{ P_{sr}(k) \} \sin(kja) \}
\]

(11)

for large \( j \), the integrand oscillates rapidly. The integration techniques can be classified into two categories: (i) the \textit{nonoscillatory techniques}, which integrate the product of the density matrix elements by exponential as a whole; and (ii) the \textit{oscillatory techniques}, which consider separately the trigonometric components. Two quadratures are implemented in the PLH code. The Gauss-Legendre (GL) [15], which do not take into account explicitly the cosine and sine parts of the last equation, and the Filon quadrature [16], which offers advantages in terms of accuracy and flexibility over the first one, since it takes into account the trigonometric functions. The Filon scheme is very efficient for slowly varying density matrix elements but requires the use of many integration points to reach high accuracies.
III. RESULTS

The critical step in our implementation was to make the orbital coefficients \( C_{pj} \) smooth functions of the equidistant \( k \) points so that the derivatives \( \partial C_{pj}(k) / \partial k \) can be obtained, and to calculate the current contribution \( P_I \) to the polarization and the corresponding term in the single-particle Hartree-Fock equation. Each SCF iteration in the PLH code consists of \( isubmx \) Filon subiterations (in our case \( isubmx = 6 \)) and the Filon quadrature is assumed to converge when the difference between the values obtained by using \( 2^i k \) and \( 2^{i-1} k \) points, where \( i \) is the number of the corresponding subiteration, does not differ by a value greater than a default threshold at the \( i \)-th iteration. For this reason, it was not very easy to collect, in the correct order, the orbital coefficients obtained by solving the equation \( F(k) C(k) = S(k) C(k) \varepsilon(k) \) at each \( (2^{isubmx} + 1) k \) points. After some rearrangements the coefficients were smoothed as a function of \( k \) and numerical stable derivatives, \( \partial C_{pj}(k) / \partial k \), were obtained. In the case of \( \text{H}_2 \) chain with a very large unit cell (e.g. \( a = 20 \) a.u.) the value obtained for the polarizability in the presence of external electric field is in agreement with the results of Champagne [17].

IV. CONCLUSIONS

The implementation of a vector potential approach, which enables the calculation of the polarization in the presence of external electric field, in an \textit{ab initio} LCAO-SCF algorithm was briefly outlined. This was generally possible since the constructed model Hamiltonian contains all essential elements of an \textit{ab initio} Hartree-Fock one. Despite some critical steps in the implementation, SCF convergence was achieved and the total polarization in the case of large \( \text{H}_2 \) chain was obtained. In this case only the charge term \( (P_\rho) \) contributes to the polarization, since there is no current \( (P_I = 0) \). Calculations of the charge flow, \( P_I \), contribution and the total polarization, \( P_{tot} \), for \( \text{H}_2 \) and other regular polymers are in progress.

ACKNOWLEDGMENTS

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Coupled Perturbed HF/KS calculation of the dielectric constant of crystalline systems. The case of six members of the garnet family.

Meyer A.*, Ferrero M.*, Valenzano L.*, Zicovich-Wilson C. M.†, Orlando R.** and Dovesi R.*

* Dipartimento di Chimica IFM, Università di Torino and NIS - Nanostructured Interfaces and Surfaces - Centre of Excellence, http://www.nis.unito.it, Via P. Giuria 7, 10125 Torino, Italy
† Facultad de Ciencias Universidad Autónoma del Estado de Morelos, Av. Universidad, 1001, Col. Chamilpa, 62209 Cuernavaca (Morelos), Mexico.
** Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale, Viale T. Michel 11, 1-15121 Alessandria, Italy

Abstract. The dielectric constant \( \varepsilon \) of pyrope \((\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3)\), grossular \((\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3)\), andradite \((\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3)\), almandine \((\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3)\), spessartine \((\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3)\), and uvarovite \((\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3)\) garnets has been calculated by using for the first time the CPHF/KS computational scheme recently implemented in the CRYSTAL code. Garnets are large unit cell (80 atoms in the primitive cell) highly symmetric (Ia\(\overline{3}\)d space group) compounds of relevant importance in geology and mineralogy. An all electron Gaussian type Basis Set has been adopted for all atoms. For the four compound containing transition metal atoms the unrestricted formulation of the HF or KS equations has been used. The Basis Set effect has been explored, as well as the influence of the adopted functional, that ranges from LDA to HF through GGA (PBE) and hybrids PBE0 and B3LYP.

Keywords: dielectric constant, garnets, CPHF, CPKS, all electron, ab initio


INTRODUCTION

Garnets \((\text{X}_3\text{Y}_2\text{Si}_3\text{O}_{12})\) are important rock-forming silicates, as major constituents of the Earth’s upper mantle and relevant phases of high-pressure metamorphic rocks in the Earth’s crust. [1] Building blocks are \(\text{SiO}_4\) tetrahedra sharing corners with \(\text{YO}_6\) octahedra, whereas \(\text{X}^{2+}\) cations are in dodecahedral coordination. The primitive cell contains 80 atoms.

The Coupled Perturbed Hartree-Fock (CPHF) and Kohn-Sham (CPKS) method formulated for systems with periodicity ranging from 0-D (molecules) to 3-D (crystalline compounds) through 1-D (polymers) and 2-D (layers, slabs) has recently been implemented [2, 3, 4] in a development version of the CRYSTAL program [5]. The scheme, here applied to the calculation of the dielectric tensor \( \varepsilon \), is highly efficient, as it fully exploits the point symmetry of the system, the latter being \( O_h \) for the SCF and \( C_{4v} \) for the CPHF calculation. This permits to investigate systems with large unit cells (80 atoms in the present case) containing heavy atoms (Fe, Mn, Cr) that require an unrestricted treatment. The field is oriented along one of the main Cartesian directions and the calculation is limited to one component, as the tensor is diagonal and isotropic in the present case. The dielectric tensor is a key ingredient for the calculation of the longitudinal orbital (LO) branch of the IR spectrum.

Gaussian type basis sets of increasing size are explored, and five different functionals, namely LDA, PBE, B3LYP, PBE0 and HF are compared. The influence of the two most important computational parameters, namely the shrinking factor \( S \) for the \( k \) points of the first Brillouin zone and the tolerances \( T_i \) controlling the truncation of the coulomb and exchange series is documented.

For table 2, 3 and 4 basis set C of table 1 has been adopted: O ((8s)(411sp)(1d)), Mg ((8s)(511sp)(1d)), Si ((8s)(6311sp)(1d)), Ca ((8s)(6511sp)(2d)), Al ((8s)(6111sp)(1d)), Fe and Cr and Mn ((8s)(64111sp)(411d)(1f)). The shrinking factor used is 2 resulting in three \( k \)-point in the irreducible Brillouin zone; the infinite sums truncation parameters are set to \( T_1=T_2=T_3=7, T_4=8 \) and \( T_5=16 \). The Broyden SCF accelerator scheme is used for calculations on almandine. An FMIXING 50 [5] is used for CPHF/KS convergence.
TABLE 1. Effect of the basis set on the andradite dielectric constant. The B3LYP functional at the B3LYP optimized geometry with basis D has been used. Basis set A is: Ca(8-65-11G), Fe(8-64-11G/411), O(8-411G), Si(8-6-311G) (see [6]). The exponents (Bohr\(^{-2}\)) of the single Gaussian functions added at each line are given (the Ca \(d\) shell is a 3G contraction). \(E_G\) is the energy gap in eV, and \(\Delta E\) is the energy lowering (mHartree per unit cell) of a given basis set with respect to the one of the previous line. The energy of basis set A is -25327.527 Hartree.

<table>
<thead>
<tr>
<th>BS</th>
<th>(\varepsilon_{xx})</th>
<th>(E_G)</th>
<th>(\Delta E)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>2.911</td>
<td>3.692</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>A+1d(<em>{Ca})+1d(</em>{Si})+1d(_{O}) ((3.9,1.3,0.38));(0.6);(0.5)</td>
<td>3.402</td>
<td>3.557</td>
</tr>
<tr>
<td>C</td>
<td>A+1d(<em>{Ca})+1d(</em>{Si})+1d(<em>{O})+1f(</em>{Fe}) ((3.9,1.3,0.38));(0.6);(0.5);(0.6)</td>
<td>3.401</td>
<td>3.583</td>
</tr>
<tr>
<td>D</td>
<td>A+2d(<em>{Ca})+2d(</em>{Si})+2d(<em>{O})+2f(</em>{Fe}) ((3.9,1.3,0.68);0.35);(1.5,0.5);(1.5,0.5);(1.5,0.5)</td>
<td>3.414</td>
<td>3.583</td>
</tr>
<tr>
<td>E</td>
<td>D+1f(<em>{Ca}}+1f</em>{Si}}+1f_{O}} (0.4);(0.7);(0.7)</td>
<td>3.426</td>
<td>3.596</td>
</tr>
<tr>
<td>F</td>
<td>D+2f(<em>{Ca}}+2f</em>{Si}}+2f_{O}} (0.6,0.3);(1.0,0.15);(1.0,0.5);(1.0,0.5)</td>
<td>3.471</td>
<td>3.562</td>
</tr>
<tr>
<td>G</td>
<td>F+1f(_{Fe}} (1.6,0.9,0.4)</td>
<td>3.474</td>
<td>3.562</td>
</tr>
</tbody>
</table>

BASIS SET AND COMPUTATIONAL TOLERANCES

Seven basis sets of increasing quality (indicated as A-F in table 1) have been considered in the case of andradite. The number of added \(d\) and \(f\) polarization functions and their exponents are given in the table. The complete basis set C is given in ref [6]. It turns out that from basis B or C on the \(\varepsilon\) variation is smaller than 2%, in spite of the large increase in the number of AO's (1640/cell for B, 2112/cell for D and 3176/cell for G). The effect of the computational conditions has been checked with reference to the C basis set given in table 1. The shrinking factor \(S\) has been increased to \(S=3\) and \(S=4\) (the number of \(k\) points evaluated in the irreducible Brillouin zone goes from 3 to 4 and 8); the energy difference is 15 \(\mu\)Ha between \(S=2\) and \(S=3\) (from \(S=3\) to \(S=4\) the difference is three orders of magnitude smaller), whereas \(\varepsilon\) goes from 3.4135 (\(S=2\)) to 3.4124 (\(S=3,4\)). The other important parameters are the ones controlling the truncation of the exchange series (see ref [5]), indicated as (T4,T5), that for the results reported in the tables 2, 3, 4 have been set to (8,16). Case C above has been rerun with (10,20) and (15,30) for (T4,T5): the effect on energy is -4 mHa for the first step and -2 mHa for the second, whereas \(\varepsilon\) moves to 3.408 and 3.414, respectively.

GEOMETRY

There are only four geometrical parameters to be optimized in the garnet unit cell: the cell edge \(a\) and the three oxygen fractional coordinates \(O_x, O_y\) and \(O_z\). The results are shown in table 2. LDA always underestimates \(a\) by 0.5 to 1.2 % while the other functionals overestimate \(a\) by 1.5 % (PBE), 1.0 to 1.5 % (B3LYP), up to 0.3 % (PBE0) and 0.4 to 1.0 % (HF). PBE0 gives in general the best description also for \(O_x, O_y\) and \(O_z\), resulting the more accurate functional in describing geometry.

As regards pure DFT calculations of almandine, an incorrect metallic state is found. This prevents from performing the CPKS calculations.

DIELECTRIC CONSTANT

Calculated and experimental dielectric constants \(\varepsilon\) are reported in table 3 and 4 where optimized and experimental geometries have been used respectively. The sum over states (SOS) approximation as well as the band gap \(E_G\) are
TABLE 2. Optimized and experimental geometries of the six end members. \(a\) in Å, \(O_x\), \(O_y\) and \(O_z\) are fractional coordinates.

<table>
<thead>
<tr>
<th></th>
<th>pyrope</th>
<th>grossular</th>
<th>andradite</th>
<th>almandine</th>
<th>spessartine</th>
<th>uvarovite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVWN</td>
<td>(a) 11.3728</td>
<td>11.7288</td>
<td>11.9316</td>
<td>11.3788</td>
<td>11.4874</td>
<td>11.8651</td>
</tr>
<tr>
<td></td>
<td>(O_x) 0.0319</td>
<td>0.0368</td>
<td>0.0381</td>
<td>0.0332</td>
<td>0.0338</td>
<td>0.0378</td>
</tr>
<tr>
<td></td>
<td>(O_y) 0.0524</td>
<td>0.0472</td>
<td>0.0507</td>
<td>0.0532</td>
<td>0.0501</td>
<td>0.0489</td>
</tr>
<tr>
<td></td>
<td>(O_z) 0.6530</td>
<td>0.6509</td>
<td>0.6550</td>
<td>0.6523</td>
<td>0.6519</td>
<td>0.65346</td>
</tr>
<tr>
<td></td>
<td>(O_x) 0.0319</td>
<td>0.0371</td>
<td>0.0384</td>
<td>0.0337</td>
<td>0.0340</td>
<td>0.0385</td>
</tr>
<tr>
<td></td>
<td>(O_y) 0.0498</td>
<td>0.0449</td>
<td>0.0493</td>
<td>0.0499</td>
<td>0.0479</td>
<td>0.0478</td>
</tr>
<tr>
<td></td>
<td>(O_z) 0.6535</td>
<td>0.6515</td>
<td>0.6558</td>
<td>0.6526</td>
<td>0.6522</td>
<td>0.6544</td>
</tr>
<tr>
<td>B3LYP</td>
<td>(a) 11.5475</td>
<td>11.9439</td>
<td>12.1809</td>
<td>11.6349</td>
<td>11.7147</td>
<td>12.1200</td>
</tr>
<tr>
<td></td>
<td>(O_x) 0.0322</td>
<td>0.0375</td>
<td>0.0387</td>
<td>0.0339</td>
<td>0.0345</td>
<td>0.0385</td>
</tr>
<tr>
<td></td>
<td>(O_y) 0.0490</td>
<td>0.0449</td>
<td>0.0485</td>
<td>0.0507</td>
<td>0.0480</td>
<td>0.0475</td>
</tr>
<tr>
<td></td>
<td>(O_z) 0.6533</td>
<td>0.6513</td>
<td>0.6555</td>
<td>0.6525</td>
<td>0.6522</td>
<td>0.6543</td>
</tr>
<tr>
<td>PBE0</td>
<td>(a) 11.4632</td>
<td>11.8562</td>
<td>12.0817</td>
<td>11.5365</td>
<td>11.6190</td>
<td>12.0208</td>
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<tr>
<td></td>
<td>(O_x) 0.0323</td>
<td>0.0375</td>
<td>0.0387</td>
<td>0.0339</td>
<td>0.0345</td>
<td>0.0385</td>
</tr>
<tr>
<td></td>
<td>(O_y) 0.0490</td>
<td>0.0449</td>
<td>0.0463</td>
<td>0.0479</td>
<td>0.0459</td>
<td>0.0457</td>
</tr>
<tr>
<td></td>
<td>(O_z) 0.6533</td>
<td>0.6513</td>
<td>0.6555</td>
<td>0.6525</td>
<td>0.6522</td>
<td>0.6553</td>
</tr>
<tr>
<td>HF</td>
<td>(a) 11.4460</td>
<td>11.8829</td>
<td>12.1544</td>
<td>11.5918</td>
<td>11.6586</td>
<td>12.1048</td>
</tr>
<tr>
<td></td>
<td>(O_x) 0.0329</td>
<td>0.0386</td>
<td>0.0399</td>
<td>0.0356</td>
<td>0.0356</td>
<td>0.0397</td>
</tr>
<tr>
<td></td>
<td>(O_y) 0.0490</td>
<td>0.0438</td>
<td>0.0463</td>
<td>0.0479</td>
<td>0.0459</td>
<td>0.0457</td>
</tr>
<tr>
<td></td>
<td>(O_z) 0.6536</td>
<td>0.6516</td>
<td>0.6561</td>
<td>0.6527</td>
<td>0.6522</td>
<td>0.6553</td>
</tr>
<tr>
<td>EXP</td>
<td>(a) 11.4390</td>
<td>11.8450</td>
<td>12.0510</td>
<td>11.512</td>
<td>11.6124</td>
<td>11.988</td>
</tr>
<tr>
<td></td>
<td>(O_x) 0.03291</td>
<td>0.03823</td>
<td>0.03914</td>
<td>0.0395</td>
<td>0.03510</td>
<td>0.03991</td>
</tr>
<tr>
<td></td>
<td>(O_y) 0.05069</td>
<td>0.04528</td>
<td>0.04895</td>
<td>0.04766</td>
<td>0.04737</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(O_z) 0.65331</td>
<td>0.65137</td>
<td>0.65534</td>
<td>0.65268</td>
<td>0.65261</td>
<td>0.65354</td>
</tr>
</tbody>
</table>

TABLE 3. Dielectric constant at the optimized geometry. SOS stands for sum over states and \(E_G\) (in eV) is the band gap. Experimental data from ref. [7] (uvarovite) and [8].

<table>
<thead>
<tr>
<th></th>
<th>pyrope</th>
<th>grossular</th>
<th>andradite</th>
<th>almandine</th>
<th>spessartine</th>
<th>uvarovite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVWN</td>
<td>(\varepsilon) 2.978</td>
<td>3.078</td>
<td>4.304</td>
<td>metallic</td>
<td>3.649</td>
<td>3.945</td>
</tr>
<tr>
<td></td>
<td>(SOS) 3.143</td>
<td>3.244</td>
<td>4.481</td>
<td></td>
<td>3.759</td>
<td>4.134</td>
</tr>
<tr>
<td></td>
<td>(E_G) 5.335</td>
<td>5.781</td>
<td>0.408</td>
<td></td>
<td>1.573</td>
<td>1.712</td>
</tr>
<tr>
<td>PBE</td>
<td>(\varepsilon) 2.971</td>
<td>3.026</td>
<td>4.319</td>
<td>metallic</td>
<td>3.598</td>
<td>3.827</td>
</tr>
<tr>
<td></td>
<td>(SOS) 3.086</td>
<td>3.151</td>
<td>4.444</td>
<td></td>
<td>3.654</td>
<td>3.965</td>
</tr>
<tr>
<td></td>
<td>(E_G) 4.980</td>
<td>5.369</td>
<td>0.748</td>
<td></td>
<td>2.064</td>
<td>2.042</td>
</tr>
<tr>
<td>B3LYP</td>
<td>(\varepsilon) 2.735</td>
<td>2.775</td>
<td>3.401</td>
<td></td>
<td>3.228</td>
<td>3.080</td>
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<tr>
<td></td>
<td>(SOS) 3.624</td>
<td>2.674</td>
<td>3.130</td>
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<td>2.975</td>
<td>2.882</td>
</tr>
<tr>
<td></td>
<td>(E_G) 7.367</td>
<td>7.704</td>
<td>3.583</td>
<td></td>
<td>2.764</td>
<td>5.269</td>
</tr>
<tr>
<td>PBE0</td>
<td>(\varepsilon) 2.780</td>
<td>2.791</td>
<td>3.292</td>
<td></td>
<td>3.189</td>
<td>3.070</td>
</tr>
<tr>
<td></td>
<td>(SOS) 2.594</td>
<td>2.634</td>
<td>2.975</td>
<td></td>
<td>2.894</td>
<td>2.815</td>
</tr>
<tr>
<td></td>
<td>(E_G) 7.866</td>
<td>8.276</td>
<td>4.477</td>
<td></td>
<td>3.677</td>
<td>4.160</td>
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<tr>
<td>HF</td>
<td>(\varepsilon) 2.363</td>
<td>2.356</td>
<td>2.411</td>
<td></td>
<td>2.499</td>
<td>2.470</td>
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<tr>
<td></td>
<td>(SOS) 1.902</td>
<td>1.912</td>
<td>1.926</td>
<td></td>
<td>1.969</td>
<td>1.953</td>
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<tr>
<td>EXP</td>
<td>(\varepsilon) 3.06</td>
<td>2.96</td>
<td>3.53</td>
<td></td>
<td>3.24</td>
<td>3.42</td>
</tr>
</tbody>
</table>

reported. \(E_G\) is a critical parameter since it define the denominator of the perturbative expression of \(\varepsilon\). It turns out that the difference between \(\varepsilon\) obtained with the two geometries is extremely small, the largest difference being 2% for LDA, that shows also the largest geometry modifications. We can now compare the results obtained with the various functionals referring to table 3. Pure DFT functionals overestimate \(\varepsilon\) from 0.35 to 0.78. This results must be addressed to the large underestimation of \(E_G\) provided by LDA.
TABLE 4. Dielectric constant $\varepsilon$ at the experimental geometry. Other symbols as in previous table.

<table>
<thead>
<tr>
<th></th>
<th>pyrope</th>
<th>grossular</th>
<th>andradite</th>
<th>almandine</th>
<th>spessartine</th>
<th>uvarovite</th>
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<tbody>
<tr>
<td>SVWN</td>
<td>$\varepsilon$</td>
<td>2.966</td>
<td>3.038</td>
<td>4.284</td>
<td>metallic</td>
<td>3.655</td>
</tr>
<tr>
<td></td>
<td>SOS</td>
<td>3.117</td>
<td>3.199</td>
<td>4.460</td>
<td>3.762</td>
<td>4.120</td>
</tr>
<tr>
<td></td>
<td>$E_G$</td>
<td>5.269</td>
<td>5.620</td>
<td>0.503</td>
<td>1.593</td>
<td>1.778</td>
</tr>
<tr>
<td>PBE</td>
<td>$\varepsilon$</td>
<td>2.942</td>
<td>3.012</td>
<td>4.222</td>
<td>metallic</td>
<td>3.521</td>
</tr>
<tr>
<td></td>
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<td>3.131</td>
<td>4.338</td>
<td>3.575</td>
<td>3.922</td>
</tr>
<tr>
<td></td>
<td>$E_G$</td>
<td>5.368</td>
<td>5.740</td>
<td>0.697</td>
<td>2.072</td>
<td>2.1611</td>
</tr>
<tr>
<td>B3LYP</td>
<td>$\varepsilon$</td>
<td>2.731</td>
<td>2.778</td>
<td>3.399</td>
<td>3.171</td>
<td>3.083</td>
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<tr>
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<td>2.884</td>
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<td></td>
<td>$E_G$</td>
<td>7.643</td>
<td>7.995</td>
<td>3.628</td>
<td>2.768</td>
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<td>2.752</td>
<td>2.783</td>
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<td>2.850</td>
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<td>4.492</td>
<td>2.749</td>
<td>6.229</td>
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<tr>
<td>HF</td>
<td>$\varepsilon$</td>
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<td>2.371</td>
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<tr>
<td>EXP</td>
<td>$\varepsilon$</td>
<td>3.06</td>
<td>2.96</td>
<td>3.53</td>
<td>3.24</td>
<td>3.42</td>
</tr>
</tbody>
</table>

and PBE. Hybrid functionals perform better providing an underestimation ranging from 0.13 to 0.18 (B3LYP) and from 0.17 to 0.24 (PBE0), in line with the slight $E_G$ overestimation. Since PBE0 contains an higher fraction (25% instead of 20% in B3LYP) of Fock exchange, it overestimates $E_G$ more than B3LYP and gives worse results than B3LYP. HF band gaps are extremely large, and as a consequence $\varepsilon$ is underestimated by about 30%. SOS is larger than $\varepsilon$ by 5% (LDA) and by 4% (PBE) for pure DFT while it is smaller by about 6% (B3LYP) and 5% (PBE0) for hybrid functionals. In the case of HF, SOS is 25% smaller than $\varepsilon$. This result indicates that the relaxation of the orbitals improves the results with respect to SOS, reducing the overestimated $\varepsilon$ and increasing the underestimated ones.

The present data show that CPHF/KS calculations are now feasible also for large unit cell systems as garnets. Also for this property ($\varepsilon$) hybrid functionals turn out to be superior to pure DFT functionals and HF.

REFERENCES

On The Dependence Of Bulk Properties On Surfaces

Michael Springborg*, Bernard Kirtman† and Violina Tevekeliyska*

*Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, Germany
†Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, U.S.A.

Abstract.

By modifying the surfaces of large, regular systems it is possible to modify the polarization of the macroscopic system, although the polarization can only be modified in units of a lattice vector times the elemental charge. Alternatively, when treating the system as being infinite and periodic, there is no surface. In that case the definition of the polarization contains a so-far undefined additive constant of a lattice vector times the elemental charge. We show that the two cases are equivalent, although the reasons behind the ‘unknown’ additive constants in the two cases are very different. Subsequently, we show that the response of extended systems to electrostatic fields, including internal structure, piezoelectricity, bulk charge density, and (hyper)polarizabilities, depends on the additive constants, i.e., on the surfaces.

Keywords: electrostatic fields, structural properties, electronic properties, static polarizability, static hyperpolarizabilities

PACS: 77.65.-j, 77.65.Bn, 42.50.Ct

I. INTRODUCTION

According to the physical chemistry as most of us has been taught, properties of sufficiently large systems may be separated into extensive and intensive ones of which the former are proportional to the size of the system and the latter independent of this size. When the system of our interest contains a large number, \( N \), of identical building blocks, and we consider an extensive quantity, \( Z \), one may then always define an intensive one

\[
\bar{Z} = \lim_{N \to \infty} \frac{Z(N)}{N} = \lim_{N \to \infty} \left[ Z(N+1) - Z(N) \right].
\] (1)

A special case is that of the system of our interest being a macroscopic crystal that has a regular arrangement of identical unit cells where only near the surfaces deviations from this regularity occur. For sufficiently large crystals the surfaces form a vanishingly small part of the total system and, accordingly, it appears to be reasonable to assume that \( \bar{Z} \) depends only on the inner parts of the system, i.e., that \( \bar{Z} \) is a pure bulk property independent of the surfaces.

This is indeed very often the case. Moreover, this consensus is supported by the near-sightedness of the electronic interactions [1], according to which electronic interactions have a finite spatial range. There are, however, exceptions, where the surfaces influence the values of experimental observables that usually would be consider bulk properties. In this contribution we shall give one example of this, i.e., properties for macroscopic materials exposed to an external electrostatic field. For the sake of simplicity we shall concentrate on systems that are extended in only one direction like the one shown in Fig. 1. Different surfaces are in this case obtained by modifying the donor and acceptor groups at the ends.

\[ \text{FIGURE 1. Schematic representation of a long, but finite, regular chain. Each black circle represents a building block containing one or more atoms and placed regularly along the chain axis (the } z \text{ axis). Donor and acceptor groups (D and A) may be included at the terminations. The separation into a central (C) and two terminating (L and R) parts is shown through the vertical lines.} \]

The response a system to an electrostatic field is most conveniently quantized through the dipole moment. Assuming that the field is parallel to the chain direction (i.e., the \( z \) axis), \( Z \) in Eq. (1) will be the \( z \) component of the dipole moment,
\( \mu, \) and \( \bar{Z} \) will be the \( z \) component of the polarization, \( P. \) By using the spatial separation of Fig. 1 we obtain directly

\[
\mu = \int_L \rho(\vec{r}) d\vec{r} + \int_C \rho(\vec{r}) d\vec{r} + \int_R \rho(\vec{r}) d\vec{r},
\]

where \( \rho(\vec{r}) \) is the charge density. With \( a \) being the lattice constant of the central region, a simple algebra gives

\[
P = \mu_C + Q_R \cdot a,
\]

where \( Q_R \) is the total charge of the \( L \) region and \( \mu_C \) is the \( z \) component of the dipole moment of one of the central units. Thus, the polarization depends on the charge accumulated at the surfaces — i.e., it depends on the surface.

\( Q_R \) is, however, not completely arbitrary. Any deviation from an integral number of elementary charges (we shall here use atomic units and then set \( |e| = 1 \)) is due to the electrons. But by transforming the set of occupied electronic orbitals into a set of localized ones, \( \{w_{lp}\} \) (with \( w_{lp} \) being the \( p \)th orbital localized to the \( l \)th unit), the electronic part of the dipole moment may be written as [2]

\[
\mu_e = \sum_l \sum_p \int |w_{lp}(\vec{r})|^2 d\vec{r}.
\]

Since each of the \( w \) functions is occupied by exactly one electron, different terminations can at most change the number of electrons associated with the terminations by integers, i.e., the dipole moment of the donor-acceptor chains like the one of Fig. 1 is quantities as is \( Q_R \) [3, 4]. In Eq. (4) we have separated the dipole moment or, equivalently, the polarization into a nuclear and an electronic part,

\[
P = P_n - P_e,
\]

where we have included the differences in the sign of the nuclear and electronic charges directly in the definition of the two parts of the polarization.

Alternatively, one may treat the system of Fig. 1 as being infinite and periodic. In that case, the electronic orbitals are written as Bloch waves, characterized by a \( k \) number. When the orbitals are approximated through linear combinations of pre-chosen atom-centered basis functions,

\[
\psi_j(k, \vec{r}) = \sum_p C_{pj}(k) \chi_p(k, \vec{r}),
\]

\[
\chi_p(k, \vec{r}) = \frac{1}{\sqrt{K}} \sum_l e^{ikl} \chi_{lp}(\vec{r}),
\]

with \( \chi_{lp} \) being the \( p \)th basis function of the \( l \)th unit, the electronic part of the polarization may be written as

\[
P_e = \frac{2i}{K} \sum_{jk} \langle \psi_j(k, \vec{r}) | \frac{d}{dk} | e^{-ikz} \psi_j(k, \vec{r}) \rangle
\]

\[
= \frac{2}{K} \sum_{jkl} e^{ikl} \sum_{pq} |C_{pqj}(k)|^2 \langle \chi_{0q}|z - 1a|\chi_{lp} \rangle + \frac{2i}{K} \sum_{jkl} e^{ikl} \sum_{pq} C_{pqj}(k) \langle \chi_{0q}|\chi_{lp} \rangle \frac{d}{dk} C_{pj}(k).
\]

We have here neglected spin polarization, so that the \( j \) summation goes over all doubly occupied bands. Moreover, we require that there is a gap between occupied and empty orbitals. This relation expresses the \( P_e \) as a sum of charge (\( P_p \)) and current (\( P_j \)) contributions of which the former corresponds to the electronic part of \( \mu_C \) in Eq. (3) and the latter to the charge-transfer term in Eq. (3).

However, \( P \) is not unique. Thus, the orbitals may be modified by band and \( k \) dependent phase factors,

\[
\psi_j(k, \vec{r}) \rightarrow e^{i\phi_j(k)} \psi_j(k, \vec{r}),
\]

although

\[
\phi_j(+\pi/a) - \phi_j(-\pi/a) = n_j \cdot 2\pi
\]

since

\[
e^{i\phi_j(+\pi/a)} = e^{i\phi_j(-\pi/a)}.
\]
When inserting this into the expressions for the polarization, Eqs. (5) and (7), it is seen that \( P \) contains an unknown, additive constant, \( \tilde{n} \cdot a \), with \( \tilde{n} = \sum_j n_j \).

The purpose of the present contribution is twofold. At first, we shall demonstrate that different values of the additive constant for \( P \) for the infinite, periodic system corresponds to modeling different extended, but finite systems with different terminations. Second, we shall demonstrate that the different values of the additive constant leads to different responses of the system to electrostatic fields. The latter implies that the surfaces influence the bulk properties irrespective of how small a volume the surfaces make compared to the total system.

We shall base our arguments on results from calculations using a fairly simple model that, however, contains all the essential ingredients of an \textit{ab initio} Hartree-Fock calculation. The advantages of using such a model are that extensive calculations can be carried through also for large, finite systems, and that by varying the parameters entering the model it is possible to study different types of systems. Moreover, truncation errors that often can influence a comparison between \textit{ab initio} results of long, but finite systems and those of infinite, periodic systems can easily be made irrelevant for model systems.

\section{II. COMPUTATIONAL STUDIES}

The model we are considering is similar to the ones we have used in our earlier studies \cite{5, 6, 7}. We study a linear \( -\text{A} = \text{B} \) chain, i.e., a chain with alternating atoms and bond lengths. For the infinite, periodic system, two parameters describe the structure, i.e., the lattice constant, \( a \), and a parameter \( u_0 \) that describes the bond-length alternation, so that alternating atoms are displaced by \( +u_0 \) and \( -u_0 \) away from the equidistant positions. The system has 4 electrons per repeated unit, and the nuclear charges are 2. For the calculation of the electronic properties we use a Hartree-Fock approximation as well as a basis set of orthonormal atom-centered functions with two functions per atom. \( \hat{h}_0 \) is the one-electron operator without the external field and \( \hat{v} \) the two-electron operator. According to our model, the one-electron matrix element \( \langle \chi_{mq} | \hat{h}_0 | \chi_{lp} \rangle \) is assumed to be non-zero only for \( (q,m) = (p,l) \) (in which case it is a constant) and for \( m = l \pm 1 \) (in which case it depends linearly on the interatomic distance). Of the two-electron matrix elements, only \( \langle \chi_{iq} | \hat{v} | \chi_{jq} \rangle \) is assumed to be non-zero. Matrix elements for the dipole moment are calculated by setting \( \langle \chi_{mq} | \chi_{lp} \rangle = \delta_{mn} \delta_{ql} z_{mq} \), where \( z_{mq} \) is the \( z \) coordinate of the atom where the function is centered. For the finite chains we model different terminations by modifying the on-site energies \( \langle \chi_{mq} | \hat{h}_0 | \chi_{lmq} \rangle \) for \( m \) representing the first or last atom of the chain. In the calculations below we could thereby change the end-to-end electron transfer by 2 electrons. The electronic energy is augmented by an elastic term which contains 2nd and 4th order terms in nearest- and next-nearest-neighbor bond lengths. The constants of this term are determined by requiring that the structure of the infinite, periodic system for \( E_{\text{DC}} = 0 \) has certain pre-chosen values for \( a \) and \( u_0 \). For the infinite, periodic chains we used \( K = 80 \) \( k \) points, and for the finite chains we used \( N = 40 \) and \( N = 41 \) units.

For the infinite, periodic chain in the presence of an electrostatic field one has to solve the equations \cite{8, 9, 5, 6, 7}

\[
\begin{bmatrix}
E(k) - E_{\text{DC}} \cdot \left( M(k) + iS(k) \frac{\partial}{\partial k} \right)
\end{bmatrix} \cdot \tilde{C}_j(k) = e_j(k) \cdot \tilde{S}(k) \cdot \tilde{C}_j(k),
\]

(11)

where \( E_{\text{DC}} \) is the strength of the electrostatic field. Moreover, \( \tilde{C}_j(k) \) is the (field-dependent) \( j \)th column of the matrix \( \tilde{C}(k) \), and

\[
\begin{align*}
S_{qp}(k) & = \sum_l e^{ikl} \langle \chi_{0q} | \chi_{lp} \rangle \\
M_{qp}(k) & = \sum_l e^{ikl} \langle \chi_{0q} | z_l \chi_{lp} \rangle = \sum_l e^{-ikl} \langle \chi_{0q} | z_l \chi_{0p} \rangle \\
F_{qp}(k) & = \sum_l e^{ikl} \langle \chi_{0q} | \hat{F} | \chi_{lp} \rangle
\end{align*}
\]

are the overlap, unit cell dipole, and Fock matrix elements, respectively. Here \( \hat{F} \) is the usual Fock operator which depends on the field through the orbital coefficients. Because of the derivative with respect to \( k \), Eq. (11) is not a normal matrix-eigenvalue problem. In order to solve the equation we have developed an efficient and numerically stable approach\cite{5, 6, 7} that shall not be discussed in detail here except for one aspect. Our approach is based on a smoothing procedure whereby \( \tilde{C}_j(k) \) is modified by a band \( (j) \) and \( k \)-dependent phase factor, making the evaluation of \( \frac{\partial}{\partial k} \tilde{C}_j(k) \) numerically stable. With this approach the phases of \( \tilde{C}_j(k) \) are continuous as a function of \( k \). Thereby it has...
also become possible to derive analytical expressions for the derivatives of the total energy as a function of structure even for $E_{DC} \neq 0$ [6]. Applying the above-mentioned smoothing procedure will result in a value for the polarization that will lie in a certain range of length $a$. In order to modify this range by an integer times $a$, the orbitals of one or more bands are given additional phase factors, $e^{iakn_j}$, with $n_j$ being an integer. Then, the phases become discontinuous across the border of the Brillouin zone, although the phase factors remain continuous. For the sake of completeness we add that these discontinuities lead to an additional term, $-E_{DC} \sum_j n_j$, in the derivative of the total energy with respect to the lattice constant compared to the expression we have presented earlier [6].

![Graph](image)

**FIGURE 2.** Results from a set of representative calculations for the model. The open and closed circles are for finite chains with 40/41 units, whereas all other symbols are for periodic chains with 80 $k$ points. The finite-chain results differ in an end-to-end transfer of two electrons. For the periodic chains, ×, triangles, squares, stars, and + marks results for the integer $\tilde{n}$ being equal to 0, 1, $-1$, 2, and $-2$, respectively. In some panels, the results have been modified by an integer times twice the lattice constant in the field-free case, $a_0$, so that they lie on top of each other.

Representative results from the model calculations are shown in Fig. 2. One of the two major results is that the two
sets of finite-chain results lie on top of the periodic-chain results. The two different finite chains differ in the number of electrons accumulated at the terminations: in one case two electrons have been transferred from one end to the other compared to the other case. For the periodic chains, the electronic part of the polarization has been modified by \( n \cdot a \) by modifying the phases of the electronic orbitals as described above.

The second major finding is that the results depend on the values of \( n \) or, alternatively stated, on the charges accumulated at the terminations. This is, e.g., true for the lattice constant \( a \) and the internal structural parameter \( u_0 \) (for the finite chains their values were extracted from the structure of the central parts), which in turn means that piezoelectric properties like the volume change of a crystal due to an electrostatic field depend on the surfaces.

\( n_A \) is the number of excess electrons (according to a Mulliken population analysis and relative to the neutral atom) on a central A atom, which also depends on the surfaces. Thus, in the presence of an electrostatic field the electronic distribution in the inner parts of a macroscopic crystal depends on the surfaces, independent of the size of the crystal. Also the total number of electrons accumulated at the terminations and relative to the neutral case (denoted \( n_R \)) shows a dependence on the terminations beyond that of the two electrons being transferred from one end to the other.

Since the total polarization possesses a different dependence on the field strength for different values of \( \tilde{n} \) (for the infinite, periodic chains) or for different terminations (for the finite chains), also the polarizability and the hyperpolarizability will depend on the surfaces. By decomposing the polarization into the current term from the electrons (i.e., \( P_I \)) and the charge term from the electrons (\( P_\rho \)) plus the contribution from the nuclei (\( P_n \)) it is seen that both parts depend on the terminations.

**FIGURE 3.** As Fig. 2, but keeping the lattice constant fixed. The left panels are for the initial structure, and the right ones after relaxing \( u_0 \).

The dependence of the bulk quantities on the surfaces is an indirect effect and is solely due to the fact that the lattice constant depends on \( \tilde{n} \). This can be seen by performing periodic-chain calculations for which \( a \) has been kept fixed at the field-free value, \( a_0 \). The results are shown in Fig. 3. In this case, all value of \( \tilde{n} \) lead to the same results. Moreover, by comparing with Fig. 2 it is seen that relaxing \( a \) in general leads to stronger variations in the property of interest as a function of field strength. Keeping also \( u_0 \) fixed (see the left panels in Fig. 3) gives an even weaker dependence on the field strength.
III. CONCLUSIONS

The purpose of this presentation was twofold. At first we have established the connection between the polarization as calculated from the dipole moment of large, but finite system and as calculated by considering an infinite, periodic system. Second we have demonstrated that for large, finite systems exposed to external electrostatic potentials the properties of the inner parts depend on the nature of the surfaces, irrespective of the size of the system.

It turns out that the dipole moment of large, finite systems differing in the surfaces cannot take arbitrary values but only ones that differ by a lattice vector times the elementary charge. On the other hand, also the polarization when being calculated for the truly infinite and periodic system is limited to take discrete values; again differing by a lattice vector times the elementary charge. Although the additive constants have very different origins we could demonstrate that the two approaches are absolutely equivalent so that choosing different values for the additive constants for the infinite, periodic systems corresponds to modeling finite systems with different surfaces / terminations. Since it computationally is orders of magnitude more efficient to consider the former systems, this connection is important not only from a conceptual point of view.

The polarization can be considered the carrier of information for the response of the system to electrostatic fields and, therefore, it may be suggested that systems with different surfaces, or equivalently, different values for the polarization, show different response properties to electrostatic fields. This was indeed found to be the case and we arrived at the conclusion that when the systems are exposed to electrostatic fields the changes of the bulk properties depend on the surfaces / terminations.

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Linear and nonlinear second order susceptibilities of molecular crystals.

Edith Botek†, Benoît Champagne†, Małgorzata Olejniczak†‡, Magdalena Pecul†

† Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles, 61, B-5000 Namur, Belgium.
‡ Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

Abstract. First and second order susceptibilities have been investigated in previous works [1,2,3] for molecular crystals presenting very interesting features for nonlinear optics. Among them, 3-methyl-4-nitroaniline (MNA), 3-methyl-4-nitroaniline-1-oxyde (POM) and urea. In the first one, stacking unit cells along the a-axis (parallel to the dipole moment of the constituting molecular pairs) yield a strong enhancement of the effective first hyperpolarizability of the cluster, while stacking along the other directions leads to the opposite behavior. In the case of POM, the effective $\beta_{abc}$ value is close to the molecular response of an isolated molecule whereas all other tensor components vanish by symmetry upon packing. The urea crystal presents a supplementary feature related to intermolecular interactions through hydrogen bonding. Its microscopic properties were evaluated employing the supermolecule approach by means of the TDHF/AM1 procedure and the macroscopic quantities were obtained by adopting the multiplicative scheme corrected for missing correlation effects by DFT and coupled cluster calculations. Such combination appears to be an efficient tool to investigate, at least at a semiquantitative level, the linear and NLO properties of molecular crystals.

Keywords: molecular crystals, TDHF/AM1, supermolecule approach, multiplicative scheme

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PROCEDURE OF CALCULATION

The calculations of (hyper)polarizabilities were carried out by means of the semiempirical TDHF/AM1 procedure (MOPAC2000 program [4]), the Hartree-Fock (HF) method, density functional theory (DFT) schemes with the B3LYP and Cam-B3LYP exchange-correlation functionals as well as the coupled cluster singles-and-doubles (CCSD) approach. For the ab initio calculations the Dalton program [5] has been employed. The basis sets used range from cc-pVDZ, and 6-311G*, through the pVTZ basis set of Sadlej to the t-aug-cc-pVTZ basis set.

From the tensor components of the clusters, the packing effects on the property $\Pi$ ($\Pi = \alpha, \beta$) of an “averaged” urea molecule can be estimated by the ratio:

$$R_{\text{cluster}} = \frac{\Pi_{\text{cluster}}}{N \times \Pi_{\text{unit}} / 4}$$

where $\Pi_{\text{cluster}}$ and $\Pi_{\text{unit}}$ correspond to the (hyper)polarizabilities of the cluster and of the unit (containing 4 urea molecules) respectively, and N is the number of molecules stacked in the cluster. For two and three-dimensional clusters, within the multiplicative scheme, the estimated ratios are approximated from the ratios of the corresponding one-dimensional clusters by means of their products:

$$R_{\text{estimated}} = R^a \times R^b$$
and
\[ R_{estimated}^{Ia \times Jb \times Kc} = R_I^{a} \times R_J^{b} \times R_K^{c} \]  \hspace{1cm} (3)

where a, b and c account for the crystal directions and I, J, K denotes the number of units along each corresponding direction. The effective property \( \Pi \) of the cluster reads then as:
\[ \Pi_{estimated}^{cluster \ eff} = R_{estimated}^{Ia \times Jb \times Kc} \times \Pi_{unit \ cell} \]  \hspace{1cm} (4)

where, for the crystal, with the extrapolated ratios, is given by:
\[ \Pi_{estimated}^{crystal \ eff} = R_{(I \to \infty)}^{I} \times R_{(J \to \infty)}^{J} \times R_{(K \to \infty)}^{K} \times \Pi_{unit \ cell} \]  \hspace{1cm} (5)

Finally, the macroscopic susceptibility of the crystal can be estimated from:
\[ \chi^{(x)} = \frac{F^{\Pi} \Pi_{estimated}^{eff \ - \ crystal}}{e_0 V_{unit \ cell}} \]  \hspace{1cm} (6)

where \( x = 1, 2 \) corresponding to \( \Pi = \alpha, \beta \), respectively and \( F^{\Pi} \) denotes the correction accounting for the impact of the electron correlation, as estimated from DFT or \textit{ab initio} calculations on small systems. Such correction is evaluated as:
\[ F^{\Pi} = \frac{\Pi_{ab \ initio \ / \ DFT}}{\Pi_{AM1}} \]  \hspace{1cm} (7)

The unit cell of urea in its standard set is presented in Figure 1.

RESULTS AND DISCUSSION

AM1 (hyper)polarizabilities of the urea molecule, of the different dimers interacting in the clusters as well as the unit of four molecules were compared with DFT and CCSD \textit{ab initio} calculations demonstrating the effectiveness of AM1 to describe some degree of electron correlation at a low computational cost. This preliminary analysis justifies its further application in a supermolecule approach. It is noticed that the packing ratios for small 1D, 2D, and 3D clusters are all close to 1. ‘R’ ranges from 0.892 to 1.058 for the polarizability, and from 0.878 to 1.169 for the first hyperpolarizability. Thus, in a first approximation, the (hyper)polarizability of urea clusters displays almost an additive character. This observation needs, however, to be modulated by noticing that the deviation from additivity increases with the size of the cluster, especially when packing along \( c \). The R packing ratios are then compared to their estimates using the multiplicative scheme (Eqs. 2 and 3), demonstrating that this scheme leads to errors on the polarizability smaller than 5% for each crystallographic direction. For the first hyperpolarizability, the error is even smaller, with a maximum of 2.6%. However, the error presents the trend to increase with the size of the clusters. For larger 1D clusters the optical properties remain nearly additive. Indeed, the largest deviations from unity are displayed by the packing ratios of \( \alpha_{cc} \) when packing molecules along the \( c \) axis (\( R \sim 1.3 \)), which coincides with the direction of the dipole moment. For such component also the largest difference between the \( b \) and \( c \) packing ratios is obtained, resulting in an 83% variation between the \( \alpha_{cc} \) values for 10\( b \) and 10\( c \) clusters. Similar effects are observed for \( \beta_{abc} \) (Table 1) with an increase in the effective first hyperpolarizability by about 30% when packing along the \( c \) axis and a decrease by about 10% when packing along the other directions. This \( \beta_{abc} \) enhancement when packing molecules along the \( c \) axis can be related to the strong intermolecular interactions and, in particular, to the cooperative effects of the hydrogen bonds.

In summary, on finite urea clusters, contrary to the case of MNA, we have observed a rather small packing-induced deviation of the polarizability and first hyperpolarizability \( \beta_{abc} \) from additivity. Thus, although this statement is restricted by the size of the computationally affordable clusters (3\( a \times 3\( b \times 3\( c \)), we conclude that the multiplicative scheme should be reliable in this case and could be used to estimate the
susceptibilities of the crystal by means of eq. (6). Indeed, the global performance of the presented scheme differs for the linear and nonlinear responses: an underestimation of the experiment is obtained for the linear susceptibility, meanwhile a good agreement of theory and experiment is attained for the second order nonlinear susceptibility.

**FIGURE 1.** The unit cell of urea crystal. The unit cell parameters are \( a=b=5.5890 \, \text{Å}, \quad c=4.6947 \, \text{Å}, \) and \( V=146.648 \, \text{Å}^3 \) [6].

**TABLE 1.** \( \beta_{abc} \) (a.u.) tensor component (\( \lambda=1064 \, \text{nm} \)) calculated at AM1 level and corresponding crystal packing ratios (\( R \)). For 2D and 3D clusters, the \( R \)-factors calculated directly from Eq. (1) are compared to those estimated within the multiplicative scheme by using Eqs. (2) and (3) while the associated error (E) is determined from \( E(\%)=100(R_{\text{multi}}-R)/R \).

<table>
<thead>
<tr>
<th>Cluster</th>
<th>( \beta_{abc}(-2\omega; \omega, \omega) )</th>
<th>( R )</th>
<th>( R_{\text{multi}} )</th>
<th>E[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 unit cell</td>
<td>-225</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 unit cells along b (2b)</td>
<td>-380</td>
<td>0.965</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 unit cells along c (2c)</td>
<td>-500</td>
<td>1.111</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 unit cells along b (3b)</td>
<td>-533</td>
<td>0.948</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 unit cells along c (3c)</td>
<td>-789</td>
<td>1.169</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a x 2b</td>
<td>-624</td>
<td>0.924</td>
<td>0.931</td>
<td>0.8</td>
</tr>
<tr>
<td>2b x 2c</td>
<td>-840</td>
<td>1.067</td>
<td>1.072</td>
<td>0.5</td>
</tr>
<tr>
<td>2a x 2b x 2c</td>
<td>-1377</td>
<td>1.020</td>
<td>1.035</td>
<td>1.5</td>
</tr>
<tr>
<td>3b x 2a</td>
<td>-867</td>
<td>0.907</td>
<td>0.914</td>
<td>0.9</td>
</tr>
<tr>
<td>3b x 2c</td>
<td>-1177</td>
<td>1.046</td>
<td>1.053</td>
<td>0.6</td>
</tr>
<tr>
<td>3a x 3b</td>
<td>-1200</td>
<td>0.889</td>
<td>0.898</td>
<td>1.0</td>
</tr>
<tr>
<td>3a x 3b x 3c</td>
<td>-4150</td>
<td>1.025</td>
<td>1.050</td>
<td>2.4</td>
</tr>
</tbody>
</table>
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Determining The Size Dependence Of Structural Properties Of Clusters

Yi Dong and Michael Springborg

Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, Germany

Abstract.
Problems related to the determination of the structure of the global total-energy minimum for clusters are discussed through three examples. For isolated gold clusters it is shown that low-symmetry structures result due to covalent bonding. Subsequently, Si$_N$Ge$_M$ and (HAIO)$_N$ clusters are treated for which the occurrence of so called homotops leads to additional computational complexity. For the former it is found that the structures are not directly related to those of the pure monatomic clusters, and for the latter the results are shown to be in agreement with available experimental information on nanostructured HAIO. In order to illustrate and analyze the results, various descriptors are introduced and applied.

Keywords: clusters, structural properties, energetic properties

PACS: 36.40.-c, 61.46.-w, 31.15.xv

I. INTRODUCTION

Clusters can be considered as intermediates between small molecules and macroscopic solids. Their size is so small that the thermodynamic limit has not been reached. Therefore, the properties of the clusters cannot be obtained through a simple interpolation between those of the small molecules and those of the solids. Instead, the size dependence of the properties often shows a fairly irregular behavior. This fact makes clusters interesting for many technological applications, once the size dependence has been understood. On the other hand, since the clusters are at most metastable, it is difficult to obtain the required information through experimental studies and theoretical studies can provide a useful complement to the experimental ones.

Theoretical studies of the size dependence of the properties of clusters are, however, far from trivial. This is due to the fact that the structure of a given cluster in most case is completely unknown combined with a not too small size of typical clusters (that may contain from around 10 atoms to several 1000s of atoms). As a consequence of the first issue (in the ideal case) an unbiased search in a multi-dimensional structure space has to be carried through. Since, however, the number of different metastable structures grows essentially exponentially with size of the cluster, the identification of the structure of the global total-energy minimum becomes an almost impossible task for just intermediate-sized clusters. In addition, the computational demands for calculating the total energy for a given structure grows with cluster size to some power, typically 3. In combination, these challenges can only be met by using structure-optimization methods that have been developed specifically for the problem at hand, combined with efficient, often approximate, total-energy methods (see, e.g., [1, 2, 3, 4] for further discussion of these issues).

A further challenge is to extract useful information from the calculations. Assuming that we have optimized the structure for a certain range of sizes, we will end up with a large set of coordinates of the nuclei for the individual clusters as well as their total energies. Simply drawing all the cluster structures does rarely bring useful insight, as also is the case when plotting the total energy (eventually per formula unit) as a function of cluster size. Instead, in order to identify trends in the chemical and physical properties it is necessary to devise special descriptors for this.

It is the purpose of the present contribution to present a few examples of our own studies where we have addressed these challenges for specific systems. We shall briefly outline our computational approach in the following section, and afterward present results for clusters with one, two, and three types of atoms, i.e., on Au$_N$, (SiGe)$_N$, and on (HAIO)$_N$ clusters.
II. COMPUTATIONAL METHODS

In order to reduce the computational needs for the calculation of the total energy for a given system and structure we apply a parametrized density-functional method that has been described in detail elsewhere [5, 6, 7]. It is based on a frozen-core approximation so that only the valence electrons are explicitly treated in the calculations. Moreover, in our calculations we use a non-self-consistent version. According to this method, the relative total energy of a given compound with a chosen structure is written as the difference in the orbital energies of the compound minus those of the isolated atoms,

\[ \sum_i \epsilon_i - \sum_m \sum_i \epsilon_{mi}, \]  

(1)

where \( m \) is an atom index and \( i \) an orbital index, augmented with pair potentials,

\[ \sum_{m_1 \neq m_2} U_{m_1, m_2} (|\vec{R}_{m_1} - \vec{R}_{m_2}|), \]  

(2)

where \( \vec{R}_m \) is the position of the \( m \)th atom.

The orbital energies are calculated by expanding the electronic orbitals in a set of atom-centered basis functions. The single-electron (Kohn-Sham) operator \( \hat{h} \) contains the kinetic-energy operator as well as the potential. The latter is approximated as a superposition of the potentials of the isolated atoms,

\[ V(\vec{r}) = \sum_m V_m (|\vec{r} - \vec{R}_m|), \]  

(3)

and subsequently we assume that the matrix element \( \langle \chi_{m_1 n_1} | V_m | \chi_{m_2 n_2} \rangle \) vanishes unless at least one of the atoms \( m_1 \) and \( m_2 \) equals \( m \). Here, \( \chi_{nn} \) is the \( n \)th atomic orbital of the \( n \)th atom. Finally, the pair potentials \( U_{m_1, m_2} \) are obtained by requiring that the total-energy curves from parameter-free density-functional calculations on the diatomic molecules are accurately reproduced. With these approximations all relevant information on the above-mentioned matrix elements can be extracted from calculations on isolated two-atomic systems.

With this method we can obtain the total energy of a given structure, and by calculating also the forces acting on the atoms, i.e., the derivatives of the total energy with respect to nuclear coordinates, also the structure of a local total-energy minimum can be identified. In order to search for the structure of the global total-energy minimum for the isolated clusters we have used a method based on genetic algorithms. Our version of the genetic algorithms is as follows. Suppose that we have optimized the structure of the cluster with \( N \) units. From this structure we construct a first generation consisting of \( P \) independent clusters for the \( (N + 1) \)-unit system by randomly adding the atoms of one further unit and letting each of these structures relax to its nearest total-energy minimum. Subsequently, a new set of clusters is constructed by cutting each of the original ones randomly into two parts that are interchanged (under the constraints mentioned above) and, subsequently, allowed to relax. Out of the total set of \( 2P \) structures, the \( P \) ones of the lowest total energy are kept as the next generation. This procedure is repeated until the lowest total energy is unchanged for a large number of generations.

III. AU CLUSTERS

Au is a metal and, accordingly, it may be expected that the structure of gold clusters is based on metallic bonding which would lead to the preference of closed-packed structures. Indeed, in an earlier set of calculations we studied the properties of gold clusters for which the interatomic interactions were approximated through a simple embedded-atom potential whereby electronic degrees of freedom are ignored. In this case we found that the structures of the lowest total energy were determined first of all by the requirement of close packing and high coordination [8].

On the other hand, in many cases low-coordinated gold atoms are found, suggesting that covalent bonding and directional bonds are important. A proper description of those requires the inclusion of electronic effects in the interatomic interactions. In order to study those we have, therefore, used the approach of the preceding section for the study of gold clusters. At first, we considered all clusters with up to 20 atoms [9, 10], but have later extended the study to Au\(_N\) clusters with \( N \leq 58 \) [11].

We found that the binding energy per atom is an increasing function of \( N \) up to around \( N \approx 20 \), which is a small number. For \( N > 20 \), the binding energy per atom is an irregular, only slowly increasing function of \( N \). Moreover, for
none of the clusters of our study we found 12-fold coordinated gold atoms (the number for the fcc crystal structure), but only lower values. This confirms that gold can exist in low-coordinated situations.

In order to analyze the structural properties we have found it useful to consider the radial distances. For any cluster with \( N \) atoms, we use the coordinates of the atoms, \( \{ \vec{R}_m, m = 1, 2, \ldots, N \} \), in defining the center,

\[
\vec{R}_0 = \frac{1}{N} \sum_{m=1}^{N} \vec{R}_m \tag{4}
\]

and, subsequently, for each atom its radial distance,

\[
r_m = |\vec{R}_m - \vec{R}_0| \tag{5}
\]

FIGURE 1. The radial distances (in a.u.) of Au\(_N\) clusters as functions of \( N \). For each value of \( N \) one small horizontal line indicates that at least one atom of the Au\(_N\) cluster has that value as its radial distance. The thick curve shows the radius of a sphere with the atom density as in crystalline Au.

Already the radial distances themselves give some information on the structures of the clusters, cf. Fig. 1. Thus, for none of the Au\(_N\) clusters we have only few different values of the radial distances, implying that none of these structures have a high symmetry. Moreover, for clusters with \( N \) between roughly 10 and 25, no atom has low values for the radial distances, i.e., these structures are what has been called ‘golden cages.’ As discussed elsewhere [11] these findings are in agreement with earlier studies on gold clusters, whereby in most of those cases either only some few cluster sizes were considered or a less detailed structure optimization was carried through.

There is, however, one aspect where our approach partly fails. The structure of the lowest total energy for Au\(_N\) clusters is planar up to \( N \) slightly above 10, whereas we find the transition from planar to purely three-dimensional structures to take place already at \( N = 7 \), although the planar structures were found to have total energies only slightly
above those of the three-dimensional ones. This problem may be ascribed to our approximate description of the total energy and suggests that an improvement could be to reoptimize more of the structures from our calculations using more sophisticated total-energy methods.

We can also use the radial distances in quantifying the structural properties of the clusters. As shown elsewhere [11] they can be used in describing to which extent the clusters resemble fragments of the fcc crystal or of a large icosahedron. Moreover, they can be used in quantifying whether the Au$_N$ cluster resembles the cluster with $N - 1$ atoms plus an extra one, as well as giving the overall shape of the cluster. It is often useful to define a so called similarity function, $S$. When comparing two objects with $N$ and $M$ atoms we determine for each object separately its radial distances and sort those in increasing order. Subsequently, from

\[ q = \frac{1}{\min(M,N)} \left[ \sum_{i=1}^{\min(M,N)} \left( \frac{r_{i,M}}{u_M} - \frac{r_{i,N}}{u_N} \right)^2 \right]^{1/2} \]  

$S$ is defined as

\[ S = \frac{1}{1 + u}. \]  

$S$ approaches 1 (0) if the two objects are very similar (different). $\{r_{i,M}\}$ and $\{r_{i,N}\}$ are the sorted radial distances for the two objects. Moreover, $u_M$ and $u_N$ are length scales which we often choose as 1 Å or 1 a.u. We shall here not give examples of the similarity functions but instead refer the interested reader to [11].

IV. SIGE CLUSTERS

In clusters of Si and Ge atoms the chemical bonds are covalent and directional. Since the most stable crystal structure of the pure elements is that of diamond and, moreover, the lattice constants for crystalline Si and Ge are very similar it may be expected that pure Si and Ge clusters as well as the mixed clusters have structures that resemble those of the crystals. In a first study of the properties of Ge-Si clusters we, therefore, considered structures that were constructed as relaxed, finite parts of the diamond crystal structure [12, 13]. For the mixed clusters we considered more different distributions of the two types of atoms and found that the most stable ones were the pure mixed clusters, whereas core/shell and purely segregated clusters were less stable.

However, as we have seen above for the Au clusters, the structures of those semiconductor clusters may have very little in common with those of the macroscopic materials. Therefore, we decided in a more recent study to carry through unbiased structure optimizations for Si$_2$N, Ge$_2$N, and Si$_N$Ge$_N$ clusters [14]. For the mixed systems the additional complication due to the existence of so called homotops shows up. Homotops are different structures of clusters with more types of atoms, having the same geometric arrangement of the atoms, but differing in the distribution of the different types of atoms [15]. The number of homotops can be large: for a Si$_N$Ge$_N$ cluster it equals $\frac{(2N)!}{(N!)^2}$, and, therefore, their existence leads to dramatic increases in the computational requirements.

Our study [14] gave indeed that the structures were quite different from that of the diamond structure. It turned out that the mixed clusters were more compact than those of the pure elements that showed some tendency towards an elongated shape. Moreover, in the mixed clusters we found first of all Si–Si and Si–Ge covalent bonds and only few Ge–Ge bonds.

When studying structural similarity (for instance between the pure clusters of the two elements) we have to take into account that the structures may be essentially identical except for a scaling. This can be taken into account by using different length units $u_M$ and $u_N$ above for the two different elements although a unique definition is hardly possible. However, even with this limitation, a similarity analysis can be carried through and gives, for example, that the mixed clusters resemble more the pure Si than the pure Ge clusters (see [14]).

V. HALO CLUSTERS

HALO is a nanostructured material with a 1:1:1 content of hydrogen, aluminum, and oxygen, and which has been of our interest for some time [16, 17, 18]. The (experimental) information about the stoichiometry makes the theoretical studies possible, but also in this case the existence of homotops complicates the computations significantly. Their
number for a H$_N$Al$_O$O$_N$ cluster is \( \binom{3N+1}{N} \). Thus, for Au, (SiGe), and (HAIO) clusters with, e.g., 12 atoms in total the number of homotops increases from 1, via 924, to 34650, which clearly illustrates the increase in computational needs.

For HAIO there are two further aspects that deserve to be mentioned. At first, the material is nanostructured but does not consist of isolated clusters. This means that the clusters most likely are interacting with each other, so that an exact treatment of this material would require the treatment of the inter-cluster interactions. Second, upon heating the material loses hydrogen and it may be expected that the resulting Al-O system segregates into Al$_2$O$_3$ and Al. Also a theoretical treatment of this would require treating the macroscopic system.

In our studies we have so far found that for isolated, finite HAIO clusters with up to 26 formula units hydrogen is sitting on the surface whereas the core consists of aluminum and oxygen with heteroatomic bonds. As far as possible, the hydrogen atoms prefer to be attached to aluminum, and not to oxygen. When, alternatively, considering planar, quasi-two-dimensional structures it is found that these are of comparable stability as the largest finite clusters we have studied. This may explain why both types of materials can be synthesized (see, e.g., [17]).

When two HAIO clusters are interacting the hydrogen atoms move away from the region between the two clusters, whereas the oxygen and aluminum atoms tend to fill the gap between the two clusters. Finally, when removing hydrogen we find that AlO clusters are stabler than non-interacting Al$_2$O$_3$ and Al clusters, although their interactions may change this conclusion.

VI. CONCLUSIONS

In this short presentation we have discussed the problems related to determining the structure of the global total-energy minimum for clusters with one or more types of atoms. Furthermore, we have discussed briefly approaches for analyzing the outcomes of the computations. We considered three different examples. At first, we discussed the properties of pure gold clusters where it was found that covalent bonding was responsible for the existence of structures with low-coordinated atoms. Subsequently, the covalently bonded semiconductor clusters, Si$_{2N}$, Ge$_{2N}$, and Si$_N$Ge$_N$ clusters were treated. We found that although there were similarities between the different materials, there were also significant differences and, in particular, that the structures of the mixed clusters were not simply related to those of the pure ones. For those, as well as for our last example (HAIO)$_N$, the existence of homotops led to significant increases in the computational requirements. For HAIO we found structural motifs that were in agreement with those deduced from experimental information.

REFERENCES

The effect of the Vibrational Contributions to the Non-Linear Optical Properties of Small and Medium size molecules

Aggelos Avramopoulos, Heribert Reis, Manthos G. Papadopoulos

e-mail: aavram@eie.gr; hreis@eie.gr; mpapad@eie.gr.

Abstract The vibrational contributions to the linear and nonlinear optical properties (L&NLO) of some selected systems are reported. The Bishop-Kirtman perturbation approach as well the Numerov-Cooley technique were employed for the computation of the vibrational properties. Electron correlation and relativistic effects have been considered. The results show that the vibrational contributions are essential for the reasonably accurate description of the L&NLO properties and in particular of the first and second order hyperpolarizabilities.

Keywords: Non linear optical properties, (hyper)polarizabilities, vibrational contributions, relativistic effect
PACS: 31.15Ar, 42.65 -k

I. Introduction

Over the recent years many research groups have focused their scientific interest on the field of the non-linear optics. Their efforts and extensive studies involve the design, synthesis, characterization and measurement of the L&NLO properties aiming at the production of more efficient photon-manipulating materials [1-8]. Therefore it is of fundamental importance to develop methods and to compute reliable results for the L&NLO properties of molecules, which may serve as test cases, for studies involving more complex systems with scientific and industrial interest. Most of the published computational studies are based on the calculation and understanding of the electronic contribution. However, in the last few years there is a growing interest [9,10,11] in the development of methods for the calculation and interpretation of the vibrational contributions to the electronic polarizabilities and hyperpolarizabilities. It has been found that vibrational properties can be of major importance, and thus a careful study needs to be performed [12].

The goal of the present paper is to present a brief survey on some of our recent results on this topic. Small and medium size molecular systems were selected in order to discuss their vibrational contributions to the polarizability and (hyper)polarizabilities, in connection with the electronic counterpart.

II. Computational Methods

In this section we shall briefly present the theoretical techniques we employ for the computation of the vibrational properties. The total value of a property \( P \), where \( P=\mu, \alpha, \beta, \gamma \), involves the following contributions:

\[
P = P_{\text{el}} + P_{\text{vib}} = P_{\text{el}} + P_{\text{vib}} + P_{\text{zpva}} + P_{\text{nr}} + P_{\text{curv}}
\]

where \( P_{\text{el}} \) corresponds to the pure electronic contribution, \( P_{\text{vib}} \) is the pure vibrational correction (\( p_{\text{vib}} \)) and \( P_{\text{zpva}} \) refers to the zero-point vibrational averaging correction (\( p_{\text{zpva}} \)), \( P_{\text{nr}} \) is the relaxation contribution and \( P_{\text{curv}} \) the curvature contribution. \( P_{\text{vib}} \) is associated with the difference between the electronic contribution of a “frozen”molecule and a vibrating one [13]. \( P_{\text{vib}} \) is associated with the change of the electronic energy which is caused by the field-induced modification of the...
molecular geometry and \( P^{\text{zero}} \) is connected with the change of the zero-point vibrational energy (directly) and the geometry relaxation (indirectly) [14]. Bishop and Kirtman developed a perturbation theory approach (BKPT) for the evaluation of the vibrational corrections [15,16,17]. Within this approach the vibrational averaging of a given property \( P \) over the ground vibrational state of the system is given by:

\[
P^{\text{zero}} = [P]^{(0)} + [P]^{(1)}
\]

and

\[
[P]^{(0)} = \frac{\hbar}{4} \sum_{\alpha, \beta} \left( \frac{\partial^2 P}{\partial \alpha \beta} \right)
\]

\[
[P]^{(1)} = \frac{\hbar^2}{4} \sum_{\alpha, \beta} \left( \frac{\partial^2 P}{\partial \alpha^2} \right)
\]

where, \( \omega_\alpha \) is the harmonic frequency, \( F_{\alpha \beta} \) is the cubic force constant and \( Q_\alpha \) is the normal coordinate. In the BKPT approach the pure vibrational (pv) contributions to the dipole polarizability and dipole hyperpolarizabilities are given by the following expressions:

\[
\alpha^{\text{pv}} = \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} = \alpha^{\text{el}} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)}
\]

\[
\beta^{\text{pv}} = \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(1,0)} + \mu^{(0,1)} = \beta^{\text{el}} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)}
\]

\[
\gamma^{\text{pv}} = \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)}
\]

In \([\alpha]^{n,m}\), \( n \) and \( m \) denote the orders of the electrical and mechanical anharmonicities respectively. Analytical expressions for \([\alpha]^{n,m}\) are given in ref. 15. The vibrational properties given by Eqs 5-7 are computed by employing energy derivatives up to the fourth order, dipole moments derivatives up to the third order, polarizability derivatives up to the second order, and first order hyperpolarizability derivatives. Another approach used for the computation of the vibrational contributions involves the Numerov-Cooley integration technique as suggested by Dykstra and Malik [18]. The energy eigenvalue problem for the vibrational wavefunction can be written as follows:

\[
[T + E(r,F)] y_v(r,F) = \epsilon(F) y_v(r,F)
\]

where \( T \) is the vibrational Kinetic operator, \( \epsilon(F) \) the energy eigenvalue, \( E(r,F) \) the distance and field-dependent BO electronic energy and \( y_v(r,F) \) the field-dependent vibrational wavefunction of the given level. By taking the n-order derivative of eq. 8 with respect to the field \( F=F_0 \) leads to the n-order total property, that is electronic + vibrational. The following analytical expressions give the total values for the polarizability (\( \alpha \)), first (\( \beta \)) and second (\( \gamma \)) hyperpolarizabilities:

\[
\alpha_{zz} = \alpha^{\text{el}} + \alpha^{\text{pv}}
\]

\[
\beta_{zz} = \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)}
\]

\[
\gamma_{zz} = \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)} + \mu^{(0,0)} + \mu^{(2,0)} + \mu^{(1,1)} + \mu^{(0,2)}
\]
\[ \alpha^{\nu} = 2<\left( \frac{\partial^2 \gamma_\nu(r,F)}{\partial F^2} \right)_{F=0} | \mu(r,0) | y_\nu(r,0) > \]  
(10)

and \[ \alpha^{el+\alpha^{\nu}} = <y_\nu(r,0) \left( \frac{\partial^2 \mu(r,F)}{\partial F^2} \right)_{F=0} | y_\nu(r,0) > \]  
(11)

\[ \beta_{zz} = \beta = \left( \frac{\partial^2 \varepsilon_0(F)}{\partial F^3} \right)_{F=0} = \beta^{\nu} + \beta^{el+\alpha^{\nu}} \]  
(12)

where \[ \beta^{el+\alpha^{\nu}} = <y_\nu(r,0) \left( \frac{\partial^2 \mu(r,F)}{\partial F^2} \right)_{F=0} | y_\nu(r,0) > \] and \[ \beta^{\nu} = 2<\left( \frac{\partial^2 \gamma_\nu(r,F)}{\partial F^2} \right)_{F=0} | \mu(r,0) | y_\nu(r,0) > + 2<\left( \frac{\partial \gamma_\nu(r,F)}{\partial F} \right)_{F=0} | \mu(r,0) | y_\nu(r,0) > + 4<\left( \frac{\partial \gamma_\nu(r,F)}{\partial F} \right)_{F=0} \left( \frac{\partial \mu(r,F)}{\partial F} \right)_{F=0} | y_\nu(r,0) > \]  
(13)

\[ \gamma_{zzz} = \gamma = \left( \frac{\partial^3 \varepsilon_0(F)}{\partial F^4} \right)_{F=0} = \gamma^{\nu} + \gamma^{el+\alpha^{\nu}} \]  
(14)

\[ \gamma^{\nu} = 2<\left( \frac{\partial^3 \gamma_\nu(r,F)}{\partial F^3} \right)_{F=0} | \mu(r,0) | y_\nu(r,0) > + 6<\left( \frac{\partial^2 \gamma_\nu(r,F)}{\partial F^2} \right)_{F=0} | \mu(r,0) | \left( \frac{\partial \gamma_\nu(r,F)}{\partial F} \right)_{F=0} > + 4<\left( \frac{\partial \gamma_\nu(r,F)}{\partial F} \right)_{F=0} \left( \frac{\partial \mu(r,F)}{\partial F} \right)_{F=0} | y_\nu(r,0) > \]  
(15)

with \[ \gamma^{el+\alpha^{\nu}} = <y_\nu(r,0) \left( \frac{\partial^3 \mu(r,F)}{\partial F^3} \right)_{F=0} | y_\nu(r,0) > \]  
(16)

The \( \mu(r,0) \), \( \mu(r,0) \), and \( \gamma(r,0) \) correspond to the electronic dipole moment, polarizability, first and second hyperpolarizability functions, respectively. Discussion on the theoretical framework and presentation of the derivation of the preceding formulas for the dipole moment and (hyper)polarizabilities can be found in refs [19,20]. This approach allows to compute benchmark results, which are of infinite order in the electrical and mechanical anharmonicities. Thus employing this approach, one may assess the validity of the finite order BKPT method.

### III. Results and Discussion

#### 1. Diatomics

The \( zpva \) correction is small for \( \alpha_{zz} \). For \( \beta_{zzz} \) and \( \gamma_{zzzz} \), at the CCSD(T) level, it has a remarkable magnitude (Table 1 [21]). In particular at the CCSD(T) level, the \( zpva \) correction has a value, which is comparable with the electronic counterpart.
The pv contribution to $\alpha_{zz}$ is small, but not negligible. The pv contribution for $\beta_{zzz}$ is large, but smaller than the corresponding electronic counterpart. The pv contribution to $\gamma_{zzzz}$ at the HF level, is larger than the electronic counterpart. The reverse trend is observed at the CCSD(T) level.

The coinage metal hydrides

Table 1. The pure vibrational (pv) and zero-point vibrational (zpva) contributions to the parallel polarizability and (hyper)polarizabilities of some diatomics\textsuperscript{a} [20,21]. For comparison the electronic contribution is given. All property values are given in a.u.

<table>
<thead>
<tr>
<th></th>
<th>KH</th>
<th>CuH\textsuperscript{c}</th>
<th>AgH\textsuperscript{c}</th>
<th>AuH\textsuperscript{c}</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>pv/el.</td>
<td>zpva</td>
<td>pv/el.</td>
<td>zpva</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF\textsuperscript{b}</td>
<td>16.92/50.79</td>
<td>0.94</td>
<td>0.90 / 40.42</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[0.85]\textsuperscript{d}/[39.31]\textsuperscript{d}</td>
<td>[1.36]\textsuperscript{d}</td>
</tr>
<tr>
<td>CCSD(T)\textsuperscript{b}</td>
<td>11.46/83.70</td>
<td>2.62</td>
<td>0.38 / 37.33</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[0.27]\textsuperscript{d}/[36.42]\textsuperscript{d}</td>
<td>[1.08]\textsuperscript{d}</td>
</tr>
<tr>
<td>$\beta_{zzz}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF\textsuperscript{b}</td>
<td>-1451/1913</td>
<td>82</td>
<td>-204/837</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[-174]\textsuperscript{d}/[745]\textsuperscript{d}</td>
<td>[53]\textsuperscript{d}</td>
</tr>
<tr>
<td>CCSD(T)\textsuperscript{b}</td>
<td>-1942/7265</td>
<td>510</td>
<td>-67/468</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[-52]\textsuperscript{d}/[416]\textsuperscript{d}</td>
<td>[17]\textsuperscript{d}</td>
</tr>
<tr>
<td>$\gamma_{zzzz}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF\textsuperscript{b}</td>
<td>694.2 (2)\textsuperscript{f} / 361.6 (3)\textsuperscript{e}</td>
<td>159.4 (2)\textsuperscript{e}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)\textsuperscript{b}</td>
<td>-1207.2 (2)\textsuperscript{f} / 1635.1 (3)\textsuperscript{e}</td>
<td>1454.1 (2)\textsuperscript{f}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The zpva corrections to $\alpha_{zz}$ is small, but not negligible [21]. For example in the case of AuH, it is 3.5% of the total $\alpha_{zz}$ (el. + pv + zpva contributions). The zpva correction to $\beta_{zzz}$ is smaller than the pure vibrational and the electronic counterparts. As an example we note that the zpva correction for AuH, at the CCSD(T) level is 8.1% of the total property (Table 1).

The pv contribution to $\alpha_{zz}$ is small, but this contribution to $\beta_{zzz}$ is considerably larger, but still smaller than the electronic counterpart.

Correlation contribution. In all cases, correlation, at the CCSD(T) level, reduces all the considered contributions (el., pv and zpva). In the case of $\beta_{zzz}$, correlation has a great effect on all the studied properties.
Table 2. The first hyperpolarizability and second hyperpolarizability components (in $10^3$) and their average values of HgS, computed using MP2 and coupled cluster methods. All values are in a.u.

<table>
<thead>
<tr>
<th></th>
<th>HgS$^*$</th>
<th></th>
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<th></th>
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<td></td>
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<tr>
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<td>119.0</td>
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<td>106.7</td>
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<td></td>
</tr>
<tr>
<td>MP2</td>
<td>925.5</td>
<td>4965.4</td>
<td>4089.9</td>
<td>-442.8</td>
<td>-100.6</td>
<td>-189.8</td>
</tr>
<tr>
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<td>1359.7</td>
<td>-100.5</td>
<td>-8.4</td>
<td>-40.2</td>
</tr>
<tr>
<td>CCSD(T)</td>
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<td>2130.8</td>
<td>1341.5</td>
<td>-68.0</td>
<td>39.2</td>
<td>-7.2</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>2002.5</td>
<td>-105.0</td>
<td>-53.4</td>
<td>-75.4</td>
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<tr>
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<td>-3030.4</td>
<td>438.6</td>
<td>87.9</td>
<td>178.0</td>
</tr>
<tr>
<td>CCSD</td>
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<td>-1414.9</td>
<td>-1003.5</td>
<td>103.4</td>
<td>6.9</td>
<td>38.4</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>31.3</td>
<td>-1752.2</td>
<td>-1013.7</td>
<td>75.2</td>
<td>-35.3</td>
<td>10.5</td>
</tr>
<tr>
<td><strong>ZPVA contribution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)$^d$</td>
<td>15.5</td>
<td>4.0</td>
<td>21.0</td>
<td>(-1.0)</td>
<td>(4.1)</td>
<td>(2.3)</td>
</tr>
<tr>
<td>CCSD(T)$^e$</td>
<td>-0.2</td>
<td>-1.4</td>
<td>-1.1</td>
<td>(-0.1)</td>
<td>(0.0)</td>
<td>(0.0)</td>
</tr>
<tr>
<td><strong>Pure vibrational contribution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)$^d$</td>
<td>-44.1</td>
<td>-176.6</td>
<td>-158.9</td>
<td>9.8</td>
<td>-5.4</td>
<td>1.8</td>
</tr>
<tr>
<td>CCSD(T)$^e$</td>
<td>-3.9</td>
<td>-44.8</td>
<td>-31.6</td>
<td>8.1</td>
<td>0.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Total</td>
<td>-887.1</td>
<td>-495.8</td>
<td>-1362.0</td>
<td>59.8</td>
<td>112.5</td>
<td>103.6</td>
</tr>
<tr>
<td>CCSD(T)$^d$</td>
<td>-153.7</td>
<td>-139.2</td>
<td>-268.0</td>
<td>29.2</td>
<td>25.6</td>
<td>36.9</td>
</tr>
<tr>
<td>CCSD(T)$^e$</td>
<td>-43.7</td>
<td>-139.2</td>
<td>-268.0</td>
<td>29.2</td>
<td>25.6</td>
<td>36.9</td>
</tr>
</tbody>
</table>

$^a$ Results obtained by employing the Pol basis sets for Hg and S [22,24]  
$^b$ Values calculated according to equation: $Q_{el}(M) = Q_{el}(SCF) + Q_{corr}(M)$, where M stands for the correlation method (M) and Q for the electronic value.  
$^c$ Values calculated according to the following differences: $Q_{el,sc}(SCF) - Q_{el,sc}(SCF)$, which defines the relativistic correction to the pure electronic value and $Q_{corr,sc}(M) - Q_{corr,sc}(M)$, which defines the interference between the relativistic and electron correlation effects.  
$^d$ Nonrelativistic results.  
$^e$ Relativistic results which include the relativistic correction and the mixed relativistic-correlation contribution computed at the CCSD(T) level of theory.

From the results of table 2 it can be seen that, similar to previous cases (table 1), the considered vibrational contributions are smaller than the electronic counterpart. The relativistic correction, similar to AuH case (table 1), is necessary for the qualitative and reliable estimation of both electronic and vibrational contributions. The mixed correlation – relativistic contributions are quite substantial. In all cases correlation has a noteworthy contribution, especially to the vibrational contributions, $zpva$ and pv. Finally let us note that the relativistic effect has a remarkable effect on the vibrational contributions of the considered properties. It can be seen that for the second hyperpolarizability the average $zpva$ relativistic value is zero [24].

2. Pyrrole

**Electronic properties.** We observe that correlation has a remarkable effect on $\beta_{vec}$ and to a less extent on $\gamma$ [25].

**Vibrational properties** These properties have been computed at the HF level [25]. The $zpva$ correction is small for all the considered properties. However, the pv contribution to $\beta_{vec}$ and $\gamma$ is large, that is the pv contribution is 1.8 and 14.5 times larger than the corresponding electronic properties for $\gamma$ and $\beta_{vec}$, respectively.
Table 3. Electronic and vibrational contributions to $\alpha$, $\beta_{vec}$ and $\gamma$ of pyrrole

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$</th>
<th>$\beta_{vec}$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Electronic Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>53.70</td>
<td>27.5</td>
<td>16345</td>
</tr>
<tr>
<td>MP2</td>
<td>55.24</td>
<td>34.7</td>
<td>20255</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>54.87</td>
<td>44.0</td>
<td>18888</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Vibrational Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zpva/HF</td>
<td>1.65</td>
<td>1.4</td>
<td>183</td>
</tr>
<tr>
<td>pv/HFc</td>
<td>6.89</td>
<td>398.3</td>
<td>29933</td>
</tr>
</tbody>
</table>

$^a$ The Pol basis set has been employed for the computation of the electronic properties [22].

$^b$ The calculations were performed with the 6-311G** basis set.

$^c$ The vibrational properties have been calculated by employing fourth order derivatives for energy, third order derivatives for the dipole moment, second order derivatives for the polarizability, and first order derivatives for the first hyperpolarizability.

3. 3-aminoacroleine

In this study we consider the effect of the conformations on L&NLO properties. The original study [26] involves 4 isomers, but here we present two extreme cases: the first isomer (I), which involves an intramolecular H-bond and the second (II), which involves a trans arrangement of the -CHO and the –NH$_2$ groups at the CC double bond (Fig. 2).

Figure 2. The structures of 3-aminoacroleines (I and II) conformers.
Table 4. The Electronic and pv contributions to $\alpha$ and $\beta$ of 3-aminoacroleine$^a$ (in a.u.).

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Electronic Contribution$^b$</th>
<th>PV contribution$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>I</td>
<td>50.99</td>
<td>16.4</td>
</tr>
<tr>
<td>II</td>
<td>53.89</td>
<td>85.4</td>
</tr>
</tbody>
</table>

$^a$ The Molecular plane is defined by X and Z axis. The Z axis corresponds to the direction of the dipole moment.

$^b$ The computations have been performed by employing the PolX basis set [22], at the HF level.

The very large vibrational contributions to both $\alpha$ and $\beta$ are likely to be due to the failure of the perturbation theory. This failure is attributed to the harmonic approximation which underlies the BKPT method. A similar failure has been found for H-bonded dimmers [27]. Torrent Sucarrat et. al. [28] proposed a variational approach which is able to treat successfully molecules with electrical and/or mechanical anharmonicities.

4. Acetonitrile

Static zpva as well as static and frequency-dependent pv contributions to the electric properties of acetonitrile were computed in a study aimed at predicting the macroscopic susceptibilities of liquid acetonitrile [29]. The derivative terms contributing to eqs. 5-7 were computed either as numerical derivatives of the electric properties with respect to normal coordinates or as derivatives of the gradient and Hessian with respect to the applied external field. The latter method is more convenient for high order properties required for zpva, as for example the first and second derivative of $\beta$ and $\gamma$ with respect to normal coordinates. The reason is that the number of single computations for field derivatives is always the same, while the required number for normal coordinate derivatives increases strongly with the size of the molecule.

The contributions were computed with different members of Dunning’s correlation-consistent basis sets $n$-aug-cc-pVNZ (abbreviated with $(n)aNZ$ in the Tables) and at different levels of electronic correlation. As can be seen in Table 4, dependence of the contributions on the size of the basis is modest, while electronic correlation, computed at the MP level, is more pronounced.

Table 5. Average static PV and ZPVA contributions to $\alpha$ and $\gamma$ and to the vector component of $\beta$ in the direction of the dipole moment of acetonitrile.

<table>
<thead>
<tr>
<th></th>
<th>aDZ/RHF</th>
<th>daDZ/RHF</th>
<th>aTZ/RHF</th>
<th>aDZ/MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{av}^{pv}$</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41</td>
<td>0.24</td>
</tr>
<tr>
<td>$\beta_{av}^{pv}$</td>
<td>35.92</td>
<td>34.71</td>
<td>34.12</td>
<td>15.85</td>
</tr>
<tr>
<td>$\gamma_{av}^{pv}$</td>
<td>1012</td>
<td>1003</td>
<td>981</td>
<td>1148</td>
</tr>
<tr>
<td>$\alpha_{av}^{zpva}$</td>
<td>0.84</td>
<td>0.85</td>
<td>0.83</td>
<td>0.80</td>
</tr>
<tr>
<td>$\beta_{av}^{zpva}$</td>
<td>-3.68</td>
<td>-3.81</td>
<td>-3.71</td>
<td>-2.33</td>
</tr>
<tr>
<td>$\gamma_{av}^{zpva}$</td>
<td>187</td>
<td>218</td>
<td>195</td>
<td>316</td>
</tr>
</tbody>
</table>
With the exception of $\beta$, the electronic properties are considerably larger than the vibrational contributions, e.g. at the MP2/daDZ level, the electronic $\alpha_{xx}, \beta_{xx}, \gamma_{xx}$ were found to be 29.17 au, 22.66 au and 3585 au. This becomes even more pronounced for the frequency-dependent properties, which were computed for the pv contributions in the so-called infinite frequency limit and were computed, at the MP2/adZ level, for SHG and EFISH to be: $\beta^{pv}_{||}, \gamma^{pva}_{||} = 0.6$ au, -273 au at $\lambda = 1064$ nm, and 0.06 au and -104 au, respectively, at $\lambda = 514.5$ nm. Nevertheless, the addition of the pv and zpva contributions to the electronic counterpart has a non-negligible effect on the total properties.

5. p-Nitroaniline

As part of a study of the macroscopic susceptibilities of p-Nitroaniline (pNA) in different solvents (p-dioxane, tetrahydrofuran and cyclohexane) [30] the vibrational contributions of pNA were computed, too. The same numerical field derivative method was applied as in the acetonitrile study [29]. Unfortunately, this method does not allow the complete determination of all the derivatives required for a full calculation of the pv contributions according to eqs. 5-7. The fourth-order normal coordinate (NC) derivative of the energy, as well as the third order NC derivative of the dipole moment and polarizability are not easily accessible with the method employed, thus some terms contributing to the bracketed terms in eqs. 5-7 are not available. In the case of acetonitrile it could be shown that the expansion is nearly converged already at the double-harmonic level, for which all the required derivative terms are available, but for pNA it turned out that the pv contributions were not converged at all at this level, as shown in Table 6.

Table 6. Static pv and zpva contributions to the dipolar (hyper)polarizabilities of pNA at the double harmonic (DH) level; numbers in parenthesis show pv contributions including some terms of higher-order anharmonicity; $\alpha, \beta$ in au, $\gamma$ in $10^3$ au.

<table>
<thead>
<tr>
<th></th>
<th>pv</th>
<th>6-31G** / RHF</th>
<th></th>
<th>pv</th>
<th>6-31G** / B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{xx}$</td>
<td>50 (186)</td>
<td>1674 (8354)</td>
<td>$\beta_{xxx}$</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>10 (33)</td>
<td>-56 (1154)</td>
<td>$\beta_{yyy}$</td>
<td>2.3</td>
<td>0.5</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>31 (141)</td>
<td>-8 (6319)</td>
<td>$\beta_{zzz}$</td>
<td>0.5</td>
<td>-0.1</td>
</tr>
<tr>
<td>$\alpha_{xy}$</td>
<td>56 (236)</td>
<td>1998 (8963)</td>
<td>$\gamma_{xx}$</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>$\alpha_{yz}$</td>
<td>7 (21)</td>
<td>-18 (1018)</td>
<td>$\gamma_{yy}$</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>$\alpha_{zx}$</td>
<td>32 (185)</td>
<td>8 (7682)</td>
<td>$\gamma_{zz}$</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Electronic contributions at the MP2/Sadle-pVTZ level were found to be $\alpha_{ii}=152$, 105, 57 au, $\beta_{ii}=1646$, -50, -50 au, $\gamma_{iii}(144.2, 11.4, 10.7) \times 10^3$ au ($i=x,y,z$), which are of comparable magnitude to the pv contributions at the DH level, but considerably smaller than the higher level contributions. However, it is clear that without the missing higher order derivative terms the latter numbers have to be considered preliminary results. Later work [30], using field-induced coordinates [32] indeed showed that second hyperpolarizability values obtained at the full level of anharmonicity corresponding to eqs. 5-7 differ substantially from the partial results shown in Table 5; at the 6-31G**/RHF level it was found that $\gamma_{xxx}=-3300 \times 10^6$ au. Work is currently in progress to compute even higher order contributions to the vibrational hyperpolarizabilities, in order to establish if the perturbation series converges or not.

It was established in Ref. [30] that a substantial part of the large pv contributions is due to the wagging motion of the amino group.

6. Cyclopropenone and Cyclopropenethione

Two medium size molecules, cyclopropenone ($C_3H_2O$) and Cyclopropenethione ($C_3H_2S$) will be considered for the vibrational effects on the polarizability and first hyperpolarizability [33]. Both molecules are conjugated cyclic and the $\pi$-conjugation effects govern the electronic and vibrational features. For these molecules two different interpretations of
the BKPT approach will be used in order to assess the vibrational corrections. These are the nuclear relaxation effects (\(nr\)) caused by the change of equilibrium geometry due to the presence of an electric field and a contribution due to the change of the shape of the potential energy surface named as curvature contributions (\(curv\)) \[14\]. The results are presented in table 7.

Table 7. Electronic and vibrational contributions to the parallel component of the polarizability (\(\alpha_{zz}\)) and first hyperpolarizability (\(\beta_{zzz}\)). The computations were performed by employing the HF/Pol method at fully relaxed optimized geometries In parenthesis the total mean value of the property is given. All values are in a.u.

<table>
<thead>
<tr>
<th></th>
<th>(\alpha_{el}^{el})</th>
<th>(\alpha_{el}^{el})</th>
<th>(\alpha_{curv}^{curv})</th>
<th>(\beta_{el}^{el})</th>
<th>(\beta_{el}^{el})</th>
<th>(\beta_{curv}^{curv})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropenone</td>
<td>41.79(33.12)</td>
<td>6.32</td>
<td>1.23</td>
<td>53.0(87.6)</td>
<td>-61.3</td>
<td>1.33</td>
</tr>
<tr>
<td>Cyclopropenenone</td>
<td>77.12(55.01)</td>
<td>9.95</td>
<td>1.25</td>
<td>123.0(11.2)</td>
<td>-45.2</td>
<td>6.9</td>
</tr>
</tbody>
</table>

* The z axis corresponds to the direction of the dipole moment

In agreement with previous results the \(nr\) contribution is the dominant over the \(curv\) one \[34\]. Substitution of O by S significantly increases the \(nr\) contribution to the polarizability and reduces the absolute value of the first hyperpolarizability. This can be attributed to the role of the charge transfer effects in these systems \[35\], which have an influence on the dipole moment derivatives. On the contrary substitution of O by S does not have any effect on the \(curv\) contribution to the polarizability. It is seen that for \(C_{3}H_{2}O\) the \(pv\) contribution is equal to \(-59.8\) a.u. while for \(C_{3}H_{2}S\) – 38.4 a.u. This finding is quite important, especially for the first hyperpolarizability, because the evaluation of the \(nr\) term is computationally cheaper.

7. HXeC,H, HXeOH, HXeSH

In this section we shall discuss our results on the vibrational contributions on the L&NLO properties of HXeC,H\[36\] and HXeAH, A=O,S\[37\].

HXeC,H. It has been found \[36-38\] that insertion of a rare gas atom, remarkably enhances the L&NLO. In agreement with the previous case studies, vibration has an important contribution to the total property. By computing the nuclear relaxation term, \(\alpha_{zz}^{\mu^2}\), for the parallel component of \(\alpha_{zz}^{el}\), it was found that \(\alpha_{zz}^{el} = 1.2[\mu^2]^{0.0}\) at the HF/aug-cc-pVDZ method, but at the MP2/aug-cc-pVDZ level, the corresponding results are \(\alpha_{zz}^{el} = 2.1[\mu^2]^{0.0}\). Analysis of this term revealed that Xe-C and Xe-H vibrational modes have the dominant contribution. Moreover electron correlation significantly diminishes the value of \([\mu^2]^{0.0}\) by 36.1 a.u. Similar observation was made for the \([\mu^2]^{0.0}\) harmonic term (eq. 6) of the parallel first hyperpolarizability. It was found that this term is equal to 431 (1041) and -835 (786) a.u., computed at the HF and MP2 levels, respectively. In parenthesis the electronic contribution is quoted. We may note that, as in previous cases, the vibrational contribution is more pronounced for the first hyperpolarizability, and a remarkable electron correlation effect is also observed.

HXeAH. The important contribution of the vibrational effects on L&NLO is also noted for the HXeAH, A=O,S compounds. For the parallel component of the polarizability \(a_{ap}\), it seen that at the HF level of theory \(a_{ap}\) contribution is 0.61 and 0.53 of the \(a_{el}\), for HXeOH and HXeSH, respectively. However a noticeable decrease is observed taking into account electron correlation effects at the MP2 level of theory, where \(a_{ap}\) contribution is 0.32 and 0.33 of the \(a_{el}\), for HXeOH and HXeSH, respectively. It is noted that substitution of O by S increases the \(nr\) contribution at both HF and MP2 levels. This is shown by the following values, 38.91(24.86), 70.57(50.46), for HXeOH and HXeSH, respectively. In parenthesis the MP2 MP2 value is given. More pronounced is the effect of the vibration on the first hyperpolarizability. Analysis of harmonic term shows that for HXeOH, \([\mu\alpha]^{0.0} = -0.27 (-0.82) \beta_{el}\), while for HXeSH, \([\mu\alpha]^{0.0} = 0.12 (-0.79) \beta_{el}\). In parenthesis the MP2 values are quoted. The very significant effect of electron correlation is highlighted, similar to what was observed for other cases.
III. Concluding Remarks

The vibrational contributions to the L&NLO properties of some selected small and medium size molecular systems have been presented. Two approaches for estimating the vibrational properties have been used. It has been found that in general the effect of vibration on the L&NLO has to be accounted for a proper estimation of the (hyper)polarizabilities. Electron correlation and relativistic effects have proven to be significant for the reliable and meaningful evaluation of the relevant terms.

REFERENCES

Polarizability and charge density distribution in crystalline urea

Mauro Ferrero*, Bartolomeo Civalleri* and Michel Rérat†

*Dipartimento di Chimica IFM, Università di Torino and NIS -Nanostructured Interfaces and Surfaces - Centre of Excellence, http://www.nis.unito.it Via P. Giuria 7, 10125 Torino, Italy
†Equipe de Chimie Physique, IPREM UMR5254, Université de Pau, 64000 Pau, France

Abstract. The aim of this short paper is to document the performance of some one electron Hamiltonians like HF, LDA (S-VWN), GGA (PBE) and Hybrids (PBE0 and B3LYP) in the calculation of the dielectric tensor elements of crystalline urea. Urea crystal has been chosen for two main reasons, first of all it represents a benchmark system for the discussion of linear and nonlinear optical properties of molecular crystals, then, in literature, there is a large variety of experimental and theoretical results to be compared with our calculations. The discussion is supported by electron density deformation maps that give a synoptic representation of the charge reorganization that takes act when passing from isolated molecules to the molecular crystal. The different behavior of the above mentioned Hamiltonians in the description of the electron density of the urea molecular crystal is also analyzed in terms of Born effective charges.

Keywords: urea, CPHF, periodic calculations, ab-initio, Gaussian basis sets
PACS: 31.15.A,31.15.es,42.70.Mp

INTRODUCTION

The assessment of a stable and reliable method to compute linear and non linear optical properties for periodic systems represented a long debated, challenging problem. The Coupled Perturbed Hartree-Fock method represents an elegant and efficient solution to compute analytically the derivatives of the total energy of a system under the effect of an electric field perturbation. First Genkin and Mendis [1] then Hurst and Dupuis [2] proposed such a scheme to compute linear and nonlinear dielectric properties of molecules, then the ground-breaking work of Kirtman and co-workers [3] allowed the extension of CPHF to periodic systems. This has been possible also thanks to works of Otto et al. [4, 5] that first used in this context the form for the static electric field operator within periodic boundary conditions originally proposed by Blount [6].

Recently CPHF has been implemented [7, 8, 9, 10, 11] in a development version of the CRYSTAL code [12] providing a stable and reliable tool to face the problem of modeling electric field effects in real scale solids, whereas all previous implementations (either based on CPHF [13, 14, 15] or alternatively on MTP [16, 17, 18]) were suitable for low dimensionality systems like polymers or small unit cell systems. After several contributions essentially devoted to show the correctness of our implementation and the capabilities of the method we are now in the position to propose the quantum mechanical description of technologically relevant non-linear optical materials, like molecular crystals. In this short contribution we want to analyze the urea molecular crystal that has always been considered a benchmark case in the wide range of molecular crystals with appealing linear and non-linear optical properties.

Here we limit our analysis to the polarizability (dielectric) tensor computed through the CPHF(KS) method, investigating the effect of the crystal packing on the electron density by means of deformation density maps. As a companion also dynamic Born charges are computed through localized Wannier functions [19]. This analysis was then repeated with several Hamiltonians ranging from HF, hybrids (B3LYP and PBE0) to GGA and LDA DFT functionals.

COMPUTATIONAL DETAILS

Both molecular and periodic calculations were carried out using a development version of the CRYSTAL06 code, that allows the solution of the multi-electronic problem by adopting a local basis set consisting of Gaussian Type Functions (GTF). We adopted five different Hamiltonians, namely: LDA in its SVWN form [20, 21], PBE [22] as GGA, B3LYP
TABLE 1. Comparison between HF and DFT methods for the polarizability (α_{aa} and α_{cc}) of free urea molecule and urea bulk (per molecule) and Born dynamic charges (Z_C for carbon and Z_O for oxygen atoms respectively) computed with the TZPP basis set. Dielectric tensor elements (ε_{aa} and ε_{cc}) are obtained from the polarizability tensor through the relation: ε_{ab} = δ_{ab} + \frac{4}{3} α_{ab}. Born dynamic charges are computed as the average value of the trace of the Born tensor. Polarizability components in Bohr^{-3}, Born dynamic charges in e (a.u.), and band gap, E_g in eV.

<table>
<thead>
<tr>
<th>Method</th>
<th>Molecule C_{2v}</th>
<th>α_{aa}</th>
<th>α_{cc}</th>
<th>Z_C</th>
<th>Z_O</th>
<th>α_{aa}</th>
<th>α_{cc}</th>
<th>Crystal</th>
<th>ε_{aa}</th>
<th>ε_{cc}</th>
<th>E_g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVWN</td>
<td>1.31 -0.83</td>
<td>30.460</td>
<td>40.265</td>
<td>1.92 -1.57</td>
<td>49.122</td>
<td>64.472</td>
<td>2.261</td>
<td>2.655</td>
<td>4.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>1.32 -0.81</td>
<td>30.378</td>
<td>40.060</td>
<td>1.90 -1.54</td>
<td>47.329</td>
<td>62.777</td>
<td>2.215</td>
<td>2.612</td>
<td>5.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>1.41 -0.87</td>
<td>28.737</td>
<td>37.801</td>
<td>1.93 -1.50</td>
<td>43.127</td>
<td>56.822</td>
<td>2.089</td>
<td>2.432</td>
<td>7.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE0</td>
<td>1.42 -0.88</td>
<td>28.326</td>
<td>37.224</td>
<td>1.88 -1.48</td>
<td>42.408</td>
<td>55.766</td>
<td>2.089</td>
<td>2.432</td>
<td>7.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>25.150</td>
<td>32.762</td>
<td></td>
<td>34.814</td>
<td>44.604</td>
<td>1.894</td>
<td>2.145</td>
<td>14.08</td>
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<tr>
<td>Exp.</td>
<td>34.483 \textsuperscript{a}</td>
<td>41.744 \textsuperscript{a}</td>
<td></td>
<td>2.168 \textsuperscript{b}</td>
<td>2.492 \textsuperscript{b}</td>
<td>5.7-6.2\textsuperscript{c}</td>
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</table>

\textsuperscript{a} B3LYP calculations performed with an extended aug-cc-pVTZ basis set [30, 27].

\textsuperscript{b} From data extrapolated to the static limit [31].

\textsuperscript{c} For band gap see references in ref. [32].

[23, 24, 25] and PBE0 [26] hybrids and pure HF. We choose to perform our investigations with a fixed all-electron basis set, namely the TZPP that has been obtained from the Ahlrichs’ TZ basis set by adding the set of polarization functions of the cc-pVTZ basis of Dunning. Anyway for a careful discussion of the basis set effects on the polarizabilities we refer to another parallel paper [27].

For the periodic calculations we set the shrinking factor of the reciprocal space net to IS = 4, this corresponds to 18 irreducible \vec{k} points in which the Fock matrix is diagonalized. The thresholds controlling the truncation of Coulomb and exchange series were fixed to 10^{-7}, 10^{-7}, 10^{-7}, 10^{-7}, 10^{-18} and the numerical integration grid for the DFT calculations has been set to XLGRID (for further details see [12]).

The convergence on the total energy \textit{TE} has been set to 10^{-7} and the convergence on the polarizability tensor elements to \textit{TCP} = 4. Furthermore, in order to get a smoother converge of the CP-SCF cycle, a mixing of the Fock matrix derivative between two subsequent cycles has been set to 50 % for all the Hamiltonians taken into account.

The urea molecular crystal is a noncentrosymmetric tetragonal crystal with \textit{P4}_{2}1/m space group with two molecules per unit cell. We started our analysis from the experimental geometry [28] at 12K (a=5.565 Å and c=4.684 Å) then, for each Hamiltonian, we performed a geometry optimization of internal coordinates. We kept fixed lattice parameters because of well known overestimation of the cell size when using DFT methods in combination with extended basis sets [29].

The isolated urea molecule has been considered in the \textit{C}_{2v} planar symmetry, in order to be compared with a molecule in the 3D environment.

RESULTS AND DISCUSSION

To better understand the electronic effects that influence the polarization of the charge density and to compare the different levels of theory, the total electron density of crystalline urea computed at the HF/TZPP level along with the corresponding charge density deformation with respect to a crystal of non interacting molecules are shown in Figure 1. Deformation maps for the other levels of theory with the TZPP basis set are reported as well. Figure 1 sheds some light on the effect of the crystal packing and the polarizability of urea as predicted by the various methods (see Table 1). The typical pattern of the charge density deformation due to H-bond is clearly seen. The two types of H-bond that surround the oxygen atom can easily be identified in the plane of the molecule (intrachain) and perpendicularly to it (interchain). When comparing the polarizability of the isolated molecule to the one of the molecular crystal, the effect of the intermolecular interactions appears evident, with an increase of the polarizability that ranges from 63 % for α_{aa} and 60 % for α_{cc} in the LDA case to 38 % for α_{aa} and 37 % for α_{cc} at the HF level. It is interesting to notice that TZPP basis set seems to give an accurate description of the dielectric tensor of the molecular crystal but not for the isolated molecule that requires the inclusion of diffuse functions. Even if a detailed discussion of these effects is important to clarify the dependence of dielectric properties on the basis set completeness, it is out of the purposes of the present short paper; further informations can be found in reference [27].

From the modification of the charge density upon crystal formation, one can see that LDA (i.e. SVWN functional)
FIGURE 1. Total electron density map of crystalline urea along with the deformation of the charge density with respect to a crystal of non interacting molecules computed at the HF level. For comparison, deformation maps for the other methods (i.e. VWN, PBE, PBE0 and B3LYP) are reported. The TZPP basis set have been used. Note that deformation maps have been obtained at the optimized atomic positions with fixed experimental lattice constants for each level of theory. Therefore, they partly include relaxation effects in the charge density distribution. The continuous and dashed lines refers to positive and negative density differences respectively. The contour lines are drawn at intervals of $0.001 |e|/bohr^3$.

tends to spread the electron density throughout the unit cell thus making the electron density around the oxygen atom more polarized. Therefore, along with a smaller band gap, the tendency of LDA to provide overestimated dielectric tensor elements (4.2 % and 6.5 % for $\varepsilon_{aa}$ and $\varepsilon_{cc}$ respectively) is confirmed. The tendency of LDA to delocalize the charge can also be related to the Born charges of atoms in the isolated molecule and in the urea bulk. Defining $\Delta \bar{Z}_C$ and $\Delta \bar{Z}_O$ the difference between dynamic Born charges of carbon and oxygen atoms in the isolated system and in the 3D framework, we see in Table 1 that LDA exhibits the largest variation ($\Delta \bar{Z}_C = 0.61 \, e$ and $\Delta \bar{Z}_O = -0.74 \, e$).

When passing to a semilocal GGA functional such as PBE, the deformation of the charge density around oxygen results to be less pronounced than for LDA, that in combination with a less pronounced underestimation of the band gap gives $\varepsilon_{aa}$ and $\varepsilon_{cc}$ that are 4.9 % and 2.2 % overestimated with respect to the experimental reference value.

The addition of exact exchange as in hybrid functionals tends to reduce the polarization and therefore the polarizability. In particular, at the B3LYP level, the charge density deformation is quite similar to the HF one but with a much more accurate prediction of the band gap. This combination gives the more accurate description of the dielectric tensor of the crystalline urea obtainable with the present set of computational parameters providing $\varepsilon_{aa}$ and $\varepsilon_{cc}$ underestimated by only the 2.2 % and 1.3 % respectively. An analogous description of the electron density is given by the PBE0 hybrid, that on the other side overestimates the band gap, giving a dielectric tensor slightly underestimated if compared to experimental values (3.6 % for $\varepsilon_{aa}$ and 2.4 % for $\varepsilon_{cc}$).

Charge redistribution due to crystal field is also evident in the the carbonyl group where a depletion of charge on carbon with a corresponding buildup on oxygen is observed. To give a quantitative picture of such density reorganization we use the Born charges of carbon and oxygen atoms for all the Hamiltonians we have considered and, as it is seen in Table 1, this agrees with the results obtained for charge densities. Let us consider, for instance, the carbonyl group of the isolated molecule and in the crystal, both described at the B3LYP level: oxygen atom Born charge changes from -0.87 to -1.50 $e$, while for carbon it changes from 1.41 to 1.93 $e$. Also in this case the tendency to redistribute charge reduces when passing from LDA to GGA, then hybrids and finally HF.
CONCLUSIONS

The effect of the Hamiltonians has been related to the dielectric properties and deformations of the charge density when passing from an isolated urea molecule to the 3D molecular crystal. We choose to present the results with a fixed TZPP basis set and to redirect the interested reader to a more complete study [27] that takes into account also the effect of the basis set on dielectric properties.

From this analysis it emerges that the B3LYP hybrid functional gives the more accurate description of the dielectric tensor (and of the band gap) of the crystalline urea that has been computed through the analytic CPHF method. Charge density deformation maps and Born charges provide the complementary information to discuss the electron density reorganization upon formation of the urea molecular crystal.

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REFERENCES

Prediction of the linear and nonlinear electric susceptibilities of 3-methyl-4-nitropyridine-N-oxide (POM) and meta-nitroaniline (mNA) crystals with account of electronic and molecular vibrational contributions.

Heribert Reis* and Josep M. Luis†

*Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, Vas. Constantinou 48, 11635 Athens, Greece
†Institute of Computational Chemistry and Department of Chemistry University of Girona, Campus de Montilivi 17071 Girona, Catalonia, Spain

Abstract. The quasistatic and optical dielectric permittivities as well as the second-harmonic generation and linear electro-optic signals of the molecular crystals meta-nitroaniline and 3-methyl-4-nitropyridine-N-oxide are calculated using a model which combines accurate ab–initio molecular properties and classical electrostatic interactions to account for the intermolecular effects. A simple distribution scheme is employed for the electric properties to account for size and shape effects. Using only electronic (hyper)polarizabilities, good agreement with experimental data is obtained for all the susceptibilities which involve electric fields at optical frequencies. The effect of intramolecular vibrational contributions is taken into account additionally in the case of the quasistatic permittivities and the linear electro-optic effects. The full nuclear relaxation part to the molecular vibrational contributions is computed using field-induced coordinates (FICs). The addition of the intramolecular vibrational effects to the electronic ones make a substantial contribution to the computed susceptibilities and increase the agreement with experimental values considerably. However, discrepancies to the experimental values remain and are probably due to the effects of intermolecular phonons.

Keywords: Molecular crystals, electric susceptibilities, Vibrational hyperpolarizabilities, meta-nitroaniline,3-methyl-4-nitropyridine-N-oxide

PACS: 42.65.An,77.22.Ch,77.22.Ej,78.20.Bh

The theoretical prediction of nonlinear optical (NLO) properties of molecular materials is an active matter of research. Methods to compute the electronic NLO properties of single molecules are quite advanced and are being applied in a nearly routinely fashion, at least for molecules of small to medium size. Electronic contributions are the only relevant contributions if the process being studied involves only electric fields at optical frequencies, with the exception of effects where two or more frequency arguments add to zero, like IDRI. Once static or low-frequent fields are involved, it becomes necessary to consider vibrational contributions to the NLO properties, too. Although their calculation is more involved than those of the electronic contributions, feasible methods have been developed recently [1], which are applicable to molecules of medium sizes. In contrast, methods for the calculation of macroscopic NLO susceptibilities are still more scarce and in a stage of active development. Additionally, most of the methods developed so far are restricted to the electronic response only. Here we want to report on a first step to take into account also the vibrational contribution by considering the molecular vibrational response. In addition we show that the interaction model we employ is able to predict the experimental electronic response in good approximation.

Our approach to compute the macroscopic susceptibilities consists of computing accurate ab–initio molecular properties of a single molecule, which are then used in an electrostatic interaction model, termed the rigorous local field (RLF) model [2] to compute the macroscopic susceptibilities. The first and second-order susceptibilities (χ(1) and χ(2)) in the RLF model are given by:

χ(1) ≤(−ω; ω) = \frac{1}{\varepsilon_0 v} \sum_k \alpha_k (−ω; ω) \cdot d_k (ω),
(1)

χ(2) ≤(−ω; ω_1, ω_2) = \frac{1}{2\varepsilon_0 v} \sum_k d_k (ω)^T \cdot \beta (−ω; ω_1, ω_2) d_k (ω_2) d_k (ω_1),
(2)

where v is the volume of the unit cell (uc), with k labeling the different molecules in the uc, d_k are local field factor...
tensors [2], \( \alpha, \beta \) are the polarizability and first hyperpolarizability tensors, respectively, of molecule \( \kappa \), and \( \omega_i \) are the frequencies of the electric fields involved in the linear or nonlinear process considered. The molecular properties \( \alpha, \beta \) are the properties of a molecule in the undisturbed crystal, that is, they are subject to the influence on the molecular environment in the crystal. In our approach, only electrostatic effects are considered, which give rise to permanent local fields on the molecules due to the permanent multipoles and the static (hyper)polarizabilities of the surrounding molecules. For POM and mNA, permanent local field and field gradient were computed in quadrupolar approximation, using dipoles, quadrupoles and polarizabilities up to quadrupole-quadrupole order. In addition, fields and field gradients due to permanent octopoles and hexadecapoles were computed, too. For POM, which has a nearly vanishing dipole moment, permanent fields and field gradients also due to higher multipoles up to the order considered were found to be small. For mNA, which has a sizeable permanent dipole moment, permanent field effects are found to be quite large, while the field gradient effects are nearly negligible.

In molecular crystals consisting of molecules of the size of POM and mNA, the one-site multipole expansion for the electric potential is inadequate, and some kind of distribution of the electric properties over the molecule needs to be applied. In our case, we employed the simple approach based on the "submolecule" model pioneered by Luty [3], where the properties are equally distributed over a set of conveniently chosen parts (the submolecules) of the molecule. For POM, we mostly chose a distribution over 11 submolecules (one at each second-row) atom, while for mNA we chose 10 submolecules, again one at each second-row atom, except for the permanent local field and field gradient determination, where we chose 8 submolecules (one at the centre of mass of the nitro group and one on each of the other second-row atoms). This was necessary because the 10 submolecule model gave unreasonably large electric fields on the oxygen atoms, probably due to short distances in the crystal. Additionally to the submolecule model, we considered for POM also a fully distributed model for multipoles and polarizabilities developed by Stone and Misquitta [4], which is, however, only applicable with DFT. Due to the limitation of the corresponding program to polarizabilities, no permanent field effects nor second-order susceptibilities could be computed with this approach.

The static molecular electronic properties required for the calculation of the permanent local fields and field gradients were computed for POM at the MP2 level with a small basis set (D95(p,d) [5]), which was found to yield nearly the same properties as the considerably larger basis set developed by Sadlej (Pol). Accordingly, the diagonal frequency dependent polarizabilities and the dominant terms of the first hyperpolarizability for POM could be computed at the analytical CCSD level using the D95(p,d) basis. For mNA, substantial differences were found between properties computed with D95(p,d) and with Pol, thus all the static electronic properties of mNA were calculated at the MP2/Pol level, and multiplied with scaling factors computed at the RPA/Pol level to account for the frequency dispersion.

In the case of the quasistatic dielectric constant (\( \varepsilon - 1 = \chi^{(1)} \)) and the linear electro-optical (or Pockels) effect, where quasistatic electric fields are involved, corresponding molecular vibrational effects were added to the pure electronic contributions. In all cases, the nuclear relaxation (NR) part of the total vibrational contribution, either in static (for \( \alpha(0) \)) or in infinite frequency approximation (for \( \beta(-\omega; \omega, 0) \)) was computed using field-induced coordinates (FICs) [6], at the MP2 level with the 6-31G** basis. In addition, for POM selected components of the static curvature function (ZPVA + C-ZPVA [11]) were computed at the MP2/6-31G** level using a finite field based approach detailed in Ref. [7]. The permanent field effect was taken into account by scaling factors obtained from the

<p>| TABLE 1. Selected calculated components of ( \alpha ) and ( \beta(-\omega; \omega, 0) ) (( \lambda = 632.8 ) nm) of the free POM and the free and in-crystal mNA molecules; all units in au. |
|---|---|---|---|---|---|
| | POM | | mNA | | |
| | ( \alpha_{xx}(0) ) | 155.31 | 14.46 | 3.01 | 130.87 | 22.96 | 135.71 |
| | ( \alpha_{yy}(0) ) | 112.78 | 5.33 | 3.48 | 114.17 | 15.34 | 113.68 |
| | ( \alpha_{zz}(0) ) | 55.84 | 28.46 | 0.46 | 72.88 | 15.87 | 56.53 |
| | ( \beta_{xx}(-\omega; \omega, 0) ) | 2298 | 227 | - | 142 | 1211 |
| | ( \beta_{yy}(-\omega; \omega, 0) ) | 168 | 22 | - | -42 | 191 |</p>
<table>
<thead>
<tr>
<th></th>
<th>( \beta_{zz}(-\omega; \omega, 0) )</th>
<th>-106</th>
<th>153</th>
<th>-</th>
<th>49</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>CCSD/D95(p,d)</td>
<td></td>
<td>MP2/6-31G**</td>
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</table>
corresponding static electronic properties. One may consider the sum of the NR and the electronic contribution as the first and the curvature as the second term in a development series for the full electric property ($\alpha$ and $\beta$) [1]. From the computed values for POM it appears that this series is converging both for the diagonal components of $\alpha$ and, albeit more slowly, $\beta$.

Table 1 shows selected components of the computed electronic and vibrational contributions to $\alpha$ and $\beta$. Both POM and mNA contain groups which give rise to vibrational motions of quite low frequency (amino, nitro, methyl-group), which may lead to very large vibrational contributions, even to divergence of the perturbation series. Nevertheless, the vibrational contributions for POM and mNA are of reasonable magnitude, in general they are smaller than the electronic ones; this holds also for the static $\beta$ components, which are not shown in the Table.

Very good agreement between our computed and experimental optical susceptibilities is obtained, as shown in Table 2. The computed $\chi^{(2)}$ values obey Kleinman symmetry in good approximation, which is also observed experimentally, at least for POM [8]. Our values for POM also compare favourably with those of other models to calculate macroscopic susceptibilities [9, 10].

As a more elaborate distribution model, we computed fully distributed polarizabilities for POM using the constrained density-fitting algorithm published by Misquitta and Stone [4]. With a fully distributed model, charge-charge and dipole-charge polarizabilities appear in addition to the dipole-dipole polarizabilities and the calculation of the first susceptibility is a bit more complicated than in Eq. 1 [13]. Using the PBE0 functional with the Pol basis set, we obtained $\chi^{(1)}_{ii} = 1.494, 1.905, 1.372(i = a,b,c)$, compared to $1.829, 2.252, 1.588$ for the 17 submolecule model with the same input data. The values of the fully distributed model are rather low in comparison with experiment and the submolecule model seems to fare better. On the other hand, a fully distributed description of the permanent field may change the in-crystal polarizabilities in a different way than the average field used in the submolecule treatment. A computation of the distributed field effect on polarizabilities requires at least distributed first hyperpolarizabilities, which are not yet available, thus it is still premature to draw conclusions about the suitability of this distribution model for the computation of the susceptibility of the molecular crystals.

Predicted static linear susceptibilities and linear electrooptic signals, with and without vibrational contributions, are compared with experiment in Table 3. In all cases, molecular vibrational contributions increase agreement with the experimental values, but substantial differences remain, especially for the EO signal of mNA. Although the inclusion of the curvature effect may change those values, where they have not been considered yet, slightly, the main reason for the remaining discrepancies is probably the neglect of contributions due to the intermolecular phonons. Work is in progress to consider this effect, too. However, the fact that intramolecular contributions alone have quite a large effect on the susceptibilities, as shown in this work, make it plausible that the usual separate consideration of inter- and intramolecular vibrations in molecular crystals can only be a first approximation.

**ACKNOWLEDGMENTS**

Financial support from the HPC Europa Transnational Access Program is gratefully acknowledged, as well as support from the European Center for Parallelism of Barcelona (CEPBA), where part of the computations were performed.

**Linear and nonlinear electric susceptibilities of POM and mNA**
TABLE 3. Comparison of calculated (with (Full) and without (NoVib) vibrational contributions) and experimental (quasi)static linear ($\chi^{(2)} \equiv \chi^{(1)(0)}$) and linear electrooptic ($\chi^{(2)} \equiv \chi^{(2)}(-\omega; \omega, 0)/(\text{pm/V})$, $\lambda = 632.8$ nm) susceptibilities.

<table>
<thead>
<tr>
<th></th>
<th>POM</th>
<th>mNA</th>
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<tr>
<td></td>
<td>NoVib</td>
<td>Full</td>
</tr>
<tr>
<td>$\chi^{(1)}_{aa}$</td>
<td>1.680</td>
<td>2.151</td>
</tr>
<tr>
<td>$\chi^{(1)}_{bb}$</td>
<td>2.160</td>
<td>2.873</td>
</tr>
<tr>
<td>$\chi^{(1)}_{cc}$</td>
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<tr>
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</tr>
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<tr>
<td>$\chi^{(2)}_{bca}$</td>
<td>–13.1</td>
<td>–12.4</td>
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REFERENCES

**Theoretical Model for Infrared Spectra of Hydrogen-Bonded 2,4-Dithiouracil Crystal**

Marek J. Wójcik*, Jacek Kwiendacz and Marek Boczar

*Faculty of Chemistry, Jagiellonian University, 30-060 Kraków, Ingardena 3, Poland*

**Abstract.** Theoretical model describing infrared spectra of the N-H(D) stretching bands in 2,4-dithiouracil and its deuterated derivative is presented. The model takes into account anharmonic coupling between the high-frequency N-H(D) stretching and the low-frequency N···S stretching vibrations, resonance interaction between two equivalent hydrogen bonds in the dimer, anharmonicity of the potentials for the low-frequency vibrations in the ground and excited state of the N-H(D) stretching mode, Fermi resonance between the N-H(D) stretching and the first overtone of the N-H(D) bending vibrations, and electrical anharmonicity.

**INTRODUCTION**

Hydrogen bonding represents an important type of intermolecular interaction. In particular, it plays the crucial role in biological systems. The structures of DNA, proteins, and many other biomolecules highly depend on the net of weak interactions, especially hydrogen bonds.

Vibrational spectra provide the most commonly used criteria for the presence and the properties of hydrogen bonds. The most significant spectral changes resulting from H bond formation occur in the IR spectra, especially in the region of the \( \nu_s \) stretching bands. These are the decrease in the frequency of the \( \nu_s \) stretching mode, increase of its intensity, broadening of the bands and appearance of a complex fine structure. The mechanisms of these phenomena are a subject of many theoretical studies [1-11].

In the present paper theoretical model of the hydrogen-bonded cyclic dimers, based on Wójcik model [4], including mechanical and electrical anharmonicity, is presented. In the crystal structure of 2,4-dithiouracil such cyclic planar dimers are present [12].

**THEORETICAL MODEL**

Let us consider a dimer of 2,4-dithiouracil. Our model assumes strong interaction between the N-H stretching vibration and the N···S stretching vibration, the occurrence of Fermi resonance between N-H stretching fundamental mode and the first overtone of N-H bending vibration, and the Davydov interaction between two equivalent hydrogen bonds. The mechanical and electrical anharmonicities are taken into account by using Morse potential functions in the N···S stretching mode description and including the non-linear components in the expansion of dipole momentum operator. As two vibrational modes include the N···S stretching vibration in each dimer, both modes are be taken into account in computations.

Let us consider one of the cyclic dimers of 2,4-dithiouracil. We denote by \( q_{s,i}, q_{b,i} \) and \( Q_i \) (\( i=1,2 \)) the coordinates of N-H stretching, N-H in-plane bending and N···S hydrogen bond stretching vibrations, respectively. The corresponding frequencies are denoted by \( \nu_s, \nu_b \) and \( \nu_{\sigma} \).

The vibrational Hamiltonian can be written as:

\[
\hat{H} = \hat{T}(Q_i) + \hat{T}(Q_2) + \hat{h}_{s,1} + \hat{h}_{s,2} + \hat{h}_{b,1} + \hat{h}_{b,2} + \hat{V}_{\text{res}} + \hat{V}_{\text{anh}},
\]

where \( \hat{T}(Q_i) \) are the kinetic energy operators for the low-frequency vibrations \( \nu_{s,i} \), \( \hat{h}_{s,j} = \hat{T}(q_{s,j}) + U(q_{s,j}, Q_j) \) are the vibrational Hamiltonians of the N-H stretching vibrations \( \nu_s \) (\( U \) is the potential energy), \( \hat{h}_{b,i} = \hat{T}(q_{b,i}) + U(q_{b,i}, Q_i) \) are the vibrational Hamiltonians for the N-H bending vibrations \( \nu_b \),

*Corresponding author. E-mail address: wojcik@chemia.uj.edu.pl. Fax +48-12-634-05-15.*
\( \tilde{V}_{\text{res}}(q_{s,i},q_{s,j}) \) is the exchange resonance interaction potential between two equivalent hydrogen bonds and \( \tilde{V}_{\text{anh}} \) is the anharmonic coupling potential between the N-H stretching and N-H in-plane bending vibrations.

In the adiabatic approximation applied to the ground state of the N-H stretching vibrations the total vibrational wave function \( \Psi_m \) has the form:

\[
\Psi_m = \alpha_m^0 \phi_{s,i}^0 \phi_{s,2}^0 \phi_{b,1}^0 \phi_{b,2}^0 = \alpha_m^0 \pi_0, \tag{2}
\]

where \( \phi_{s,i}^0(q_{s,i},Q_{i}) \) are the eigenfunctions of the Hamiltonians \( \hat{h}_{s,i}^0 \) with eigenvalues \( \varepsilon_{s,i}(Q_{i}) \), \( \phi_{b,i}^0(q_{b,i}) \) are the eigenfunctions of the Hamiltonians \( \hat{h}_{b,i}^0 \) with the eigenvalues \( \varepsilon_{b,i} \) and \( \alpha_m^0(Q_{1},Q_{2}) \) are the vibrational wave functions of the \( v_a \) vibrations.

In the first excited state of N-H stretching vibrations the total vibrational function \( \Psi_n^+ \) can be expressed in the four-component form:

\[
\Psi_n^+ = \alpha_1 \phi_{s,i}^+ \phi_{b,1}^+ \phi_{s,2}^+ \phi_{b,2}^+ + \beta_1 \phi_{s,i}^+ \phi_{b,1}^+ \phi_{s,2}^+ \phi_{b,2}^+ + \alpha_2 \phi_{s,i}^+ \phi_{b,1}^+ \phi_{s,2}^+ \phi_{b,2}^+ + \beta_2 \phi_{s,i}^+ \phi_{b,1}^+ \phi_{s,2}^+ \phi_{b,2}^+, \tag{3}
\]

where the superscript "+" marks the excited state of \( v_s \) and the first overtone of \( v_b \) vibrations. The wavefunctions \( \alpha_1(Q_{1},Q_{2}) \) and \( \beta_1(Q_{1},Q_{2}) \) of the \( v_b \) vibrations are not yet specified.

To simplify notation let us introduce:

\[
\pi_1 = \phi_{s,i}^+ \phi_{b,1}^+ \phi_{s,2}^+ \phi_{b,2}^+, \quad \pi_2 = \phi_{s,i} \phi_{b,1} \phi_{s,2} \phi_{b,2}, \tag{4}
\]

Then the total vibrational function \( \Psi_n^+ \) takes the form:

\[
\Psi_n^+ = \alpha_1 \pi_1 + \beta_1 \pi_2 + \alpha_2 \pi_3 + \beta_2 \pi_4. \tag{5}
\]

To determine the wave functions \( \alpha_1(Q_{1},Q_{2}) \) and \( \beta_1(Q_{1},Q_{2}) \) the variational principle is applied to the Schrödinger equation with Hamiltonian (1) and wave function (3). For the \( v_s \) and \( v_a \) vibrations the crude adiabatic approximation is used:

\[
[\hat{T}(Q),\phi_{s,i}] = 0. \tag{6}
\]

The effective Hamiltonian \( \hat{H}^{\text{eff}} \) for the hydrogen bonds stretching vibrations \( v_s \) can be written as:

\[
\hat{H}^{\text{eff}} = \begin{bmatrix}
\hat{T}(Q_1) + \hat{T}(Q_2) + \varepsilon_{s,1} + \varepsilon_{b,1} + \varepsilon_{s,2} + \varepsilon_{b,2} & V_{\text{anh}} & V_{\text{res}} & 0 \\
V_{\text{anh}} & \hat{T}(Q_1) + \hat{T}(Q_2) + \varepsilon_{s,1} + \varepsilon_{b,1} + \varepsilon_{s,2} + \varepsilon_{b,2} & 0 & 0 \\
V_{\text{res}} & 0 & \hat{T}(Q_1) + \hat{T}(Q_2) + \varepsilon_{s,1} + \varepsilon_{b,1} + \varepsilon_{s,2} + \varepsilon_{b,2} & V_{\text{anh}} \\
0 & 0 & V_{\text{anh}} & \hat{T}(Q_1) + \hat{T}(Q_2) + \varepsilon_{s,1} + \varepsilon_{b,1} + \varepsilon_{s,2} + \varepsilon_{b,2}
\end{bmatrix}, \tag{7}
\]

where \( V_{\text{res}} \) denotes the matrix element of resonance interaction between two equivalent hydrogen bonds, and \( V_{\text{anh}} \) is the matrix element of Fermi resonances between the first excited state of N-H stretching vibration and the first overtone of the N-H in-plane bending vibration. These matrix elements are defined as:
\[ V_{\text{res}} = \langle \pi_3 | \hat{V} | \pi_1 >_{q_i,q_b} = \langle \pi_1 | \hat{V} | \pi_3 >_{q_i,q_b} \]
\[ V_{\text{anh}} = \langle \pi_2 | \hat{V} | \pi_1 >_{q_i,q_b} = \langle \pi_4 | \hat{V} | \pi_3 >_{q_i,q_b} = \langle \pi_3 | \hat{V} | \pi_2 >_{q_i,q_b} \]

The integrals in these matrix elements are equal due to the C2 symmetry of the system.

The Q-dependent eigenvalues \( \varepsilon_{s,i} \) of the Hamiltonians \( \hat{h}_{s,i} \) determine effective potentials for the low-frequency hydrogen bond stretching vibrations \( v_s \) in the ground state and the first excited of the \( v_s \) vibrations respectively. Usually the harmonic approximation is assumed and these potentials are defined by parabola equations. When the mechanical anharmonicity is taken into account, the \( \varepsilon_{s,i} \) energies should be described in different way.

Let us describe the potential for the N···S stretching vibration by the Morse curves:
\[ \varepsilon_{s,i} (Q_i) = D(1 - \exp(-\alpha Q_i))^2, \]
\[ \varepsilon_{s,i}^+ (Q_i) = D^*(1 - \exp(-\alpha^+ Q_i)) + R = D^*(1 - b \cdot \exp(-\alpha^+ Q_i)) + R, \]
with \( b = \exp(\alpha^+ B) \). \( D \) is the dissociation energy of the N···S hydrogen bond, \( \alpha \) the curvature constant of the potential function, \( R \) the vertical excitation energy, and \( B \) is the distortion parameter.

We define the force constant \( k = 2\alpha^2 D \). Then it is possible to define the angular frequency \( \Omega \) for the vibration \( v_s \) as:
\[ \Omega = \sqrt{\frac{k}{M}}, \]
where \( M \) is the reduced mass for the N···S vibration.

We introduce dimensionless quantities:
\[ q_i = Q_i \sqrt{\frac{M\Omega}{h}}, \quad p_i = \frac{\hat{h}}{\hbar \Omega} \sqrt{\frac{1}{hM\Omega}}, \quad \gamma = \alpha \sqrt{\frac{\hbar}{hM\Omega}}, \quad d = D \sqrt{\frac{\hbar}{h\Omega}}, \quad r = \frac{R}{h\Omega}. \]
\[ r' = \frac{\varepsilon_{b,i}}{\hbar \Omega}, \quad V_{\text{res}} = \frac{V_{\text{res}}}{h\Omega}, \quad V_{\text{anh}} = \frac{V_{\text{anh}}}{h\Omega}, \]
and assume that \( \varepsilon_{b,i} \) energies are equal zero. We expand the \( \varepsilon_{s,i} \) potentials into Taylor series and neglect the terms of an order higher than \( p \) (where \( p \) is integer). Then the potential functions take forms:
\[ \varepsilon_{s,i} (Q_i) = \frac{1}{2} q_i^2 + \sum_{t=3}^{p} a_t q_i^t, \quad \varepsilon_{s,i}^+ (Q_i) = \frac{1}{2} q_i^2 + \sum_{t=0}^{p} b_t q_i^t, \]
where the coefficients \( a_t \) and \( b_t \) are defined as:
\[ a_t = \frac{1}{t!} \gamma^t d(1)^t (2^t - 2) \quad (t \geq 2), \]
\[ b_0 = r, \quad b_1 = -2d^+ b y^+ (b - 1) \]
\[ b_2 = d^+ b (y^+) (2b - 1) - \frac{1}{2} \]
\[ b_t = \frac{(-1)^t}{t!} d^+ b (y^+) (b 2^{t-1} - 1) \quad (t \geq 2) \]

According to a definition of the linear distortion parameter taken from the Maréchal-Witkowski model [1] we define by \( b_M \) a linear coefficient in the Taylor series \( (b_M = b_1) \).

The effective Hamiltonian \( \hat{H}_{\text{eff}} \) can be transformed into:
\[ \hat{h}_{\text{eff}} = \frac{\hat{H}_{\text{eff}}}{\hbar \Omega} = \begin{bmatrix}
S + B_1 + A_2 & V_{\text{anh}} & V_{\text{res}} & 0 \\
V_{\text{anh}} & S + A_1 + A_2 + r' & 0 & 0 \\
V_{\text{res}} & 0 & S + A_1 + B_2 & V_{\text{anh}} \\
0 & 0 & V_{\text{anh}} & S + A_1 + A_2 + r'
\end{bmatrix}, \]  
\[(15)\]

where:
\[ S = \frac{p_i^2}{2} + \frac{q_j^2}{2} + \frac{q_k^2}{2}, \quad A_i = \sum_{t=3}^p a_i q_i^t \quad \text{and} \quad B_i = \sum_{t=0}^p b_i q_i^t. \]  
\[(16)\]

Each dimer of 2,4-dithiouracil is invariant to the symmetry operator \( \hat{C}_2 \) corresponding to two-fold symmetry axis. Therefore four-dimensional Hamiltonian (15) can be reduced to two-dimensional Hamiltonians \( \hat{h}^{\pm} \). The method used to reduce the Hamiltonian (15) is analogous to that applied by Fulton and Gouterman [13] to the reduction of the two-dimensional vibronic equation. The Hamiltonian (15) commutes with the symmetry operator \( \hat{C}_2 \sigma_1 \), where the matrix \( \sigma_1 \) is defined as:
\[ \sigma_1 = \begin{bmatrix}
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0
\end{bmatrix}. \]  
\[(17)\]

The projection operators \( \hat{P}^\pm = \frac{1}{2} (I \pm \hat{C}_2 \sigma_1) \) project out the eigenvectors of the operator \( \hat{C}_2 \sigma_1 \) from the functional basis \( [\alpha_1 \quad \beta_1 \quad \alpha_2 \quad \beta_2]^T \). The eigenvectors of the Hamiltonian (13) transform to:
\[ \frac{1}{\sqrt{2}} \begin{bmatrix}
\alpha_i \pm \hat{C}_2 \alpha_2 \\
\beta_i \pm \hat{C}_2 \beta_2 \\
\pm \hat{C}_2(\alpha_i \pm \hat{C}_2 \alpha_2) \\
\pm \hat{C}_2(\beta_i \pm \hat{C}_2 \beta_2)
\end{bmatrix} = \begin{bmatrix}
\alpha^\pm \\
\beta^\pm \\
\hat{C}_2 \alpha^\pm \\
\hat{C}_2 \beta^\pm
\end{bmatrix}. \]  
\[(18)\]

The vectors \( [\alpha^\pm \quad \beta^\pm]^T \) are the eigenvectors of two-dimensional reduced Hamiltonians \( \hat{h}^\pm \):
\[ \hat{h}^{\pm} = \begin{bmatrix}
S + B_1 + A_2 + V_{\text{res}} \hat{C}_2 & V_{\text{anh}} \\
V_{\text{anh}} & S + A_1 + A_2 + r'
\end{bmatrix}. \]  
\[(19)\]

The Hamiltonians \( \hat{h}^\pm \) cannot be reduced any further.

IR intensities of the fundamental transitions of the N-H stretching vibrations can be expressed as:
\[ I \sim |\langle \Psi_m^\prime | \hat{\mu} | \Psi_n^\prime \rangle|^2 \exp \left( -\frac{E_m}{kT} \right) \]  
\[(20)\]

where \( \Psi_m^\prime \) and \( \Psi_n^\prime \) are the wavefunctions of the ground and the first excited state of the N-H stretching vibrations respectively, and \( \hat{\mu} \) is the dipole moment operator.

When the electrical anharmonicity is taken into account, \( \hat{\mu} \) can be defined as:
\[ \hat{\mu} = \mu_0 + C(q_{x,1} + q_{x,2}) + C'(q_{x,1}^2 + q_{x,2}^2) + C''(q_{x,1} q_{x,1} + q_{x,2} q_{x,2}) + C'''(q_{x,1} Q_1 + q_{x,2} Q_2) + C''''(q_{x,1} Q_2 + q_{x,2} Q_1) + D(q_{b,1} + q_{b,2}), \]  
\[(21)\]

where:
We neglect the terms of higher order. With the wavefunctions $\Psi_m$ and $\Psi_n^+$ defined by (2,3), the formula (20) takes a form:

$$I_{m \rightarrow n} = \left| \langle \alpha_m^0 | 1 \pm \hat{C}_2 \beta \rangle_{\alpha, \alpha} + \delta_1 < \alpha_m^0 | 1 \pm \hat{C}_2 \beta \rangle_{\alpha, \alpha} + \delta_2 < \alpha_m^0 | (1 \pm \hat{C}_2)Q_1 \beta \rangle_{\alpha, \alpha} + \delta_3 < \alpha_m^0 | (1 \pm \hat{C}_2)Q_2 \beta \rangle_{\alpha, \alpha} \right|^2 \exp \left( \frac{-E_m}{k_B T} \right),$$

where $\delta_i$ coefficients ($i=1,2,3$) are defined as:

$$\delta_1 = \frac{D_3}{D_1 + D_2}, \quad \delta_2 = \frac{D_4}{D_1 + D_2}, \quad \delta_3 = \frac{D_5}{D_1 + D_2},$$

with:

$$D_1 = < \varphi_{s1} | C \varphi_{s1}^* >_{q_{s1}} = < \varphi_{s2} | C \varphi_{s2}^* >_{q_{s2}}$$
$$D_2 = < \varphi_{b1} | D \varphi_{b1}^* >_{q_{b1}} = < \varphi_{b2} | D \varphi_{b2}^* >_{q_{b2}}$$
$$D_3 = < \varphi_{s1} | C^* \varphi_{s1}^* >_{q_{s1}} = < \varphi_{s2} | C^* \varphi_{s2}^* >_{q_{s2}}$$
$$D_4 = < \varphi_{s1} | C^* \varphi_{s1}^* >_{q_{s1}} = < \varphi_{s2} | C^* \varphi_{s2}^* >_{q_{s2}}$$
$$D_5 = < \varphi_{s1} | C^* \varphi_{s1}^* >_{q_{s1}} = < \varphi_{s2} | C^* \varphi_{s2}^* >_{q_{s2}}.$$

The intensity of the transition is dependent on a sum of Franck-Condon integrals between the wavefunction $\alpha_m^0$ and the wavefunctions $\alpha^\pm$ and $\beta^\pm$. The contributions of the terms derived from the electrical anharmonicity and the overtone bending transitions are expressed by the coefficients $\delta_i$ ($i=1,2,3$).

Presented equations allow us to compute theoretical energies and intensities of the vibrational transitions, which represent the structure of the $\nu$ band. The energy of transition from the ground state of the N-H stretching vibration $\Psi_m$ to the excited state of this mode $\Psi_n^+$ takes the form:

$$E_{m \rightarrow n} = E_{n}^+ - E_m^-, \quad (26)$$

where the energy is expressed in quanta of the slow stretching mode, and the intensity of the transition $I_{m \rightarrow n}$ is described by the formula (20).

Numerical solutions of the Hamiltonians (19) give us a set of energies and intensities of vibrational transitions (23,26), therefore it can be presented as a vibrational spectrum. After imposing Gauss functions with the same half-width on each transition, the sum of such functions gives the theoretical contour of the simulated band, which can be easily compared with the normalized experimental band shape.

When the potentials $\varepsilon_{i,j}(Q_i)$ are expressed in the Taylor series, the overlap integrals of type $\langle \chi_k(Q_i) | Q_i^l | \chi_j(Q_i) \rangle$ (where $\chi_k$ is a k-th eigenfunction of the harmonic oscillator and n is a positive integral number) appear. The exact values of these integrals can be obtained from:

$$\begin{cases} 
< \chi_i | x^i | \chi_j > = W\left( j, t, \frac{1}{2} (i - j + t) \right) & \text{for } i+j+t \text{ non-negative even number} \\
< \chi_i | x^i | \chi_j > = 0 & \text{otherwise}.
\end{cases}$$

The coefficients W satisfy the following recursion formulas:
\[
\begin{align*}
W(n,k,0) &= \sqrt{\frac{(n-1)\ldots(n-k+1)}{2^k}} \\
W(n,k,k) &= \sqrt{\frac{(n+1)(n+2)\ldots(n+k)}{2^k}} \\
W(n,k+1,i) &= W(n,k,i) \sqrt{\max\left(0, \frac{n-k+2i}{2}\right)} + W(n,k,i-1) \sqrt{\max\left(0, \frac{n-k+2i-1}{2}\right)}
\end{align*}
\]

for \( n, k, i \) non-negative integer numbers, \( 0 < i < k+1 \).

Described model was successfully applied to reproduce experimental spectra of 2,4-dithiouracil crystal and its deuterated derivative [14].

**REFERENCES**

Elongation Cutoff Technique At Kohn-Sham Level Of Theory: An Efficient Sparse Matrix Algebra Approach To Linear Scaling

Jacek Korchowiec

K. Guminski Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, POLAND

This is the standard font and layout for the individual paragraphs. The style is called "Paragraph." Replace this text with your text. The "Enter" key will take you to a new paragraph. If you need to insert a hard line break within the paragraph, please use Shift+Enter, rather than just tapping the "Enter" key.

Huge progress in computer technology brings about conditions for \textit{ab initio} computational methods to be of practical value in chemistry, biochemistry and material science. The application of conventional Hartree-Fock (HF) or Kohn-Sham (KS) calculations to huge molecular systems is limited due to undesired scaling behavior. The expense of a given method is usually expressed as a $N^a$, where $N$ and $a$ are the number of basis functions applied in the calculations and scaling exponent, respectively. In this presentation the elongation cutoff (ELG/C) technique and its scaling behavior is presented \cite{1}. The ELG/C technique is an extension of elongation (ELG) method \cite{2} that takes the full advantage of localized KS molecular orbitals. The ELG/C KS scheme is based on local exchange-correlation space approximation. Such approximation improves efficiency of the method without introducing additional numerical errors. It is demonstrated that the ELG/C method substantially speeds up the quantum-chemical calculation at KS level of theory. The majority of CPU time is spent for constructing the KS matrix, therefore, it is especially well suited for parallel performance. A comparison of ECT timings for model systems with the reference calculations is given. The analysis includes the overall CPU (central processing unit) time and its most time consuming steps, as well as the accuracy of the method.

REFERENCES

Generalized Van Vleck Perturbation Theory Study of Chlorine Monoxide

Timothy J. Dudley, Jesse J. Howard, and Mark R. Hoffmann

Chemistry Department, University of North Dakota, Grand Forks, ND 58202-9024, USA

Abstract. The second order generalized Van Vleck perturbation (GVVPT2) variant of multireference perturbation theory for molecular electronic structure theory was used to study the ground and first excited states of the atmospherically important molecule chlorine monoxide (ClO). Unlike multiconfigurational self-consistent field (MCSCF) results, GVVPT2 shows that the $A^2^1^T$ state has a local minimum, in agreement with experiment. This study supports the growing evidence that GVVPT2 can be used to study complex electronic structures, including those involving excited states and radicals.

Keywords: Multireference perturbation theory; electronic structure theory; excited states; potential energy surfaces; atmospheric chemistry.

PACS: 31.15.ae; 31.15.vn; 31.15.xp; 31.50.Bc; 31.50.Df.

INTRODUCTION

While multireference configuration interaction (MRCI) techniques are able to treat nondynamic and dynamic electron correlation sufficiently well for most systems, the computational effort (i.e., “cost”) of performing such calculations becomes prohibitively expensive for most polyatomic systems with moderate-sized or larger basis sets. This is primarily due to the construction of Hamiltonian matrix elements between excited configurations. Since the effects of dynamic correlation are supposed to be relatively small, treatment of such effects through perturbation theory ought to be reliable. First-order (in the wavefunction) approximations to such theories describe dynamic correlation through interactions between qualitatively correct zero-order reference functions and singly- and doubly-excited configurations only, where the majority of the correlation effects arise.

Especially when there are multiple low-lying electronic states in close proximity, one should expect that some of the singly- and doubly-excited configurations that will be used to describe electron correlation will be energetically low-lying. Such near degeneracies are notorious for causing divergent perturbation expansions, referred to as the intruder-state problem. More specifically, such intruder states are referred to as front-door intruders. In order to avoid such intruder states, Kirtman [1] suggested that an “extended model space” be formed that includes such low-lying zero-order states, and that only the low-lying states of interest within the model space be perturbatively corrected by the zero-order states lying outside the model space, using generalized van Vleck perturbation theory (GVVPT). Consequently, these low-lying zero-order external states, which have now become high-lying model space configurations, form a buffer zone. In such a scheme, the total configuration space is divided into three orthogonal subspaces

$$L_t = L_M \oplus L_Q = L_p \oplus L_S \oplus L_Q$$

Beginning in 1992, Hoffmann and coworkers [2] have investigated concrete realizations of generalized Van Vleck perturbation theory involving zero-functions constructed from MCSCF solutions to the model space problem. When the configuration state functions (CSFs) that are used to construct the zero-order low-lying states of interest (i.e., the primary states) comprise the model space, the secondary states correspond to MCSCF states that are not optimized (also often called the MCSCF complementary space). The framework that Kirtman suggested allows flexibility in choices made for the specification of the perturbative corrections, e.g., Møller-Plesset- or Epstein-Nesbet-like realizations are possible, and level shifts can be introduced. We have investigated some of these options.
and have arrived at a robust and generally applicable method that we refer to as GVVPT2. Since a complete description of the derivation and formalism of the GVVPT2 method has been given previously [2,3,4], in this work we only mention salient features.

Chlorine-containing compounds are believed to be a major contributor to the oxidation of many chemical species in the troposphere, though it is not well understood through what reaction pathways this occurs [5]. Thus, in order to understand many important processes in atmospheric chemistry, information about the ground and excited states of numerous chlorine-containing compounds is required. The simplest of the molecular chlorine-containing species are diatomics, such as HCl and chlorine monoxide (ClO). Since ClO is a radical, it is capable of reacting with other radicals readily. The first excited state corresponding to the same symmetry type as the ground state, \( ^2\Sigma^+ \), exhibits a potential energy minimum at a Cl-O bond distance significantly larger than the ground state. The corresponding potential energy curve presumably correlates to the dissociation limit involving a ground state chlorine atom and an excited oxygen atom. Experiments have shown that the vibrational states of the excited state minimum exhibit predissociation effects [6]. Therefore, ClO is able to produce atomic chlorine effectively through chemical interactions and simple photolysis.

The predissociation of ClO can be understood in terms of the breakdown of the Born-Oppenheimer approximation of electronic potential energy surfaces. The ground state potential energy curve has a minimum corresponding to a bound chlorine-oxygen species with a leading configuration of \( \sigma^2\pi^1 \). A simple bond-breaking process leads to formation of atomic chlorine and atomic oxygen, both in their ground states. Excitation from the ground state minimum to the first excited state corresponds to a \( \pi \rightarrow \pi^* \) transition. Though this transition disrupts the \( \pi \)-bond structure of ClO, the chlorine-oxygen \( \sigma \)-bond remains intact, leading to a bound excited state structure with an elongated bond. In the excited state, a further elongation that leads to bond-breaking gives atomic chlorine in its ground state and atomic oxygen in an excited state [4].

Based on symmetry considerations, the ground state dissociation limit, Cl (\( ^3\Pi \)) + O (\( ^3\Pi \)), correlates to nine doublet Born-Oppenheimer PESs, four of which correspond to two doubly degenerate \( ^3\Pi \) states [4]. One of these \( ^3\Pi \) states is the ground state, while the other corresponds to an excited electronic state. Since the first excited state at the ground state equilibrium geometry correlates diabatically to an excited dissociation limit, the second state correlating to the ground state dissociation products must lie higher in energy at the ground state equilibrium geometry, and therefore must cross the first excited state. However, for diatomic molecules, states of the same symmetry cannot cross. Rather, the states repel one another in the region where the crossing would occur, forming an avoided crossing. For the ClO molecule, this avoided crossing forces the first excited state to correlate to the ground state dissociation products, forming a quasibound excited state structure. Hence, the onset of predissociation at higher vibrational levels of the first excited state minimum.

Ab initio techniques that are able to describe excited states and especially multi-surface phenomena accurately are not abundant. MCSCF methods, while able to produce an avoided crossing in cases where one is rigorously required, often times produce poor results due to their lack of inclusion of dynamic correlation. Previous studies of ClO have indicated the absence of a bound stationary point on the \( ^3\Pi \) surface at the CASSCF level [7], in obvious contradiction to experiment. Highly accurate MRCISD calculations have been reported for this system and predict the existence of a minimum on the first excited state surface [7]. Such calculations offer a standard by which other techniques can be assessed. The purpose of this study is to evaluate the effectiveness of GVVPT2 in describing nearly degenerate excited states. Results obtained at the GVVPT2 level will be compared to previously reported results to determine whether the treatment of dynamic correlation at the GVVPT2 level is sufficient.

**RESULTS**

MCSCF calculations were performed using cc-pVTZ and cc-pVQZ basis sets, and all valence electrons and orbitals. The CFSs comprising the MCSCF configuration space defined the model space for the subsequent GVVPT2 calculations. State-averaged (SA-) MCSCF calculations were used. Using equal weights in the SA-CASSCF calculation does not produce optimum energies for any single state, just their average. In order to obtain a near-optimum state, it is necessary to heavily weight a single state in the SA-CASSCF calculation. Since the first excited state is of principal interest, SA-CASSCF calculations that favored the first excited state were performed. It is important to include a small amount of weight on all states below the one of interest and ones that may be nearly degenerate to the state of interest, in this case, the second excited state [8]. Thus, SA-CASSCF calculations were performed using a weighting scheme in which the first excited state was a factor of 5 times more heavily weighted than both the ground and second excited state. Figure 1 depicts the changes in the first excited state due to changes in the weighting scheme.
Although there is an appreciable separation between the ground state PESs using different weighting schemes, in a region from the potential energy minimum to considerably larger bond lengths, the difference between PESs is relatively constant [4]. A similar conclusion can be made for the excited state surface, but the separation between surfaces is considerably smaller. Note that the absence of a potential energy minimum on the excited state surface is not a consequence of how one treats nondynamic correlation for each state.

The inability of the CASSCF method to generate even qualitatively correct results means that dynamic correlation is required to obtain accurate energies and accurate results pertaining to geometrical structure. GVVPT2 includes dynamic correlation using a set of orbitals generated at the MCSCF level. Thus, GVVPT2 calculations depend on the weighting scheme used at the MCSCF level. The curves at the GVVPT2 level are expected to be less dependent on the weighting scheme than at the MCSCF level. This is because some of the nondynamic correlation energy lost through optimizing multiple states simultaneously is regained during the calculation of dynamic correlation energy. Unlike conventional multireference perturbation theories, in which the coupling between the perturbed primary states and the unperturbed secondary states is set to zero, and consequently only the primary states are re-optimized amongst themselves during a multi-root calculation, GVVPT2 diagonalizes the full effective Hamiltonian [1,2,3,4]. Figure 1 (right) contains PES plots of the first excited states of ClO generated at the GVVPT2 level with different weighting schemes at the underlying SA-CASSCF level. For the excited state, even though the curves are not exactly parallel to one another in the region of the minimum, the deviation between the curves is considerably less than it was at the MCSCF level (cf. Fig. 1 left). More significantly, a potential energy minimum is now apparent for both curves.

### Spectroscopic Parameters

The spectroscopic parameters generated at the GVVPT2/cc-pVTZ and GVVPT2/cc-pVQZ levels are presented in Table 1, along with corresponding experimental parameters [9]. Increasing the basis set size appears to decrease the bond lengths of ground and excited state structures, while the effects on the energy are surprisingly minimal. The basis set dependence is in accord with previous studies [7].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>cc-pVTZ</th>
<th>cc-pVQZ</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_e ) (Å)</td>
<td>1.585</td>
<td>1.567</td>
<td>1.57</td>
</tr>
<tr>
<td>( T_v ) (eV)</td>
<td>4.93</td>
<td>4.97</td>
<td>-</td>
</tr>
<tr>
<td>( \omega_0 ) (cm(^{-1}))</td>
<td>870.5</td>
<td>962.2</td>
<td>854</td>
</tr>
<tr>
<td>( R_e ) (Å)</td>
<td>1.864</td>
<td>1.814</td>
<td>1.86</td>
</tr>
<tr>
<td>( T_e ) (eV)</td>
<td>4.25</td>
<td>4.26</td>
<td>3.96</td>
</tr>
<tr>
<td>( R_e^2 ) (Å)</td>
<td>2.152</td>
<td>2.148</td>
<td>-</td>
</tr>
<tr>
<td>( E_0 ) (eV)</td>
<td>0.23</td>
<td>0.33</td>
<td>-</td>
</tr>
</tbody>
</table>
CONCLUSIONS

A series of calculations have been reported for the ClO radical at the GVVPT2 level using both the cc-pVTZ and cc-pVQZ basis sets. Spectroscopic constants have been calculated for the ground state and the lowest excited state of the same symmetry. The ground state equilibrium bond length is calculated to be 1.585 Å using the cc-pVTZ basis set and 1.567 Å using the cc-pVQZ basis set, both comparing well to the experimental value of 1.57 Å. Unlike CASSCF calculations, GVVPT2 calculations were able to determine excited state stationary points. However, the bond lengths are sensitive to basis set size, in this case, $R_e = 1.864$ Å at the cc-pVTZ level and $R_e = 1.814$ Å at the cc-pVQZ level. The depth of the potential well on the excited state curve is relatively insensitive to increasing the number of valence and polarization functions in the basis set. The harmonic vibrational frequency, $\omega_h$, is quite sensitive to both basis set effects and the weighting scheme at the MCSCF level [4].

Though a complete analysis of the ClO radical’s lowest lying states at the GVVPT2 level is not yet available, it is clear that GVVPT2 is able to give a quantitatively correct description of this system. Based on these results, it is reasonable to conclude that GVVPT2 can provide a much more accurate picture of excited states than MCSCF techniques. Though not discussed in this study, the cost of performing GVVPT2 corrections is comparable to the cost of MCSCF calculations [3], and significantly less than that of MRCI calculations (e.g., on the order of $pn$, where $n$ is the number of one-electron basis functions and $p$ is the number of CI iterations). While this is not of primary concern for molecules as small as ClO, application of MRCI techniques to larger halogen-containing systems becomes prohibitively expensive quickly. Since consideration of dynamic correlation is an essential aspect in describing the excited states of even the simplest of halogen-containing species, one must assume it will be important for larger species. Thus, GVVPT2 appears be an important tool to obtaining an accurate description of both geometrical parameters and energetic properties for larger chlorine-containing species, including molecules of atmospheric relevance.

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On Two Recent Developments Of The Polarizable Continuum Model: Molecules And Correlating Their Electrons.

R. Cammi

Dipartimento di Chimica G.I.A.F., Università of Parma, 43100 Parma, Italy

This talk will introduce two recent developments in describing the effect of the solvent on the molecular response properties obtained by using the continuum solvation model introduced by our group since 1981 [1-2], and called Polarizable Continuum Model (PCM). One of the two developments regards the descriptions of the molecular response functions at extreme pressure conditions and the other one regards the extension of the Coupled-cluster method to the description of the electron correlation of PCM solvated molecules.

The reasons to extend to PCM model to molecules under extreme pressure stay in its capability to describe at QM level the repulsive component of the solute-solvent interaction, and in the recent experimental and theoretical interest in the chemistry at extreme pressure conditions [4-6], where the repulsive (i.e. Pauli) component dominates the intermolecular interactions.

The reason to extend the PCM at the Coupled-cluster level concerns the description of the interplay between electronic correlation and solvation effects. To this end we have developed a Couple-cluster method [8] that introduces two different computational level: 1) the “energy only” scheme, PTE, in which the “solvated” HF orbitals are used to calculate the CC correlation energy, (2) the iterative scheme ,PTDE, in which the solvated correlated CC density is used to have a self-consistent reaction field. The CC-PCM method differs from the Christainsen-Mikkelsen [9] implementation of the Coupled-cluster with a Multipolar Continuum solvation model (CC-MPE) by the choice of the Hartree-Fock reference state of the molecular solute.

The talk will touch the theoretical basis of these new developments, and it will present some numerical applications concerning the evaluation of vibrational and electronic response functions.

REFERENCES

Experimental and Theoretical Investigations of Reference Molecules for Nonlinear Optics: The example of Acetonitrile

Elena Bogdan 1, Vincent Rodriguez 1, Frédéric Castet 1, Laurent Ducasse 1, Aurélie Plaquet 1,2, Benoît Champagne 2

1 Institut des Sciences Moléculaires, Université de Bordeaux, 351 Cours de la Libération, 33405 Talence (France)
2 Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix (FUNDP), rue de Bruxelles, 61, 5000 Namur (Belgium)

Abstract. We present a joint experimental and quantum chemical investigation on the first hyperpolarizability of the acetonitrile molecule, which is used as an external reference in Hyper-Rayleigh scattering (HRS) experiments. The measured HRS response is compared with calculations using the Finite Field (FF) procedure in combination with the Hartree-Fock and MP2 methods. Solvent effects are accounted for by using the Polarizable Continuum Model, while frequency dispersion effects are included by using a multiplicative correction scheme.

Keywords: Nonlinear optics, Hyper-Rayleigh Scattering, Quantum-chemical calculations.

PACS: 42.65.An; 42.65.Ky; 31.15.Ar.

INTRODUCTION

The off- and on-resonant nonlinear optical (NLO) phenomena are essential for future applications in the field of photonics, such as high-speed optical switching and computing, three-dimensional optical storage, three-dimensional photolithography, photonic crystals, optical limiting, or photodynamic therapy. The macroscopic NLO phenomena originate from the microscopic nonlinear polarization, which is described by the molecular hyperpolarizabilities. In the presence of an external electric field \( F \), the change in the dipole moment \( \mu \) is expanded in a power series of \( F \) (for simplicity, the frequency dependence of the fields is not explicitly written):

\[
\mu_i = \sum_j \alpha_{ij} F_j + \sum_{jk} \beta_{ijk} F_j F_k + \sum_{jkl} \gamma_{ijkl} F_j F_k F_l + ... \tag{1}
\]

where the indices \( i, j, k, ... \) depict the coordinates \( x, y \) and \( z \). The \( \alpha_{ij} \), \( \beta_{ijk} \), and \( \gamma_{ijkl} \) coefficients are referred to as the polarizability, the first hyperpolarizability, and the second hyperpolarizability, respectively. These coefficients are at the origin of various physical and chemical phenomena, e.g., \( \beta_{66}(-2\omega,0,0,0) \) and \( \gamma_{666}(-3\omega,0,0,0) \) characterize the second and third harmonic generations (SHG and THG). The search for molecular and material systems providing high second order responses has motivated lots of work in the recent years, the macroscopic responses being conditioned both by the first hyperpolarizability \( \beta \) of the molecular bricks and by their supramolecular arrangement.

There are two experimental techniques to probe the molecular first hyperpolarizability: the electric field induced second harmonic generation (EFISHG) and the Hyper-Rayleigh scattering (HRS). The EFISHG technique consists of measuring the light intensity at a frequency twice the fundamental frequency of an incident laser pulse generated by a solution submitted to a static electric field. This method gives information on the projection of the vector part of \( \beta \) on the dipole moment vector, so that only a combination of tensorial components of \( \beta \) can be obtained. The HRS method allows measurements for no dipolar and/or ionic molecules, which are out of reach of the standard EFISHG. The intensity of the scattered light is proportional to the square of the incident intensity, the proportionality factor implying a mean value of components of the \( \beta \)-tensor. Therefore, the HRS method allows obtaining different independent tensor components of the first hyperpolarizability, which is not possible by EFISHG. In both of these techniques, the determinations of the absolute \( \beta \) values are accomplished with respect to the second
order response of reference compounds, e.g. acetonitrile, ethanol, or carbon tetrachloride. As a part of a broader project aiming at reinvestigating such reference compounds, we present here a preliminary study of the first hyperpolarizability of the acetonitrile molecule combining HRS experiments and quantum-chemical calculations.

**EXPERIMENTAL AND COMPUTATIONAL ASPECTS**

**Hyper Rayleigh Scattering Experiments**

Acetonitrile was obtained from Aldrich with a purity of 99.9% (HPCL grade). The incident radiation at 1064 nm was obtained from a Nd:YAG laser producing trains of \( \approx 65 \) ps, \( \leq 50 \mu \text{J} \) pulses at a repetition rate of 2kHz (PL2200 Laser, EKSPLA). The scattered light was collected at 90° and focused into a Jobin-Yvon Horiba spectrographvi.

In the hyper-Rayleigh scattering (HRS) technique, the first hyperpolarisability, \( \beta \), is derived from the intensity of the incoherent scattered light at optical frequency 2\( \omega \) on incidence of an intense laser pulse at \( \omega \). For a single molecule, the HRS light intensity, \( I_{2\omega} \), is proportional to the square of the incident light, \( I_{\omega} \), and to the first hyperpolarizability. Assuming an elliptically polarized incident light propagating along the X direction, described by the rotation angle \( \Psi \) of the plane of polarization onto a fixed quarter waveplate with vertical fast axis vii, i(d), the intensity of the harmonic light scattered at 90° along the Y direction and vertically polarized V (along the Z axis) is given by:

\[
I_{2\omega} \propto \beta_{ZYY}^2 \cos^4 \Psi + \beta_{ZZZ}^2 \sin^4 \Psi + \sin^2 \Psi \cos^2 \Psi \left( \beta_{ZXY} + \beta_{ZYZ} \right)^2 - 2\beta_{ZXX} \beta_{ZZY} \left( \right)
\]

where the brackets indicate averaging over all possible molecular orientations. Hence, linearly polarized incident beams are described by \( \Psi = 0 \) (horizontal, H) or \( \Psi = \pi/2 \) (vertical, V) giving then the standard HV and VV scattering geometries, respectively. The macroscopic averages in equation (1) can be related to the components of the molecular first hyperpolarizability tensor using Bersohn’s expressions vii. If we consider the acetonitrile molecule with a C\(_3\) molecular symmetry and assuming Kleinman conditions (the HRS optical excitation at \( \lambda =1064 \) nm is far from any absorption band), there are three independent components, \( \beta_{ZXX} = \beta_{XXZ} \), \( \beta_{YYY} \), and \( \beta_{ZZZ} \). Thus, from Eq. 1 the elliptical polarization of the fundamental light introduces the following quartic dependence in \( \cos \Psi \) in the expression of the scattered light intensity:

\[
I_{2\omega} \propto \left( \beta_{ZYY}^2 \right) \cos^4 \Psi + \left( \beta_{ZZZ}^2 \right) \sin^4 \Psi + \sin^2 \Psi \cos^2 \Psi \left( \beta_{ZXY} + \beta_{ZYZ} \right)^2 - 2\beta_{ZXX} \beta_{ZZY} \left( \right)
\]

with \( R = \beta_{ZXX}/\beta_{ZZZ} \). Comparisons between experimental measurements and theoretical estimates are made by considering the square root of the HRS intensity for plane-polarized incident light observed perpendicularly to the propagation direction, as well as the associated depolarization ratios:

\[
\beta_{HRS}(-2\omega,\omega,\omega) = \sqrt{\left( \beta_{ZXX}^2 + \beta_{ZZZ}^2 \right)} = \sqrt{\left( I_{YY}^{2\omega} + I_{HV}^{2\omega} \right)}
\]

\[
DR = \frac{\beta_{ZXX}^2}{\beta_{ZYY}^2} = \frac{I_{YY}^{2\omega}}{I_{HV}^{2\omega}}
\]

**Quantum-chemical Calculations**

The molecular geometry has been optimized at the B3LYP/6-311G* level. The components of the static \( \beta \)-tensor have been calculated using the numerical finite field (FF) procedureviii in combination with the Hartree-Fock (HF) level, including no correlation effects, as well as the second-order Möller-Plesset (MP2) level. The dynamic \( \beta \)-tensor at 1064 nm has been computed using the time-dependent Hartree-Fock (TDHF) scheme, which consists in expanding the matrices of the TDHF equations in Taylor series of the external dynamic electric field and in solving
these analytically order by order \(x\). Different basis sets were employed (6-31G*, 6-31+G*, aug-cc-pvDZ, and aug-cc-pvTZ) in order to measure the impact of including polarized and diffuse functions on the second-order NLO response. Solvent effects were included by using the Polarizable Continuum Model with the integral equation formalism (IEFPCM)\(^x\), and acetonitrile as solvent. The HRS first hyperpolarizability including all correlation, solvent and frequency dispersion effects has been estimated by adopting the percentage or multiplicative correction scheme, which has been shown to be suitable for different systems\(^x\)ii:

\[
\beta^{\text{corr}}_{\text{solv}}(-2\omega;\omega,\omega) \approx \beta^{\text{corr}}_{\text{mp2}}(0,0,0) \times \frac{\beta^{\text{mp2}}_{\text{CDFT}}(-2\omega;\omega,\omega)}{\beta^{\text{mp2}}_{\text{CDFT}}(0,0,0)} \tag{6}
\]

All calculations were performed using Gaussian03\(^x\)ii, as well as homemade codes to improve the accuracy of the numerical derivations implied in the FF procedures. All first hyperpolarizability values are consistent with the convention B of Ref. \(^x\)iii.

**PRELIMINARY RESULTS AND PERSPECTIVES**

The first hyperpolarizability of acetonitrile measured from HRS at 1064 nm, \(\beta_{\text{HRS}}\), is equal to 20 a.u. (atomic units), while the independent \(\beta\)-tensor components are \(\beta_{xxx} = 0\), \(\beta_{zzz} = 10.5\) a.u., and \(\beta_{zzz} = 34.4\) a.u. The depolarization ratio \(\text{DR}\) amounts to 8.98, which is the signature of the pure dipolar character of the molecule. The theoretical values of \(\beta_{\text{HRS}}\) and \(\text{DR}\) calculated at the HF and MP2 levels using the different basis sets listed above are reported in Table 1.

<table>
<thead>
<tr>
<th>(\lambda = \infty)</th>
<th>Gas phase</th>
<th>Liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta_{\text{HRS}})</td>
<td>(\text{DR})</td>
<td>(\beta_{\text{HRS}})</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>12</td>
<td>2.27</td>
</tr>
<tr>
<td>6-31+G(d)</td>
<td>10</td>
<td>1.93</td>
</tr>
<tr>
<td>aug-cc-pvdz</td>
<td>4</td>
<td>1.60</td>
</tr>
<tr>
<td>aug-cc-pvtz</td>
<td>4</td>
<td>1.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\lambda = 1064) nm</th>
<th>Gas phase</th>
<th>Liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta_{\text{HRS}})</td>
<td>(\text{DR})</td>
<td>(\beta_{\text{HRS}})</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>12</td>
<td>2.31</td>
</tr>
<tr>
<td>6-31+G(d)</td>
<td>10</td>
<td>1.94</td>
</tr>
<tr>
<td>aug-cc-pvdz</td>
<td>5</td>
<td>1.59</td>
</tr>
<tr>
<td>aug-cc-pvtz</td>
<td>4</td>
<td>1.58</td>
</tr>
</tbody>
</table>

# using equation 6

At the HF level in the gas phase, the static \(\beta_{\text{HRS}}\) decreases as the size of basis set increases, while the associated DR values decrease. Including electron correlation at the MP2 level has for consequence to enhance the static \(\beta_{\text{HRS}}\) and the depolarization ratios, except for the smallest 6-31G(d) basis set where a small decrease is observed. At both the HF and MP2 levels, accounting for solvent effects leads to an increase of the static \(\beta_{\text{HRS}}\) with respect to the gas phase values. The same trend is found for the DR, except when using 6-31G(d), are significantly exalted by the polarizable medium. Frequency dispersion effects have a negligible impact on \(\beta_{\text{HRS}}\) and on the associated DRs when the molecule is considered in the gas phase. However, when solvent effects are taken into account, the dynamic \(\beta_{\text{HRS}}\) values are significantly reduced with respect to the static limit, as a result of the difference between the dynamic and static solvent dielectric responses. The opposite trend is observed when considering the DR, which are significantly exalted by frequency dispersion at \(\lambda = 1064\) nm.

Finally, considering the results obtained with the best level of calculation, \(i.e.\) IEFPCM/MP2/aug-cc-pvtz, we obtain \(\beta_{\text{HRS}} = 21\) a.u. and DR = 6.50, in good agreement with experiments. This points out that a precise description of the NLO properties of molecular systems requires using correlated methods together with extended basis sets, as
well as including both solvent and frequency dispersion effects. The calculated DR value remains nevertheless underestimated compared to the experimental one, very close to the limit value of 9. That no saturation in the DR values is observed when increasing the size of the basis set indicates that larger basis sets are needed to improve the agreement with experiment. In particular, a recent theoretical study has revealed that the d-aug-cc-pVTZ basis set is appropriate for NLO studies of medium-size molecules such as acetonitrile. In addition, the performance of higher levels of theory, such as the fourth-order Møller-Plesset or the coupled-cluster levels will be addressed.

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A general toolbox for the calculation of higher-order molecular properties using SCF wave functions at the one-, two- and four-component levels of theory

Kenneth Ruud*, Radovan Bast*, Bin Gao*, Andreas J. Thorvaldsen*, Ulf Ekström† and Lucas Visscher†

*Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway
†Department of Chemistry, Vrije Universiteit, Faculty of Sciences, De Boelelaan 1081a, 1081 HV Amsterdam, The Netherlands

Abstract. We outline a new approach for the calculation of higher-order molecular properties for self-consistent field (SCF) wave functions (or Kohn–Sham density-functional theory) expressed in time- and perturbation-dependent basis sets. The approach is based on an atomic-orbital-based, open-ended quasienergy derivative formalism, and is applicable for use in linear scaling SCF calculations. In order to enable the calculation of any response property, we have also developed open-ended one- and two-electron integral derivative programs, as well as a program that can calculate derivatives of exchange-correlation functionals to any order using automatic differentiation. These modules have been interfaced to both the Dalton and DIRAC programs. This allows us to calculate molecular properties at the one-, two- and four-component levels of theory using a common theoretical framework and code.

Keywords: Response theory, atomic orbital basis, integral derivatives, exchange-correlation kernels, automatic differentiation

PACS: 31.15.A-, 31.15.ap, 31.15.ee, 33.15.Kr

INTRODUCTION

The advances in laser technology, computational methodology and computer power have lead to an increasing interest in higher-order molecular properties, with nonlinear optical properties [] and nonlinear birefringences [] being prominent examples of such properties. The pioneering work of Bishop and Kirtman on the perturbation theory approach for calculating pure vibrational contributions to nonlinear optical properties also highlights the need for flexible schemes for calculating higher-order molecular properties for basis sets that may be both time- and perturbation dependent [1, 2]. As an example, the pure vibrational contribution to the second hyperpolarizability γ requires in the leading-order anharmonic approximation the calculation of fifth-order derivatives through the second geometrical derivative of the (in general frequency-dependent) first hyperpolarizability. The zero-point vibrational contribution to γ would, even within the harmonic approximation, require the sixth-order energy derivative through the second geometry derivative of the second hyperpolarizability.

The group of Champagne has made important contributions to the development of analytical methods for the calculation of higher-order, frequency-dependent molecular properties including contributions from geometrical derivatives [3, 4, 5]. Krykunov and Autschbach have introduced an approach in which time- and perturbation-dependent basis sets can be utilized for second- and third-order energy corrections [6]. These contributions have been important in the development of analytical methods for calculating molecular properties. However, both implementations have been done in the molecular orbital basis, and some aspects of the implementations are not optimal in terms of the computational effort needed to calculate the energy derivatives [7].

In this paper, we outline our strategy to attack the important and challenging task of calculating molecular properties of arbitrary order for time- and perturbation-dependent basis sets. We will also summarize the steps we take in order to develop all the necessary building blocks of such an open-ended computational procedure.
AN AO-BASED QUASIENERGY DERIVATIVE THEORY

The formalism we employ has recently been presented for the specific case of nonrelativistic Kohn–Sham density functional theory [7], but it has also been extended to the four-component relativistic framework [8]. The starting point for deriving (hyper)polarizability gradients in this approach is the quasienergy gradient formula [7]

$$Q^a = \frac{d}{da}Q = \left\{ \frac{d}{dg}E(D) - \text{Tr} S g W \right\}_t,$$

(1)

where $Q$ in our case is the Hartree–Fock (or Kohn–Sham DFT) quasienergy, $Q^a$ its derivative with respect to a nuclear displacement parameter $g$ (perturbation strength), which makes a (generally) time-dependent perturbation of both the Hamiltonian and the atomic orbital (AO) basis. $E(D)$ the generalized Hartree–Fock (or Kohn-Sham DFT) energy expressed in terms of the AO density matrix $D$, $S^a = \frac{d}{dg}S$ the geometry derivative of the overlap matrix, and $W$ the generalized energy-weighted density matrix (see Ref. [7] for the definition of these quantities). $\{ \ldots \}_t$ denotes the time average of the quantity inside the brackets.

Eq. (1) can be considered an extension of Pulay’s expression for the molecular gradient [9] to time-dependent basis sets. However, the generalized SCF energy $E(D)$ in Eq. (1) depends in the case of time-dependent basis sets on an additional matrix $T$ arising from the time dependence of the AOs. In the Hartree–Fock case this is given by

$$E(D) = h_{\text{nuc}} + v_{\text{nuc}} + \text{Tr}(h + V - \frac{1}{2}T)D + \text{Tr} \frac{1}{2}G(D)D, \quad (2)$$

$$T_{\mu\nu} = \langle \chi_{\mu} | \dot{\chi}_{\nu} \rangle - \langle \dot{\chi}_{\mu} | \chi_{\nu} \rangle, \quad \dot{\chi}_{\mu} = \frac{d}{dt} \chi_{\mu}, \quad (3)$$

where $h_{\text{nuc}}$ is the nuclear repulsion energy, $v_{\text{nuc}}$ the potential energy between the nuclei and the external fields, $h$ the integral matrix of the one-electron Hamiltonian, $V$ the integral matrix of the electron-field interaction, and $G$ the two-electron integral operator (Coulomb and exchange). Since $\frac{1}{2}T$ is a Hermitian matrix, $E(D)$ is a real-valued function of time. Note that for the unperturbed system (static, no fields), $T$, $V$ and $v_{\text{nuc}}$ are zero.

Expressions for higher-order molecular properties can be obtained from Eq. (1) by straightforward differentiation. In the case of the Hartree-Fock electric dipole gradient, we get

$$Q^{ga} = \frac{d}{da}Q^a = \left\{ \frac{d}{dg}v_{\text{nuc}} + \text{Tr} (V^{ga}D + h^{ga}D^a + G^{ga}(D^a - S^a W^a)) \right\}_t,$$

(5)

where we have taken advantage of the fact that it is only the electric field $a$ which is time dependent and not $g$. Similar expressions can be obtained for higher-order molecular properties. For all orders, the perturbed density matrices $D^a$, $D^{ab} \ldots$ can be determined by solving the same set of linear sets of equations [7]. We emphasize that the above equations have been derived in the atomic orbital basis, allowing for the use of linear scaling technology if available [10].

The formulas that are derived by repeated differentiations of Eq. (1) will fulfill the so-called $n + 1$ rule, in which the perturbed density of order $n$ can be used to determine the energy correction to order $n + 1$. Whereas this approach is advantageous if one of the perturbations have a large number of components (such as nuclear displacements), the much stronger $2n + 1$ rule should be used when the number of components are comparable for the different perturbations. Both possibilities are implemented in our program [7, 11].

In the formulas above, all formulated in the atomic orbital basis, no assumption has been made regarding the detailed nature of the Hamiltonian of the unperturbed system. The formalism is therefore equally applicable to non-relativistic Hamiltonians as it is for two-component relativistic Hamiltonians, such as the X2C Hamiltonian [12], and four-component relativistic Hamiltonians [8], such as the Dirac–Coumb or Dirac–Coulomb–Gaunt Hamiltonians. By utilizing matrix libraries capable of hiding the exact nature of the matrices (their size, symmetry and whether real, complex or quaternion algebra is employed), we may utilize the same code for both one-, two- and four-component wave functions. The only differences arise in the routines/programs that we use to calculate the energies and determine the perturbed densities. In the case of nonrelativistic wave functions, we use the Dalton program [13], whereas we use the DIRAC program for two- and four-component relativistic calculations [14].

OPEN-ENDED ONE- AND TWO-ELECTRON INTEGRAL CODES

A major challenge in the calculation of higher-order molecular properties is the appearance of a large number of different, and potentially complicated, one-electron integrals. This is in part due to the large number of molecule-field
interactions that can arise, but also due to the fact that if our basis set is perturbation dependent, derivatives of all the one-electron integrals may be required. Although one-electron integrals are fairly easy to program and computationally rather cheap, they would remain a limiting factor for studying an arbitrary molecular property.

We have therefore developed a new one-electron integral code, in which we take as a starting point the general one-electron operator

$$
\partial = C X_{AB}^{Kx_1, Ky_1, Kz_1} \sum_{A'B'M'} \left\{ \left( \frac{\partial}{\partial C_{x}} \right)^l_{x} \left( \frac{\partial}{\partial C_{y}} \right)^l_{y} \left( \frac{\partial}{\partial C_{z}} \right)^l_{z} f(r_{c}) \right\} \left( \frac{\partial}{\partial A} \right)^{n_x} \left( \frac{\partial}{\partial A} \right)^{n_y} \left( \frac{\partial}{\partial A} \right)^{n_z},
$$

(6)

where \( C \) is an arbitrary constant, such as the nuclear charge. \( A, B, C \) and \( M \) represent different nuclei or centers, and \( AB = A - B \) denotes the vector from center \( B \) to \( A \). The capital letters \( X, Y \) and \( Z \) represent the Cartesian coordinates of the nuclei, whereas the small letters \( x, y \) and \( z \) describe the coordinates of the electrons.

We allow for any derivative of this one-electron operator with respect to the nuclear positions. The derivative with respect to the different centres \( A, B, C \) and \( M \) of the one-electron integral over our generalized operator \( \partial \) in Eq. (6) thus takes the form

$$
\partial^{(A)} \partial^{(B)} \partial^{(C)} \partial^{(M)} \left\{ X_{i}(r, a, A) \right\} \partial^{(B)} X_{j}(r, b, B) \)

= C \partial^{(A)} \partial^{(B)} \partial^{(C)} \partial^{(M)} \left[ R^{K}_{AB} \int_{R^3} X_{i}(r, a, A) \langle \partial^{(C)} f(r_{c}) \rangle \partial^{(B)} X_{j}(r, b, B)\right] \]

= C (-1)^{\tau} \partial^{(A)} \partial^{(B)} \partial^{(C)} \partial^{(M)} \left[ R^{K}_{AB} \partial^{(A)} \partial^{(B)} \partial^{(C)} \partial^{(M)} \int_{R^3} X_{i}(r, a, A) \langle \partial^{(C)} f(r_{c}) \rangle \right] \]

(7)

For the details of the implementation we refer to Ref. [15].

We have also made a corresponding two-electron integral code in which an arbitrary-order geometry derivative of the two-electron repulsion integrals can be calculated. This is achieved by restricting attention to a solid-harmonic basis, as opposed to a Cartesian angular basis, since this offers a particularly simple and efficient route to geometry-differentiated integrals. This strategy is based on the observation that contracted solid-harmonic basis functions may not only be expressed as a combination of contracted Cartesian basis functions, but also from contracted Hermite basis functions [16].

**EXCHANGE-CORRELATION DERIVATIVES USING AUTOMATIC DIFFERENTIATION**

Modern exchange-correlation functionals have complicated forms. When calculating higher-order molecular properties, the derivatives of these functionals are needed to the same order as the order of the energy derivative. This may in many cases lead to highly complex expressions covering several pages of typically automatically generated code, where little control of the numerical stability of the expressions can be assured. Furthermore, these extensive codes are also prone to coding errors, and finding errors in such elaborate codes is at best difficult. To illustrate the challenges faced for higher-order derivatives of exchange-correlation functionals, consider the heptic response function (eighth-order energy correction): The derivative of the exchange-correlation functional will contain 887 unique terms (at the spin-unpolarized local density approximation (LDA) level, otherwise additional terms will arise), many of which also occur with a large number of permutations. Automatic generation of code via symbolic manipulation is therefore not likely to be a viable approach for calculating these exchange-correlation contributions, although implementations to response functions have been presented in the literature [17].

We have for this reason adopted a different approach for calculating higher-order exchange-correlation functionals [18] based on automatic differentiation [19]. In contrast to for instance symbolic differentiation, which yields explicit expressions and codes for the derivatives, automatic differentiation provides values for the derivatives without an explicit derivative code. This is achieved by teaching the computer how to perform differentiation of sums, products and other elementary functions. By using operator overloading or similar language structures, this task can also easily be programmed.

In practice, we have written a code which can represent any function normally appearing in common exchange-correlation functionals as a Taylor series, and then instruct the program on how to calculate the Taylor series of the exchange-correlation energy density as a function of a Taylor series expansion of the density variables. Since
the Taylor series is a representation of the function in terms of its derivatives, we can easily extract the relevant higher-order derivatives. We have verified that the approach yields numerically stable results for the local spin-density approximation (LSDA) functional up to at least 8th order [18], but the code is in principle unlimited in terms of the order of the derivatives and the complexity of the functional it can handle. The approach has been shown to be computationally competitive to symbolically differentiated code for lower orders, for both LDA and generalized gradient approximation (GGA) functionals, but is expected to be much more advantageous for higher orders, both in terms of development time and in terms of computational efficiency.

SUMMARY

We have outlined our strategy for building a new atomic-orbital-based response formalism, in which all the necessary building blocks are open-ended in terms of the derivatives we can calculate. Both frequency-dependent and perturbation-dependent basis sets can be used in this approach. The code is built up from independent modules with well-defined interfaces, allowing for a high level of portability of the modules between different computer programs. Indeed, the modules can be utilized using one-, two- and four-component relativistic or non-relativistic wave functions.

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Second-Order Nonlinear Optical Responses of Flexible Pyridine-Pyrimidine Foldamers

Frédéric Castet¹, Raphaël Méreau¹, Edith Botek², Benoît Champagne²

¹ Institut des Sciences Moléculaires, Université de Bordeaux, 351 Cours de la Libération, 33405 Talence (France)
² Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix (FUNDP), rue de Bruxelles, 61, 5000 Namur (Belgium)

Abstract. Using a theoretical approach combining classical molecular dynamics and quantum chemistry calculations, we investigate the impact of the dynamical disorder, as well as of the impact of chemical substitution, on the nonlinear optical responses of helical oligomers based on pyridine-pyrimidine units. The fluctuations in the Hyper-Rayleigh scattering and electric field-induced second harmonic generation responses are analyzed with respect to the geometrical changes along molecular dynamics conducted at room temperature, providing therefore an insight into the relationships between the nature of the unit cell, the thermally induced geometrical fluctuations of the system, and its NLO properties.

Keywords: helical structures, nonlinear optics, molecular dynamics, quantum chemical calculations.
PACS: 42.65.An; 42.65.Sf; 71.15.Pd.

INTRODUCTION

Helices form a specific class of chiral molecules presenting high potential for building electronics, electro-optics, and photonics devices. Various possibilities exist to obtain molecules with a helical conformation,¹ from rigid molecules, in which the minimization of steric strains leads to helix formation, to flexible molecules adopting helical conformation as a result of stabilizing intramolecular non-covalent interactions. Starting from the principle that 2,2'-bipyridine adopts a s-trans conformation, Lehn and co-workers have proposed several helical structures based on heterocycles,² including pyridine-pyridazine, pyridine-naphthyridine, pyridine-pyrimidine, and hydrazone-pyrimidine units. These systems can be considered as coiled molecular wires of nanometric size possessing electron-acceptor properties associated to the nature of their subunits and substituents. In a recent study, we have investigated the first hyperpolarizability of such conjugated organic foldamers in order to address their potential to organize chromophores in such a way to exhibit large and specific second-order NLO responses.³ In particular, we have demonstrated that the first hyperpolarizabilities of helical pyridine-pyrimidine oligomers can be exalted by adding donor substituents such as aniline groups on the pyrimidine rings, and that supramolecular assemblies presenting dipolar-, octupolar-, or Λ-shape NLO character can be built by varying the substitution rate. Combining classical molecular dynamics to quantum chemistry calculations, we have also demonstrated that the dynamical disorder strongly impacts the NLO responses of such foldamers.³ We report here complementary results, which highlight further both the impact of the substitution and the impact of the thermally induced geometrical fluctuations on the NLO responses of pyridine-pyrimidine systems (Fig. 1). The fluctuations in the Hyper-Rayleigh scattering and electric field-induced second harmonic generation responses are analyzed with respect to the geometrical changes along molecular dynamics conducted at room temperature.

THEORY AND METHODS OF CALCULATION

MD simulations were carried out in the canonical ensemble at room temperature, for 1 ns with time steps of 0.5 fs. The MMFF94 force field¹¹ is employed because it closely reproduces the structures of the helical strands, as determined from X-ray diffraction.³ Every 2.5 ps, the geometrical structure is grasped and the corresponding second
harmonic generation $\beta(-2\omega;0,0)$ tensor is calculated for a wavelength of 1064 nm at the time-dependent Hartree-Fock (TDHF) level of approximation with the semiempirical AM1 Hamiltonian. Although it does not include explicitly electron correlation effects, it was substantiated in a series of works that the TDHF/AM1 approach is a good compromise between the quality of the results and the sparing of the computational resources for the calculation of the NLO responses of medium- and large-size systems. Hyper-Rayleigh scattering (HRS) and electric field-induced second harmonic generation (EFISHG) responses are analyzed since these are usual techniques to probe $\beta$. In the case of plane-polarized incident light and observation made perpendicular to the propagation plane without polarization analysis of the scattered beam, the second-order NLO response that can be extracted from HRS data reads:

$$\beta_{\text{m}}(-2\omega;0,0) = \sqrt{\left\langle \beta_{zzz}^2 \right\rangle + \left\langle \beta_{xzz}^2 \right\rangle}$$

while the associated depolarization ratio (DR) is given by:

$$DR = \frac{\left\langle \beta_{zzz}^2 \right\rangle}{\left\langle \beta_{xzz}^2 \right\rangle}$$

This last quantity gives information on the geometry of the part of the molecule responsible for the NLO response (for an ideal D/A one-dimensional system DR = 5, for an octupolar molecule, DR = 1.5 whereas for a $\Lambda$-shape molecule, the amplitude of DR depends on the angle between the chromophore as well as on the D/A groups). Full expressions of the orientational averages of the $\beta$ tensor can be found in Ref. 9. The EFISHG measurements give information on the projection of the vector part of $\beta$ on the dipole moment vector:

$$\beta_{\alpha}(-2\omega;0,0) = \beta_{\alpha} = \frac{3}{5} \sum_{i=1}^{n} \frac{|\mu_i|}{\|\mu\|} \sum_{\eta}^{\alpha} \left( \beta_{\eta\eta\eta} + \beta_{\eta\eta\eta} + \beta_{\eta\eta\eta} \right) = \frac{3}{5} \sum_{i=1}^{n} \frac{\mu_{i\alpha}}{\|\mu\|}$$

where $\|\mu\|$ is the norm of the dipole moment and $\mu_{i\alpha}$ and $\beta_{\alpha\beta}$ the components of the $\mu$ and $\beta$ vectors. Calculations were done using the MacroModel and MOPAC packages.

![Lewis structure](image1.png)

**Figure 1:** Lewis structure (a), top (b) and side (c) views of pyridine-pyrimidine (py-pym) strands.

### NON SUBSTITUTED PYRIDINE-PYRIMIDINE HELICAL STRANDS

The distributions of the $\beta$ values reported in Fig. 2 show that the average $\beta_{\text{HRS}}$ response of py-pym is about $9 \times 10^2$ a.u., with a standard deviation $\sigma$ of $2 \times 10^2$ a.u. The average depolarization ratio is equal to 1.7, characterizing octupolar-like NLO-phores. The octupolar symmetry originates from the structure and assembly of the unit cells; three py-pym (Fig. 1) units make slightly more than one helical turn so that the system exhibits a quasi $C_3$ symmetry. This symmetry is also consistent with the fact that $\beta$ is dominated by its radial component and that the axial contribution is negligible. The average EFISHG responses of the py-pym structure is almost negligible ($0.6 \times 10^2$ a.u.), which mainly results from the fact that the mean value of the angle $\theta$ between the dipole moment ($\mu$) and $\beta$ vectors is close to $\pi/2$ (82°). The $\beta_{\text{EFISHG}}$ distribution is also characterized by a very large standard deviation ($\sigma = 3 \times 10^2$ a.u.) demonstrating the crucial role of thermal fluctuations in the EFISHG responses of helical structures. This wide distribution has for origin the large fluctuations in the $\theta$ values ($\sigma = 42^\circ$) as well as the fluctuations in the norm of $\mu$, of similar amplitude to its average value ($\mu = 1.18D \pm 1.40D$).
SUBSTITUTED PYRIDINE-PYRIMIDINE HELICAL STRANDS

The second-order NLO responses of “naked” py-pym helical strands remain globally small with respect to typical donor/acceptor systems. Nevertheless, the first hyperpolarizabilities can be exalted by adding peripheral substituents on the helical structure. As previously shown, there is a preference to substitute the pyrimidine ring rather than the pyridine ring, and to substitute it by an electron-donating group rather than by an electron-withdrawing moiety. Thus, the effects of substituting the pyrimidine rings by electron-donating aniline groups on the HRS and EFISHG responses have been investigated by using the same computational approach. The distributions reported in Fig. 3 show that the substitution enhances the average HRS hyperpolarizability by a factor of ~6 ($\beta_{\text{HRS}} = 57 \times 10^{-2}$ a.u.). The standard deviation of the $\beta_{\text{HRS}}$ values is of $11 \times 10^{-2}$, indicating that geometrical fluctuations are responsible for relative variations of ~20% in the HRS responses, similarly to what is found for non-substituted structures. In addition, the presence of substituents reinforces the octupolar character of the NLO-phore, as shown by the DR distribution that concentrates more on the 1.5-1.6 domain. Compared to the naked structure, the average EFISHG response ($2 \times 10^{-2}$ a.u.) is slightly exalted by substitution but remains however small, the average value of the angle $\theta$ between the dipole moment ($\mu$) and $\beta$ vectors keeping unchanged (81°). Here also, the $\beta_{\text{EFISHG}}$ distribution presents a very large broadening ($\sigma = 2400$ a.u.) demonstrating the crucial role of thermal fluctuations in the EFISHG responses.

CONCLUSIONS AND PERSPECTIVES

These calculations combining classical samplings to semi-empirical calculations evidence the high impact of dynamic fluctuations on the NLO properties in pyridine-pyrimidine strands. In particular, these fluctuations are responsible for relative variations of ~20% in the HRS responses. Dynamical disorder has an even more important impact on the EFISHG responses, whose mean values are close to zero. This demonstrates that geometrical
fluctuations have necessarily to be taken into account for a reliable description of NLO properties in flexible structures such as helical strands. This work also demonstrates that grafting external aniline chromophores on the helical structure leads to a significant enhancement of the average HRS hyperpolarizability, while the EFISHG response remains weak for symmetry reasons. The approach presented here will be used to investigate new foldamers including double and quadruple helices, as well as to study the effects of temperature. In addition, future work will account for solvent-solute interactions, by including explicit solvent molecules in the dynamics, and/or by using quantum chemical continuum solvation schemes in the calculation of NLO properties. These further investigations should allow proposing reliable guidelines for the synthesis of dynamical objects exhibiting large and specific NLO responses.

ACKNOWLEDGMENTS

E.B. thanks the IAP 6/27 for her postdoctoral grant. B.C. thanks the Fund for Scientific Research (F.R.S.-FNRS) for his research director position. The calculations have been performed on the intensive calculation pole “M3PEC-MESOCENTRE” of the University Bordeaux financed by the Conseil Régional d’Aquitaine and the French Ministry of Research and Technology and on the ISCF installed at the FUNDP, for which the authors gratefully acknowledge the financial support of the F.R.S.-FRFC and the ‘Loterie Nationale’ for the convention No. 2.4617.07, and of the FUNDP.

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[7] The Taylor series expansion convention was employed to define β while 1 a.u. of $\beta = 3.6213 \times 10^{-22}$ m$^4$ V$^{-1}$ = 3.20636 $\times 10^{-33}$ C$^3$ m$^3$ J$^{-2} = 8.6392 \times 10^{-33}$ esu. See Shelton, D.P.; Rice, J.E. Chem. Rev. 1994, 94, 3.
Molecular Face Theory (MFT) – The Topology Analysis Of The PAEM And Local Descriptors Of Reactivity Mapping On The Molecular Face

Zhong-Zhi Yang and Dong-Xia Zhao

School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China, zzyang@lnnu.edu.cn

The potential acting on an electron in a molecule (PAEM) is defined as the interaction energy of an electron at position \( r \) with the remaining electrons and all nuclei in a molecule. PAEM of a series of inorganic and organic molecules were investigated using ab initio method. A molecular face (MF) [1] for a molecule, like an ID card, is defined uniquely and intrinsically. Potential acting on an electron in a molecule \( V(r) \) (PAEM) was first defined. The molecular face contour is formed by all the MF points defined by:

\[
G(-I) = \{ r : V(r) = -I \},
\]

where I is the first ionization potential of the molecule. The feature of a MF is the electron density on the face contour that is calculated one by one with an ab initio method.

We have studied some local reactivity descriptors on MF for a series of inorganic and organic molecules. As an example, the molecular face (MF) of \( \text{H}_2\text{O} \) is shown in Figure 1. We wish to provide some features of the reactivity descriptors on the MF. These descriptors, besides the electron density, include the Fukui function, local softness, molecular electrostatic potential etc. For nucleophilic attack, \( f^- (P) \) is the difference in electron density between the cation and the neutral; for electrophilic attack, \( f^+ (P) \) is the difference in electron density between the neutral and anion. The Fukui function distributions on MF are also displayed in Figure 1.

**FIGURE 1.** The Electron density, \( f^- (P) \) and \( f^+ (P) \) on the MF of \( \text{H}_2\text{O} \) molecule.
ACKNOWLEDGMENTS

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REFERENCES

Critical assessment of density functional theory for computing vibrational (hyper)polarizabilities

R. Zaleśny*, I. W. Bulik*, M. Mikołajczyk*, W. Bartkowiak*, J. M. Luis†, B. Kirtman**, A. Avramopoulos‡ and M. G. Papadopoulos‡

*Theoretical Chemistry Group, Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, W. Współp. 27, 50–370 Wrocław, Poland
†Institute of Computational Chemistry, University of Girona, Campus de Montilivi, 17071 Girona, Catalonia, Spain and Department of Chemistry, University of Girona, Campus de Montilivi, 17071 Girona, Catalonia, Spain
**Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, USA
‡Institute of Organic and Pharmaceutical Chemistry, The National Hellenic Research Foundation, 48 Vas. Constantinou Avenue, 11635 Athens, Greece

Abstract. Despite undisputed success of the density functional theory (DFT) in various branches of chemistry and physics, an application of the DFT for reliable predictions of nonlinear optical properties of molecules has been questioned a decade ago. As it was shown by Champagne, et al. [1–3] most conventional DFT schemes were unable to qualitatively predict the response of conjugated oligomers to a static electric field. Long–range corrected (LRC) functionals, like LC–BLYP or CAM-B3LYP, have been proposed to alleviate this deficiency. The reliability of LRC functionals for evaluating molecular (hyper)polarizabilities is studied for various groups of organic systems, with a special focus on vibrational corrections to the electric properties.

Keywords: hyperpolarizabilities; electron correlation; vibrational corrections; density functional theory
PACS: 31.15.A–; 31.15.ap; 31.15.E–; 31.15.es; 31.15.vq

In the presence of uniform electric fields of moderate strength, the total molecular energy can be expanded into a Taylor series:

\[ E(F) = E(0) - \mu F_i - \frac{1}{2!} \alpha_{ij} F_i F_j - \frac{1}{3!} \beta_{ijk} F_i F_j F_k - \frac{1}{4!} \gamma_{ijkl} F_i F_j F_k F_l - \ldots, \]  

where \( E(0) \) denotes the energy in the absence of electric fields \( (F) \). The expansion coefficients \( (\alpha, \beta, \gamma) \) define the polarizability, and the first and the second hyperpolarizability, respectively. Within the Born–Oppenheimer approximation the property \( (P = \alpha, \beta, \gamma, \ldots) \) may be separated into electronic and vibrational contributions [4, 5]:

\[ P = P^e + P^{vib}. \]  

\( P^{vib} \), in turn, can be divided into nuclear relaxation \( P^{nr} \) and curvature \( P^{curv} \) terms [5]:

\[ P^{vib} = P^{nr} + P^{curv} \]

with \( P^{nr} \) usually being the larger of the two. The nuclear relaxation contributions to static (hyper)polarizabilities can be further partitioned [6] into various square bracket components:

\[ \alpha^{nr}(0; 0) = [\mu^2]_{\omega = 0}^0, \]

\[ \beta^{nr}(0; 0, 0) = [\mu \alpha]_{\omega = 0}^0 + [\mu^3]_{\omega = 0}^1, \]

and

\[ \gamma^{nr}(0; 0, 0, 0) = [\alpha^2]_{\omega = 0}^0 + [\mu \beta]_{\omega = 0}^0 + [\mu^2 \alpha]_{\omega = 0}^1 + [\mu^4]_{\omega = 0}^2. \]

The zeroth-order terms (as indicated by Roman numeral superscript) are sufficient to compute nuclear relaxation contributions, in the infinite optical frequency approximation, for the dc–Pockels (dc–P) effect and intensity–dependent refractive index (IDRI) [6]:

\[ \beta^{nr}(-\omega; \omega, 0)_{\omega \to \infty} = \frac{1}{3} [\mu \alpha]_{\omega = 0}^0 \]

\[ \gamma^{nr}(-\omega; -\omega, \omega)_{\omega \to \infty} = \frac{2}{3} [\alpha^2]_{\omega = 0}^0 \]
In principle, vibrational contributions to electric dipole (hyper)polarizabilities can be determined using several schemes [6–12]. The Bishop–Kirtman perturbation theory is a general framework for computing vibrational corrections through various orders of electrical and mechanical anharmonicity [13]. The essential drawback of this approach is that it requires explicit evaluation of energy and property derivatives. On the other hand, finite–field nuclear relaxation (FF–NR) methods seem to be much more computationally efficient as far as polyatomic molecules are concerned [11]. Within the FF–NR scheme, two practical choices to perform electronic/vibrational structure calculations are wave function theory (WFT) and density functional theory (DFT). While the former approach can be quite successful in predicting electronic and vibrational (hyper)polariizations, the latter was shown a decade ago to completely fail in determining electronic contributions to α, β and γ of π–conjugated systems [1–3]. An assessment of DFT to compute vibrational (hyper)polarizabilities has only recently been undertaken [14–16]. The traditional functionals are expected to fail for long chain molecules, as the evolution of electronic contributions to α, β and γ with system size is poorly reproduced [3]. On the other hand, recently proposed long–range corrected (LRC) functionals [17, 18] were
reported to cure to a large extent the overshoot problem [19–21]. To make a preliminary assessment of the reliability of predictions of vibrational contributions to (hyper)polarizabilities by the LRC functionals, we used the LC–BLYP functional for this purpose. The results of calculations for several valence–bond and charge–transfer molecules are presented in Table 1. The MP2 values, serving here as a reference, in few cases are reproduced reasonably well by the LC–BLYP functional. Based on the results obtained using the BLYP functional it is difficult to observe any systematic trends. However, in almost all cases the LC–BLYP functional represents an improvement over the BLYP functional. The results of computations of static nuclear relaxation contributions to $\alpha$, $\beta$ and $\gamma$ for other organic model systems including polymethineimine oligomers and donor–acceptor–substituted polyenes will be presented.

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Vibrational Coupled Cluster Theory

Ove Christiansen, Mikkel Bo Hansen, Peter Seidler, Mikkel Bo Hansen, Manuel Sparta, Daniele Toffoli, Eduard Matito, Werner Györffy

Department of Chemistry, University of Århus, Denmark, ove@chem.au.dk

Response theory has long been a computational mature approach for calculating electronic properties such as polarizabilities and hyperpolarizabilities.

Recently we have developed response theoretical methods for calculating of vibrational contribution to molecular properties. Using explicit quantum wave functions for describing anharmonic vibrational motion vibrational response functions can be derived, implemented and applied. Wave functions that has been used includes vibrational self consistent field (VSCF), vibrational configuration interaction (VCI), and vibrational coupled cluster (VCC).

It will be described how the total properties can be obtained as combination of vibrational and electronic response functions. Methods for constructing potential and property surfaces are also considered including new ideas allowing adaptive construction of potential energy surfaces and efficient use of derivative information.

Finally, we will describe some simple methods for including temperature effects in vibrational calculations.
Nonlinear optical properties and large amplitude anharmonic vibrational motions

Josep M. Luis,* Heribert Reis,† Manthos Papadopoulos,‡ and Bernard Kirtman‡

* Institute of Computational Chemistry and Department of Chemistry, University of Girona, Campus de Montilivi, 17071 Girona, Catalonia, Spain.
† Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, 48 Vas. Constantiinou Avenue, 11635 Athens, Greece.
‡ Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, USA.

Abstract. A general reduced dimensionality finite-field nuclear relaxation method for calculating vibrational nonlinear optical properties of molecules with large contributions due to anharmonic motions has been very recently developed. Both nuclear relaxation and curvature contributions are included. In an initial application to the umbrella (inversion) motion of NH₃, it is found that the initial convergence problems associated with a conventional single well treatment are overcome and that the particular definition of the inversion coordinate is not important.

Keywords: Nonlinear Optics, Vibrational hyperpolarizabilities, vibrational states, ammonia.

PACS: 42.65.-k, 33.15.Mt, 33.20.Tp

INTRODUCTION

Nonlinear optics phenomena are not usually observed in nature since require very high light intensities such as those provided by pulsed lasers. Nevertheless, diverse scientific and technological fields such as materials science, communications, and medicine are benefited from nonlinear optical processes. At the molecular level both the electronic and nuclear degrees of freedom can interact with an electromagnetic light wave and, as a result, NLO properties contain both electronic and vibrational contributions. Surprisingly, for many NLO processes the vibrational contribution is often comparable in magnitude, or even larger, than that due to electronic motions.

Bishop and Kirtman developed a pioneering and successful approach based on perturbation theory for evaluating the vibrational contribution to NLO properties. Recently, a variational procedure based on analytical response theory, applied initially to linear polarizabilities, has been proposed by Christiansen, et al. The feasible application of both approaches are limited to small polyatomic molecules without anharmonic vibrational modes due to enormous cost of accurate potential energy and electrical property surfaces and the converge problems caused by the vibrational anharmonicity. Another alternative procedure more adequate for medium size molecules is the finite field - nuclear relaxation (FF-NR) approach, which requires determining the relaxation of the equilibrium molecular geometry induced by a static electric field, but avoids the explicit calculation of the potential energy and property surface. The handicap caused by most of anharmonic molecules can be overcome combining the FF-NR procedure with variational methods to calculate field dependent vibrational wavefunction. However, for molecules with very large amplitude anharmonic modes, simple power series expansion of the PES in normal coordinates will not suffice, and a new procedure is required.

A new approach to calculate the vibrational hyperpolarizabilities for highly anharmonic molecules has been very recently developed. This method is based on the fact that for the molecules with anharmonic large amplitude modes only a limited number of internal coordinates will play a significant role in determining vibrational NLO properties. In the next section we give the FF-NR methodology for treating a large amplitude anharmonic vibration and provide illustrative calculations for the inversion mode of NH₃.
THEORY

Our new treatment\textsuperscript{19} is based on an FF-NR approach wherein the key motions are decoupled from all other vibrations in first-order. This method takes advantage of recent developments that combine FF-NR methodology with variational calculation of field-dependent ZPVA energies and (hyper)polarizabilities.\textsuperscript{12,13} This new approach is designed for molecules where the primary contributions arise from a limited number of nuclear motions with large anharmonic effects. Then, the dimensionality of the vibrational problem for the large amplitude modes will be the same as one would encounter in treating a relatively small molecule. Vibrational wavefunctions for the inversion motion, which are required for the FF-NR treatment, are obtained by numerical solution of the 1D Schrodinger equations including a proper expression for the kinetic energy operator.\textsuperscript{19}

In the FF-NR approach the total vibrational (hyper)polarizability is divided into nuclear relaxation ($P^\nu$) and curvature ($P^\nu$) contributions. $P^\nu$ and $P$ arise from the change in the electronic and zero-point vibrational averaging corrections caused by the field-induced relaxation of the equilibrium geometry, respectively. $P$ can be divided into two terms: the zero-point vibrational averaging ($\text{zpva}$) contribution, $P^\text{zpva}$, and the remainder $P^\text{zpva}$. The FF-NR approach yields the static $P^\nu$, $P^\text{zpva}$ and $P^\text{zpva}$, as well as $P^\nu$ and $P^\text{zpva}$ for the dynamic Pockels effect, $\beta^\text{Pockels}$, Kerr effect, $\gamma(-\omega,\omega,0,0)$, electric field-induced harmonic generation (ESHG), $\gamma(-2\omega,\omega,\omega,0)$, and degenerate four-wave mixing (DFWM) $\gamma(-\omega,\omega,-\omega,\omega)$.\textsuperscript{12}

Here the focus is on large amplitude anharmonic vibrations using the umbrella motion in ammonia as an example. In order to study this vibrational movement we choose two different inversion coordinates. The first one, previously used by Handy, is based on the angle between the three N-H bond and the trisector axis ($\theta$).\textsuperscript{20} The second coordinate, $z$, is the displacement between the plane defined by the three hydrogens and the N atom.\textsuperscript{21}

The 1D potential energy function, $V(q_{inv})$, was obtained as the electronic energy at a fixed value of the inversion coordinate, $q_{inv}$, with the geometry otherwise optimized. This eliminates all linear terms in the remaining vibrational degrees which means that the first-order coupling between the inversion coordinate and the remaining spectator coordinates is included in the effective 1D potential. In order to have a general method that can be easily applied to any molecule we decided to evaluate kinetic energy operator numerically. In order to do so we use $tnum$,\textsuperscript{22,23} which requires only the Cartesian coordinates of the atoms for any of the usual internal coordinates and readily allows for the definition of linear combinations of internal coordinates as well. In the evaluation of the numerical kinetic energy operator we chose the Wilson normalization,\textsuperscript{24-25} which has the advantage that the volume element is simply expressed as the product of the coordinates differentials. A key advantage of using $tnum$ for this project is that the same formulation of the kinetic energy operator is valid for reduced dimensionality models.\textsuperscript{23} We fit to a polynomial of $n$th degree\textsuperscript{1} our results for different components of the numerical kinetic energy operator. Repeating the procedure to determine $V(q_{inv})$ for different finite fields we obtained the expression of the he field-dependent 1D effective inversion Hamiltonian.\textsuperscript{19}

For ammonia inversion in the absence of tunneling the field-free vibrational ground state will be doubly degenerate corresponding to motion along the inversion coordinate in each of the two potential wells. These states will be split by tunneling into a quasi-degenerate symmetric and antisymmetric pair. In order to analyze the perturbing effect of a static electric field we utilize a procedure based on generalized Van Vleck quasi-degenerate perturbation theory (GVV-PT).\textsuperscript{26-29} The GVV-PT derivation show that the expansion of the ground state vibrational energies in the field, vital to define the (hyper)polarizabilities, can only be performed when the energy difference between the quasi-degenerate states is either negligible, or far larger, than the energy change induced by the field. The first case turned out to be clearly true for the ammonia molecule.

In our new procedure we combine GVV-PT and exact numerical solution of the field-dependent Schrodinger equation. The first method was used to derive the finite field equations from which the vibrational dipole moment and (hyper)polarizabilities are obtained.\textsuperscript{19} But the second method was used to obtain the lowest pair of field-dependent energies for each finite field. Then, the vibrational (hyper)polarizabilities computed with this new procedure will include all anharmonic contributions within the 1D (reduced dimensionality) approximation.

In order to solve the numerical field-dependent Schrodinger equations we used the the so-called shooting method,\textsuperscript{30} which involves writing the second-order ordinary differential equation as a coupled pair of first-order differential equations. The ordinary differential equations are integrated numerically using the Runge-Kutta method. The shooting method is an iterative procedure. The integration is repeated, using a globally convergent Newton's method to adjust values of the vibrational energy, until the wavefunction satisfies the boundary conditions and then the iterative procedure converge. Finally, the field-dependent zpva contributions to the dipole moment and (hyper)polarizabilities were computed numerically as expectation values using the field-dependent vibrational wavefunctions for the inversion doublet, and the appropriate property expression as a function of $q_{inv}$.\textsuperscript{19}
ILLUSTRATIVE EXAMPLE

Although NH₃ may be considered a simple case it does allow us to perform initial tests of the general strategy and to compare with recent work based on an expansion of the potential about one of the minima.¹⁴ We compute the vibrational (hyper)polarizabilities of NH₃ using the same level of electronic structure calculations as for our previous single well treatment¹⁴ in order to perform a proper comparison. Thus, the effective 1D potential energy function was computed using the GAUSSIAN03 suite of programs³¹ at the MP2 level with the POL basis set developed by Sadlej³² for determination of polarizabilities.

In Tables I we present the electronic and vibrational contributions to the diagonal component of the second (hyper)polarizabilities, along the C₃ symmetry axis of ammonia.¹⁹ The static electric fields used in the finite field calculations are ±0.0004, ±0.0008, ±0.0016, ±0.0032, ±0.0064, and ±0.0128, a.u. The calculations confirm that it is essential to consider the vibrational contribution to NLO properties in NH₃ and that the umbrella mode is dominant in this regard. We find that our method overcomes convergence problems associated with a conventional single well treatment. For the one-well 3N-6 results there are a big jump in the vibrational static first and second hyperpolarizability upon going from a quartic to a sextic expansion for the PES.¹⁴ Thus, we concluded that the PES should not be expanded as a power series in terms of the normal coordinate associated with a single potential well.¹⁴ Our new FF procedure solves this convergence problem. A comparison between the results shown in the second and third columns of Tables I with the data presented in the last two columns confirms that the 6th-order expansion is seriously flawed. It also suggests that the quartic expansion is satisfactory in this case. It turns out that the particular definition of the inversion coordinate is not very important with maximum differences of about 7% in $\gamma_{zzzz}^{\text{VPC-vpva}}$. In addition, the results show that for NH₃ the effect of tunneling in the NLO properties is insignificant.

### TABLE 1. Electronic and vibrational contributions to the diagonal component of $\gamma$ in the direction of $\mu$ for NH3. Our 1D results are reported for two inversion coordinates. The FVCI values for the complete set of 3N-6 normal modes were obtained using 4th-order and 6th-order expansions.⁷,¹⁴,³³ All quantities are in a.u.

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<th>Inversion Coordinate</th>
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<th>1D $\zeta$</th>
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<th>6th-order $\gamma_{zzzz}$</th>
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33. These truncations are denoted as XmMtT, where X may be the potential energy (V) or the electronic contribution to the static electrical property, m is the maximum number of coupled modes, and t is the highest power in the expansion (M and T are included for cosmetic reasons only).
Theoretical Study of the Second Hyperpolarizability of Linear Ladder-type O-, N-, S-, and B-fused Heterocyclic Oligomers

Milena Spassova¹, Valentin Monev¹, and Benoît Champagne²

¹ Institute of Organic Chemistry with Center of Phytochemistry, Sofia 1113 (Bulgaria)
² Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix (FUNDP), rue de Bruxelles, 61, 5000 Namur (Belgium)

Abstract. Density functional theory calculations were carried out to investigate the effect of oligomer length and heteroatom substitution on the static electronic longitudinal second hyperpolarizabilities \( g_L \) of a series of fused heteroles (oligo-heteroacenes with \( N = 2 \) – 10 units, and up to \( N = 14 \) for borole derivatives). At the restricted B3LYP/6-31G* level, furan, pyrrole, and thiophene fused heteroles show second hyperpolarizabilities per unit cell, \( g_L/N \), monotonically increasing with chain length, with no sign of leveling off for \( N \) as values for furan and pyrrole are very close. On the other hand, for fused borole oligomers, a very irregular chain length dependence of \( g_L/N \) is found. Considering \( \pi \)-electron deficiency and excess, we have studied aromatic and quinoid skeleton deformations of the carbon backbone and have discussed the results for \( g_L \) determined by the singlet (open-shell)/triplet diradical character of the ground state (unrestricted B3LYP/6-31G* calculations). Calculations using wavefunction approaches have also been employed.
Long-Range-Corrected UDFT Study on Second Hyperpolarizabilities of Open-Shell Singlet Systems

Ryohei Kishi,*1 Sean Bonness,1 Kyohei Yoneda,1 Takashi Kubo,2 Kenji Kamada,3 Koji Ohta,3 Benoît Champagne,4 Edith Botek,4 Takao Tsuneda5 and Masayoshi Nakano*1

1Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
2Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
3Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan
4Laboratoire de Chimie Théorique Appliquée Facultés Universitaires Notre-Dame de la Paix (FUNDP), rue de Bruxelles, 61, 5000 Namur, Belgium
5Advanced Science Institute, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Abstract. The long-range correction (LC) scheme for the electron exchange in spin-unrestricted density functional theory (DFT), combined with the Becke-Lee-Yang-Parr exchange-correlation functional, i.e., LC-UBLYP, is applied to the calculation of the static second hyperpolarizabilities ($\gamma$) of $p$-quinodimethane, $o$-dimethylenepyrrole, and $o$-dimethylenefuran, which have different diradical characters. The spin-unrestricted HF (UHF) and post-UHF electron correlation methods, e.g., spin-unrestricted Møller-Plesset $n$th-order perturbation theory [UMPn ($n = 2, 4$)], spin-unrestricted coupled cluster singles and doubles (UCCSD) and that with perturbative triples correction [UCCSD(T)] methods as well as the conventional DFT and the spin-flip CI (SF-CI) methods, are applied to the model systems in order to compare the results with that obtained by the LC-UBLYP method. It is found that for the systems having intermediate and large diradical characters, the $\gamma$ values obtained by the LC-UBLYP method are in good agreement with those obtained by the UCCSD(T) method though it fails to reproduce the UCCSD(T) result for the system with small diradical character.

Keywords: second hyperpolarizability, singlet diradical, open-shell, density functional theory, long range correction

PACS: 31.15.A-, 31.15.E-, 31.15.es

1. INTRODUCTION

Recently, we have theoretically proposed open-shell nonlinear optical (NLO) systems whose second hyperpolarizabilities ($\gamma$) can be drastically changed depending on the diradical character and spin multiplicity.1-3 We also have proposed a novel structure-property relationship for open-shell molecules since the UDFT spin-contamination is usually small. We have reported that the UBHandHLYP exchange-correlation (XC) functional method is widely used to calculate the ground state properties of open-shell molecules since the UDT spin-contamination is usually small. We have reported that the UBHandHLYP exchange-correlation (XC) functional...
turns out to qualitatively describe the variation in static $\gamma$ of the $p$-quinodimethane (PQM) model as a function of the diradical character.\textsuperscript{2} The result indicates the importance of including HF exchange term for the reliable evaluation of (non)linear optical properties of open-shell singlet systems with intermediate and large diradical characters. On the other hand, the pure and hybrid DFT with conventional XC functionals are known to cause catastrophic behavior when computing the linear and nonlinear responses of extended closed-shell systems and thus are not suitable for examining the size effects on $\gamma$.\textsuperscript{5,6} This failure was found to be related to the shortsightedness of the conventional XC functionals, which are not able to describe the ultra-nonlocality of the electronic response to electric fields.\textsuperscript{5,6} To address the serious drawback of conventional DFT, several treatments, e.g., optimized effective potential (OEP) based approach\textsuperscript{7} and novel XC functionals,\textsuperscript{8-10} have been proposed recently.

The long-range correction scheme of density functional theory (LC-DFT)\textsuperscript{8-10} is one of such novel XC functionals based on the partitioning technique of electron repulsion operator ($1/r_{12}$) into the long- and short-range parts. The LC-DFT scheme along with the general gradient approximation (GGA) functional,\textsuperscript{8} has succeeded in improving poor descriptions of the conventional DFT for excitation energies, (non)linear optical properties of super- and supramolecules\textsuperscript{8,10} though there is still room for discussion of this approach to remove the catastrophic behavior completely for largely extended $\pi$-conjugated systems.\textsuperscript{11} Because the relative increase of the weight of HF exchange is also predicted to alleviate the catastrophic behavior of NLO properties of closed-shell extended $\pi$-conjugated systems, and the LC-DFT method has not been applied to the calculation of NLO properties of open-shell singlet systems so far, the applicability of LC scheme to the calculation of $\gamma$ values of open-shell singlet systems is of great interest. In this study, we therefore apply the LC scheme combined with (U)BLYP exchange correlation functional, i.e., LC-UBLYP, to the calculation of the static $\gamma$ value of a singlet open-shell system, $p$-quinodimethane model, which is one of the simplest aromatic diradical system. We employ this model system because electron correlation and basis set dependences of $\gamma$ have been studied previously in details. In order to discuss the applicability of LC-UBLYP method to several diradical systems, we also consider two additional diradical systems involving a pyrrole or furan ring bearing two methylene groups in $\beta$ position. We compare the results with those calculated by several ab initio correlated MO and conventional DFT methods. On the basis of these results, we discuss the applicability of the LC-UBLYP method to the $\gamma$ values of diradical molecular systems with different diradical characters.

2. METHODOLOGY

We first briefly outline the LC scheme in the DFT method. In the LC scheme, the $1/r_{12}$ operator is split into two terms using the standard error function,\textsuperscript{8} i.e., $1/r_{12} = [1 - \text{erf}(\mu r_{ij})]/r_{12} + \text{erf}(\mu r_{ij})/r_{12}$, where the parameter $\mu$ determines the partitioning ratio. The first term, which corresponds short-range interaction, is described by the DFT exchange functional, while the second term accounts for the long-range interaction and is described using the Hartree-Fock (HF) exchange integral. We employ the Becke1988 exchange functional for the short-range part along with the Lee-Yang-Parr correlation functional, i.e., LC-BLYP. The LC calculations are performed on the GAMESS program with the $\mu$ of 0.33. The spin-unrestricted scheme is employed in order to take account of partial static correlation in open-shell singlet ground state. The static $\gamma$ value is calculated by the finite-field (FF) approach. Within the FF approach, the longitudinal component of the static electronic $\gamma_{ii}$ ($\gamma$) is calculated using the fourth-order numerical differentiation formula. The convergence on the total energy is fixed to $10^{-10}$ a.u. Diradical character $\gamma$ is evaluated using the Yamaguchi scheme\textsuperscript{12} represented by using the occupation numbers of UHF natural orbitals (UNOs). The LC-UBLYP results are compared with those calculated by the spin-flip (SF)-CI approaches developed by Krylov\textsuperscript{13} as well as by several conventional ab initio correlated MO and DFT methods. The SF-CIS(D) method, which takes into account the double excitation effects in a perturbative manner, can correct for the lack of dynamical electron correlation. All SF-CI results, obtained by the Q-CHEM 3.0 program package, are taken from our previous paper\textsuperscript{3} while the ab initio MO and conventional DFT results are calculated by the Gaussian 03 program package.

In order to discuss the performance of LC-DFT method, not only the $\gamma$ value itself but also the $\gamma$ density analysis\textsuperscript{14} is examined in order to clarify the spatial contribution of electrons to $\gamma$. The longitudinal $\gamma$ density, $\rho_{ii}^\gamma(r)$, is defined as the third-order derivative of electron density with the applied electric field $F$\textsuperscript{14}. The positive and negative values of $\gamma$ densities multiplied by $F^2$ correspond to the field-induced increase and decrease in the third-order charge density and induce the third-order dipole moment (third-order polarization) in the direction from positive to negative $\gamma$ density. The $\gamma$ density map, therefore, represents the relative phase and magnitude of change in the third-order charge densities between two spatial points with positive and negative $\gamma$ densities.
3. RESULTS AND DISCUSSION

Model A in Fig. 1, called \( p \)-quinodimethane (PQM), is one of the simplest aromatic singlet diradical systems. Optimized molecular geometry of model A is taken from ref. 1. According to our previous papers, \( \gamma \) value calculated at the UHF/6-31G*+p \( (\zeta = 0.0523 \) on C) level of approximation is 0.146. For comparison, \( \alpha \)-dimethylenepyrrole and \( \alpha \)-dimethyleneurran were employed. Models B and C are built from a pyrrole or thiophene ring bearing two methylene groups in \( \beta \) position, respectively (see Fig. 1). The optimized geometries of these models are taken from ref. 2. The \( \gamma \) values calculated from the UNOs/6-31G*+p \( (\zeta = 0.0582 \) on N, and 0.0719 on O) amount to 0.487 for model B, and 0.694 for model C. Thus, the \( \gamma \) value turns out to increase when the ring aromaticity decreases, starting from \( \gamma = 0.146 \) for model A with a significant contribution of benzene ring. We calculate the \( \gamma_{\text{unc}} \) component using the 6-31G*+p basis set. Table 1 summarizes the calculation results obtained using several correlated \( \text{ab initio} \) MO, hybrid DFT, and \( \text{SF-CI} \) methods as well as the LC-UBLYP method. It was already found that all the spin-restricted-based post-HF and DFT methods cannot reproduce the UCCSD(T) results due to triplet instability in the intermediate and large \( \gamma \) regions. Therefore, we here compare several spin-unrestricted based results with the LC-UBLYP result. The most reliable and therefore reference results are obtained at the UCCSD(T) level of approximation, which significantly remove the spin contamination in the UHF solution.\(^1\) The UCCSD(T) \( \gamma \) decreases in the order: model A \( (233 \times 10^2 \) a.u.\( ) > \) model B \( (225 \times 10^2 \) a.u.\( ) > \) model C \( (162 \times 10^2 \) a.u.\( ) \). Despite their larger \( \gamma \) values, models B and C present smaller \( \gamma \) values than model A, at least when considering the direction connecting the radical sites corresponding to the horizontal axis in Fig. 1. This is most probably associated with their smaller extent, due to \( \alpha \)-orthoc-connection for models B and C, in this direction.\(^2\) On the other hand, the significant decrease in \( \gamma \) for model C than model B reflects the diradical character driven variation.

It is obvious that model A shows significant electron correlation dependence of \( \gamma \) as compared to the other models. It is found that the UHF results significantly underestimate the UCCSD(T) results for models B and C though in good agreement with the UCCSD(T) result for model A. In contrast, the UMP\( n \) result is shown to significantly overshoot the UCCSD(T) result for model A, e.g., enhancement by a factor of three at the UMP2(4) level of approximation, while to undershoot those for models B and C. These results indicate that UMP\( n \) correlation methods are not enough to reproduce the CC results, where the UCCSD results are semi-quantitatively comparable to the UCCSD(T) results for all the three models. The SF-CIS and SF-CIS(D) methods approximately correspond to the UNOCASCI(2,2) and UNOCASPT2(2,2) methods, respectively, in view of the approximation scheme.\(^3\) Although the SF scheme effectively removes the spin contamination effects, the SF-CIS is shown to improve the UHF results slightly. On the other hand, the UMP2 results are shown to be significantly improved by employing the SF-CIS(D) except for model B. It turns out that for model A, the SF-CIS and SF-CIS(D) results are very close to the UCCSD(T) result, while for models B and C the SF-CIS(D) results give significantly undershoot UCCSD(T) \( \gamma \) values. From these analyses, we found that both the high-order dynamical correlation and spin contamination correction are indispensable for describing the correct \( \gamma \) dependence of \( \gamma \) in the whole \( \gamma \) value region.

Because the spin-restricted DFT solutions partially involve static correlation effects even in the system having non-zero diradical character calculated from UNOs, a broken-symmetry solution is not necessarily obtained by the DFT method. Indeed, for the B3LYP and LC-BLYP functionals, the broken-symmetry solutions are not obtained for model A. We obtain the monotonic increase of \( \gamma \) with the increase of \( \gamma \) with the B3LYP functional. The UBHandHLYP results are found to be similar to the UCCSD results except for model A. As already reported in previous paper,\(^1,3\) the UBHandHLYP methods reproduce at least qualitatively the variations in \( \gamma \) except for small values of \( \gamma \) where the \( \gamma \) values overshoot the reference values. It is found that the LBLYP and B3LYP results, which are similar to each other, undershoot the reference UCCSD(T) results by about a factor of three. On the other hand, the LC-UBLYP results are shown to be in very good agreement with the reference UCCSD(T) results for models B and C, having intermediate and large \( \gamma \), respectively. As a result, the LC-UBLYP method is found to be a promising method for the evaluation of \( \gamma \) values of \( \pi \)-conjugated diradical systems with intermediate and large diradical characters.

Fig. 2 shows the \( \gamma \) density maps calculated at the UHF, UMP2, UCCSD, UBHandHLYP, and LC-UBLYP of models B [Fig. 2(a)] and C [Fig. 2(b)]. Because the UCCSD(T) density is not available in the Gaussian 03 program, we consider the UCCSD \( \gamma \) density as the reference showing the reasonable response of density. From the UCCSD \( \gamma \) density map for model B, positive and negative \( \gamma \) densities on the both-end diradical sites as well as on the C atoms of \( \alpha \) position mainly contribute to the \( \gamma \) value [see Fig. 2(a)]. For model B, most methods, except the UHF, show similar \( \gamma \) density maps, which exemplifies similar \( \gamma \) values. In particular, the UBHandHLYP and LC-UBLYP \( \gamma \) densities are in good agreement with the UCCSD \( \gamma \) density. On the other hand, for model C, the UHF and UMP2 \( \gamma \)
densities contributing positively to $\gamma$ value are significantly reduced as compared to the UCCSD $\gamma$ density [see Fig. 2(b)]. As is expected from the calculated $\gamma$ values, the UCCSD and UBHandHLYP results are similar to each other. The LC-UBLYP and UCCSD(T) methods, which give similar $\gamma$ value for model C, are therefore expected to give similar $\gamma$ density maps. These results indicate that the LC-UBLYP method as well as the UBHandHLYP method, though the UBHandHLYP method gives a smaller amplitude of $\gamma$, is predicted to be a reliable method for the semiquantitative calculation of $\gamma$ value of $\pi$-conjugated singlet diradical systems with intermediate and large $\gamma$.

| Table 1. Electron correlation dependences of $\gamma$ values [$x 10^2$ a.u.] for models A, B, and C |
|----------------------------------|-----------------|-----------------|-----------------|
| model A                         | model B         | model C         |
| UHF                              | 261             | 70              | 27              |
| UMP2                             | 765             | 157             | 63              |
| UMP4                             | 664             | 149             | 63              |
| UCCSD                            | 278             | 188             | 120             |
| UCCSD(T)                         | 233             | 225             | 162             |
| SF-CIS                           | 214             | 89              | 46              |
| SF-CIS(D)                        | 233             | 133             | 104             |
| UB3LYP                           | 70†             | 205             | 294             |
| UBHandHLYP                       | 547             | 182             | 110             |
| LC-UBLYP                         | 74†             | 212             | 158             |

†The UDFT solution coincides with the RDFT solution.

FIGURE 1. Structures and key geometric parameters [Å] of models A, B and C, as well as the diradical character $\gamma$ calculated from UNOs/6-31G+$^\dagger$

FIGURE 2. $\gamma$ density maps of models B (a) and C (b) calculated by the UHF, UMP2, UCCSD, UBHandHLYP and LC-UBLYP methods. The yellow (blue) mesh represents the isosurface of positive (negative) $\gamma$ densities with the amplitude of 100 a.u.

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**Anharmonic Vibrational Analysis Of Water At CCSD(T) Level: Comparison Of Traditional And Explicitly Correlated Methods**

Kalju Kahn*, Bernard Kirtman*, Jozef Noga†#, and Seiichiro Ten-no¶

* Department of Chemistry and Biochemistry, UC Santa Barbara, CA 93106, USA
† Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, SK-84215 Bratislava, Slovakia
# Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-84536 Bratislava, Slovakia
¶ Graduate School of Engineering, Kobe University, Nada-ku, Kobe 657-8501, Japan

**Abstract.** Achieving the spectroscopic accuracy in ab initio calculation of harmonic vibrational frequencies and vibrational anharmonicities is challenging due to two well-understood limitations. First, accurate results require a good description of electron correlation. Second, correlated calculations require large one-electron basis sets. It is well known that the convergence of harmonic frequencies with respect to the basis set size is slow. We now report that the convergence of cubic and quartic force constants in traditional CCSD(T) calculations of H₂O with Dunning’s cc-pVXZ family of basis sets is also frustratingly slow. As an alternative, we explore the performance of R12/B, R12/C and F12/C explicitly correlated methods at the CCSD(T) level. We find that an excellent convergence of harmonic frequencies and cubic force constants is provided by all three explicitly correlated methods with modest R12 basis sets; larger R12 basis sets appear necessary for the accurate description of quartic force constants and vibrational anharmonicities in water.

**Keywords:** Coupled cluster methods, explicitly correlated methods, anharmonic vibrational analysis, water.

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**INTRODUCTION**

Spectroscopic properties such as harmonic vibrational frequencies, centrifugal distortion constants, rovibrational coupling constants, and vibrational anharmonicities can be experimentally determined to a very high accuracy for many small molecules. The calculation of such properties ab initio to a “spectroscopic accuracy,” usually understood to mean that vibrational frequencies are accurate to about 1 cm⁻¹ (12 J/mol) has proven challenging for even the most advanced computational approaches. For example, reaching average errors below 1 cm⁻¹ for the water molecule required multi-reference configuration interaction (MRCI) calculations with large active valence orbital space, followed by corrections due to core correlation, relativistic effects, quantum electrodynamics, and Born-Oppenheimer approximation.

Single reference coupled cluster methods promise to yield accurate spectroscopic parameters, at a cost lower than MRCI.[1] However, the popular CCSD(T) approach yields errors in harmonic frequencies in the range of 10–20 cm⁻¹ in many cases.[2-9] There are two major limitations to higher accuracy with the coupled cluster approach. First, the meaningful estimation of double excitation contributions requires basis sets that include functions with high angular momentum.[5] Second, the correlation contributions beyond triples are not negligible.[4,6,8,9] It has been shown that for many diatomic systems, spectroscopic accuracy can be obtained by combining the valence-only CCSD(T) results at the basis set limit with various correction terms that are evaluated with smaller basis.[5-7]. Two approaches to obtain the correlation energy at the basis set limit have emerged in recent years. First, noting that the correlation energy converges systematically in correlation-consistent basis sets, one can extrapolate from results with finite basis sets.[10] Alternatively, one could use wave functions that explicitly depend on the interelectronic
distance (R12) when evaluating contributions from single and double excitations. The latter approach defines a family of explicitly correlated CCSD-R12 methods.

Until very recently, explicitly correlated coupled cluster methods made some assumptions in order to simplify and speed up calculations. Almost two decades ago, CCSD(T)-R12[11] was implemented [12] within the standard approximation.[13] The latter uses one-particle resolution of identity (RI) approximated by the projector over the actual computational basis, which significantly simplified the coding but necessitated basis sets in which low angular momentum functions (s, p, d, f) had to be nearly fully saturated in the radial dimension. Further approximations in the handling of integrals over the commutator of the kinetic operator and the correlation factor defines approximations A, B, and C.[14] Alternatively to the “standard approximation”, Klopper proposed to use large auxiliary basis sets for the resolution of identity while more compact contracted correlation consistent sets are used for the orbital basis.[15] In earlier versions of explicitly correlated codes, the correlation factor was a linear function of interelectronic distance but in 2004 Ten-no showed that a good accuracy can be obtained with even smaller orbital basis if a non-linear correlation factor, namely the Slater type geminal (STG) is used.[16] Coupled cluster methods that use linear correlation methods are usually designated as CC-R12 while methods with non-linear correlation functional are labeled as CC-F12.

The good convergence of correlation energy in CCSD-R12 and CCSD-F12 methods has inspired several authors to apply these approaches to calculation of molecular geometries, harmonic frequencies and vibrational anharmonicities of diatomic molecules.[3,5,8,17] Also, applications of these methods to study the vibrational spectrum of polyatomic systems (including water) have been reported.[8,18,19] These studies have demonstrated that explicitly correlated calculations give good results with modest orbital basis sets but true spectroscopic accuracy has remained elusive even for a relatively simple system such as the water molecule.

The basis set and correlation treatment dependence of cubic and quartic force constants has been explored less. This is understandable because while analytic second derivatives are available at CCSD and CCSD(T) levels,[20] third and fourth order derivatives must be calculated numerically. In the case of R12 methods the lack of analytical lower derivatives implies that a large number of well-converged single point calculations must be performed to evaluate higher derivatives. We now report about basis set convergence of cubic and quartic anharmonic force constants for water, and illustrate the benefits of explicitly correlated CCSD(T)-R12 and CCSD(T)-F12 methods for anharmonic vibrational analysis.

**COMPUTATIONAL METHODOLOGY**

Geometry of the water molecule was optimized in internal coordinates at each level of theory using a Newton-Rhapson algorithm with numerically evaluated derivatives. Optimizations and vibrational analysis was performed using our custom code that interfaces to different ab initio packages that provide energy values. Our code evaluates derivatives with respect to displacements in curvilinear internal coordinates using $O(h^4)$ and $O(h^6)$ central finite difference formulas. Reliable third and fourth order derivatives required a careful choice of convergence criteria during energy evaluation and minimization. We validated our code by reproducing the analytical quadratic, cubic, and quartic force constants for water reported by Gaw and Handy at the SCF/6-31G-ext level.[21]

The determination of normal coordinates and evaluation of harmonic frequencies was performed via the familiar Wilson GF-matrix formalism[22] using the symmetrization procedure due to Miyazawa.[23] The transformation of force constants from curvilinear internal coordinates to normal coordinates was performed via B-tensor transformations as described by Hoy, Mills, and Stray.[24] Vibrational anharmonicities including the corrections for Coriolis coupling were evaluated from cubic and diagonal quartic force constants in normal coordinates according to formulae provided by Mills.[25]

The traditional and explicitly correlated single point energy evaluations were performed with the program DIRCCR12-OS,[26] recently modified to include also STG correlation factor.[27] The CCSDT and CCSDT(2) corrections[28] were evaluated with NWChem.[29] R12-optimized basis sets (referred below as spdfgh, spdfg, and spdf for oxygen) were employed in explicitly correlated calculations.[30,31] We also optimized two $i$-functions by minimizing the total energy of oxygen atom in $^3P$ state at the CCSD(T) level. The hydrogen basis was 9s6p4d3f[31] Dunning’s cc-pVXZ and aug-cc-pVXZ basis sets[32,33] were employed in traditional valence-only calculations, the largest calculation involved harmonic vibrational analysis with the pV7Z basis.[34,35]. Contributions from core electron correlation effects were assessed with aug-cc-pwCVXZ basis sets[36] in traditional CCSD(T) calculations, and with the spdfg basis in explicitly correlated CCSD(T)-R12 calculation. Published values
were used for small but important corrections for the relativistic effects [9,37], quantum electrodynamic Lamb-shift correction [38], and Born-Oppenheimer diagonal and nonadiabatic corrections [39,40].

BASIS SET CONVERGENCE OF SPECTROSCOPIC PROPERTIES

Geometries and Harmonic Frequencies

It is well known that the convergence of molecular geometry of water, especially of the angle, is extremely slow in cc-pVXZ series [9]. The convergence is somewhat better when a set of diffuse functions is added, but at least the aug-cc-pV5Z quality basis is needed to bring the bond angle within 0.1 degrees of the apparent CCSD(T) limit (104.46°). In contrast, explicitly correlated calculations predict the CCSD(T) geometry correctly with a basis set composed of only spdfg shells on oxygen (Figure 1).

![Figure 1. Convergence of bond distance.](image1)

![Figure 2. Convergence of stretching frequency.](image2)

The slow convergence of harmonic frequencies in traditional coupled cluster calculations has been noted in the past [9]. We can only add that the difference between aug-cc-pV6Z and pV7Z basis sets exceeds 1 cm⁻¹ for symmetric stretching and bending modes. The use of the explicitly correlated methods helps significantly: the basis set limit is practically achieved with the spdfg basis on oxygen (Figure 2). Comparison of R12/B, R12/C, and F12/C (STG=1) approximations reveals that the R12/B and F12/C harmonic frequencies are very similar to each other while the R12C results differ slightly. A comparison with recently published CCSD(T)-F12a and CCSD(T)-F12b results [18,19] which used auxiliary basis sets, shows a satisfactory agreement between the best CCSD(T)-F12(a,b) results from MOLPRO and our CCSD(T)-F12/C results. In summary, with the possible exception of the R12/C approximation, the explicitly correlated methods appear to provide a robust and cost-effective way to reach the basis set limit harmonic frequencies and molecular geometries in the CCSD(T) model.

Cubic and Quartic Internal Coordinate Force Constants

The basis set and correlation treatment dependence of cubic and quartic force constants is less explored than the convergence of harmonic frequencies. These constants determine vibrational anharmonicities, which are of utmost importance if quantum chemists are hoping to explain experimental spectra of molecules. In addition, the anharmonicities affect atomization energies via zero point vibrational effects as well as via the sometimes-neglected constant contribution G₀. For example, CCSD(T)/cc-pVQZ anharmonicities are part of the highly accurate ab initio thermochemistry model HEAT [41]. Our results illustrate that the convergence of individual internal coordinate cubic force constants in cc-pVXZ series is also slow and often non-monotonous. A significantly better convergence is observed in the aug-cc-pVXZ series, and aug-cc-pVQZ cubic force constants are close to the apparent basis set limit. Explicitly correlated methods consistently yield cubic force constants of near-basis-set-limit quality with the spdfg basis on oxygen; the R12/B, R12/C and F12/C methods agree with each other to better than 0.1 cm⁻¹.

The convergence of quartic force constants in the cc-pVXZ series is very slow; non-monotonous behavior persists even beyond triple-zeta basis. In some cases, the convergence is improved by augmenting the basis sets...
with diffuse functions; aug-cc-pVQZ appears the smallest basis for which reliable quartic constants can be expected. Accurate calculation of the $f_{\text{aanaa}}$ seems a particularly challenging task; here only F12/C explicitly correlated calculations produce results that do not strongly depend on the basis set.

Vibrational Anharmonicities and Fundamental Frequencies

Vibrational anharmonicities are complex functions of internal coordinate force constants and molecular geometry, and it is not clear if a slow convergence of internal coordinate force constants also implies a slow convergence of vibrational anharmonicities and zero point energies. With the exception of $x_{22}$, our calculated vibrational anharmonicities do not vary significantly when basis sets of at least triple-zeta quality are used. The $x_{22}$ term decreases monotonously both in the cc-pVXZ and aug-cc-pVXZ series (Figure 5). The three explicitly correlated methods yield anharmonicity constants that are similar to the results of largest conventional calculation.

The slow convergence of fundamental frequencies is dominated by the slow convergence of harmonic frequencies. The CCSD(T) fundamental frequencies at the basis set limit differ from experimental values by a few cm$^{-1}$ due to fortuitous cancellation of errors due to neglect of core correlation (which increases stretching frequencies by as much as 7.5 cm$^{-1}$) and neglect of correlation effects beyond triple excitations (approximate quadruple excitations via CCSDT(2)$Q$ lower stretching frequencies nearly 5 cm$^{-1}$). True spectroscopic accuracy for water is only attainable after considering these corrections along with relativistic corrections, quantum electrodynamic Lamb shift, and Born-Oppenheimer diagonal and adiabatic corrections.

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Novel Photonic Materials

Manthos G. Papadopoulos

Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue, Athens 116 35, Greece, mpapad@eie.gr.

Abstract. We consider some specific examples of derivatives, which may have applications in the photonic industry. The key properties we study are the linear and nonlinear (L&NLO) properties. The first series of derivatives involves compounds in which one or more noble gas atoms have been inserted (e.g. HArF [1], HXeCnH [2]). The second series of examples involves the L&NLO properties of [60] fullerene-chromophore dyads [3]. Besides [60]fullerene these dyads involve 2,1,3-benzothiadiazole and carbazole functional groups.

We consider some specific examples of derivatives which may have applications in the photonic industry. The key properties we study are the linear and nonlinear (L&NLO) properties. The first series of derivatives involves compounds in which one or more noble gas atoms have been inserted. (a) HArF [1]. We have found that it has very large second hyperpolarizability along the z-axis. The difference in the electronic structure, between the ground and first excited state, has been invoked to rationalize the above remarkable property. Our results provided evidence, which suggests that noble gas atoms, inserted in chemical bonds lead to derivatives, which are likely to have very large NLO properties. (b) HXeCnH [2], where n=1,2. A hierarchy of methods (e.g. HF, MP2, CCSD(T) etc.) and a series of basis sets have been employed. The electronic and vibrational properties have been considered. The bonding in HXeC2H and the change of the electronic structure, which is induced by inserting Xe, has been analyzed, in order to rationalize the observed extraordinary NLO properties. The organo-xenon derivatives have been synthesized in a Xe matrix. Thus the effect of the local field (LF), due to Xe environment on the properties of HXeC2H, has been computed. It has been found that the LF effect on some properties is significant. For the interpretation of the results we have also employed the complete active space valence bond and CASSCF/CASPT2 methods.

The second series of examples involves the L&NLO properties of [60] fullerene-chromophore dyads [3]. Besides [60]fullerene these dyads involve 2,1,3-benzothiadiazole and carbazole functional groups. Linear scaling techniques have been used to reduce the computational cost. The L&NLO properties have been computed by employing wave function techniques (e.g. HF and MP2) and density functional theory. A large variety of functionals has been employed, but only the long-range schemes avoid the large overshoot in the first hyperpolarizability values. A relationship has been established between the overshoot and the electron donating ability of the substituent. Both the electronic and the vibrational contributions have been computed. It has been found that the [60]fullerene moiety (electron acceptor) enhances the average hyperpolarizabilities. A significant increase in the above properties is also achieved by the triphenylamine moiety. The static electronic value of all the considered dyads is remarkably smaller than the nuclear relaxation contribution to the dc-Pockels first hyperpolarizability. The IDRI second hyperpolarizability is comparable to the static electronic value.

REFERENCES

On the Reliability of the Maximum Hardness and Minimum Polarizability Principles in Nontotally Symmetric Vibrations

M. Solà\textsuperscript{a}, J. M. Luis\textsuperscript{a} and M. Torrent-Sucarrat\textsuperscript{b}

\textsuperscript{a} Institut de Química Computacional and Departament de Química, Universitat de Girona, Campus Montilivi, E-17071 Girona, Catalonia, Spain
\textsuperscript{b} Departament de Química Biològica i Modelització Molecular. IQAC – CSIC. c/ Jordi Girona 18, E-08034 Barcelona, Spain.

Abstract. Our latest results on the validity of the maximum hardness and minimum polarizability principles in nontotally symmetric vibrations are briefly reviewed. These nuclear displacements are particularly interesting because they keep the chemical and external potentials approximately constant, thus closely following the two conditions of Parr and Chattaraj required for the strict compliance of the maximum hardness principle. We show that, although these principles are obeyed by most nontotally symmetric vibrations, there are some nontotally symmetric displacements that refuse following them.

Keywords: Nontotally symmetric vibrations – Maximum Hardness Principle – Minimum Polarizability Principle

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INTRODUCTION

In 1987, Pearson stated for the first time the Maximum Hardness Principle (MHP) under the form that “there seems to be a rule of nature that molecules arrange themselves to be as hard as possible”.\textsuperscript{1} The Minimum Polarizability Principle (MPP) was formulated on the basis of the MHP and a linear relationship between the softness (the inverse of the hardness) and the polarizability. The MPP affirms that the natural evolution of any system is towards a state of minimum polarizability. Both principles have been applied successfully to the study of molecular vibrations, rotations, excited states, aromaticity, and different types of chemical reactions.\textsuperscript{3–5} A formal proof of the MHP based on statistical mechanics and the fluctuation-dissipation theorem was given by Parr and Chattaraj\textsuperscript{6} under the constraints that \( \mu \) and \( \nu(\vec{P}) \) must remain constant upon distortion of molecular structure. There is no single chemical process that satisfies these two severe constraints. However, relaxation of these restrictions seems to be permissible and it has been found that in most cases the MHP still holds; even though, the chemical and external potentials vary during the molecular vibration, internal rotation, or along the reaction coordinate. Hereafter, we will refer to the generalized MHP (GMHP) or MPP (GMPP) as the maximum hardness or minimum polarizability principles that do not require the constancy of \( \mu \) and \( \nu(\vec{P}) \) during molecular changes. It is worth nothing that some failures of the GMHP and GMPP in some chemical reactions and excited states have been reported.\textsuperscript{7} In most of these cases it has been argued that the \( \mu \) and \( \nu(\vec{P}) \) change perceptibly during the process. Thus, these situations do not break the strict MHP, because this principle is rigorously valid only under constant \( \mu \) and \( \nu(\vec{P}) \).\textsuperscript{6}

The molecular motion along a nontotally symmetric vibration is an interesting case in point to analyze from the viewpoint of the MHP and MPP.\textsuperscript{3} Let us start with a molecule in its equilibrium geometry and make a displacement from equilibrium along a nontotally symmetric normal mode (see Figure 1a). In this kind of distortion, positive and negative deviations from the equilibrium structure along nontotally symmetric vibrational modes yield molecular configurations that have the same \( \eta, \mu, \alpha \), and average potential of the nuclei acting on the electrons (\( v_{\text{eq}} \)). Then, if \( Q \) represents a nontotally symmetric normal mode coordinate, it follows that \( (\delta \eta/\delta Q) = 0 \), \( (\delta \mu/\delta Q) = 0 \).
\[(\partial \alpha / \partial Q) = 0, \text{ and } (\partial \nu_{\text{en}} / \partial Q) = 0 \text{ at the equilibrium geometry. After a small displacement, } \Delta Q, \text{ from the equilibrium geometry, the average external potential may be written as:}\]

\[
\nu_{\text{ex}} = \nu_{\text{en}}^{0} + \left( \frac{\partial \nu_{\text{en}}}{\partial Q} \right) \Delta Q + K, \tag{1}
\]

and, therefore, since \[(\partial \nu_{\text{en}} / \partial Q)_{0} = 0\] is found that for small nontotally symmetric displacements \(\nu_{\text{en}}\) is approximately constant. The same applies to the chemical potential. Hence, for small distortions along nontotally symmetric normal modes, \(\mu\) and \(\nu_{\text{en}}\) are roughly constant, becoming the nuclear motion than most closely follows the two conditions of Parr and Chattaraj. According to the GMHP and GMPP, the equilibrium hardness must be a maximum, and the polarizability a minimum, for any nontotally symmetric distortion (see Figure 1a). To the best of our knowledge, all numerical calculations of hardness and polarizability along the nontotally symmetric vibration modes carried out before our studies confirmed this point.

In contrast, for totally symmetric distortions, near the equilibrium geometry the hardness keeps increasing steadily as the nuclei approach each other. Indeed, neither \(\eta\) nor \(\mu\) or \(\nu_{\text{en}}\) shows any sign of maximum or minimum at the equilibrium geometry (see Figure 1b). This is not a violation of the strict MHP since neither the chemical nor the external potentials are kept constant during this kind of distortion.

**FIGURE 1.** Schematic representation of the qualitative behavior of the energy, hardness, and polarizability in the (a) nontotally and (b) totally symmetric stretching vibrational modes of water.

**RESULTS**

In classical aromatic organic molecules, such as benzene or pyridine, there is a vibrational mode that corresponds to the bond length alternation (BLA). BLA distortions in aromatic rings reduce the delocalization of the \(\pi\)-electrons and, consequently, the polarizability of the molecule. So, it is likely that this nontotally symmetric mode can break the GMPP as well as the GMHP. So, we decided to study the behavior of some of these BLA vibrational modes, finding for the first time the existence of a nontotally symmetric vibrational mode (the \(b_{2}\) normal mode of pyridine at 1304.4 cm\(^{-1}\) evaluated at B3LYP/6-31++G(d,p) level) that breaks the GMHP and GMPP. In contrast to the examples of breakdown of the GMHP and GMPP reported to that point, this was an example of a failure of these principles for the most favorable case in which \(\mu\) and \(\nu_{\text{en}}\) keep almost constant, indicating that the strict version of the MHP cannot be straightforwardly generalized. This augment in the hardness value can be attributed to a larger destabilization of the LUMO than of the HOMO. It is worth noting that the existence of BLA modes that do not
comply with the GMHP and GMPP is not a particular feature of pyridine. We have found that several \( \pi \)-conjugated organic molecules such as benzene, naphthalene, anthracene, or phenanthrene possess BLA modes that violate the GMHP and GMPP, irrespective of the method of calculation used.\(^8\),\(^9\) However, less expected is the generalization of this breakdown to non-\( \pi \)-conjugated or even non-\( \pi \)-bonded organic and inorganic systems. Actually, we have found that systems like the hydrogen fluoride tetramer, diborane, and anionic aluminum tetramer also present nontotally symmetric vibrations, which break the GMHP and GMPP.\(^10\) Although they are not \( \pi \)-conjugated organic species, all these systems possess a certain degree of cyclic electron delocalization, even in the case of hydrogen-bonded species such as the hydrogen fluoride tetramer. However, we have also identified some molecules with an almost completely localized electronic structure (cyclobutane, chair cyclohexane) that do not follow the GMHP.\(^10\) These results are relevant since it is important to know the applicability limits of the GMHP and GMPP.

We have also proved that the diagonalization of the polarizability and hardness Hessian matrices facilitates the analysis of the breakdown of these two principles in nontotally symmetric nuclear motions.\(^9\),\(^10\) This diagonalization gives the nuclear displacements that have a more marked breakdown of the GMPP and GMHP character (see Figure 2). Figure 2 displays the two nontotally symmetric vibrational modes of benzene that do not fulfill the GMPP at the HF/6-31G level (1\(b_{2u}\) and 2\(b_{2u}\)), and the two corresponding postdiagonalization distortions (1\(b_{2u}'\) and 2\(b_{2u}'\)).\(^9\) The 1\(b_{2u}'\) displacement (0.762 \(1b_{2u} + 0.648 2b_{2u}\)) presents a negative eigenvalue. This means that the polarizability is a maximum in the equilibrium position along this nuclear motion. In this distortion, only the nuclear displacements of the carbon atoms are significant, showing a clear BLA character. This fact corroborates the importance of the BLA distortions of the heavier atoms on the breakdown of the GMPP. In contrast, the 2\(b_{2u}'\) displacement (-0.648 \(1b_{2u} + 0.762 2b_{2u}\)) has a positive eigenvalue, and in this case the displacements of the carbon atoms have been reduced and those of the hydrogen atoms have been increased. Using this technique, we have devised a set of rules to predict without calculations the existence of vibrational modes that disobey the minimum polarizability principle in aromatic and \( \pi \)-conjugated molecules.\(^9\) In addition, we have found that the polarizability and the softness (the inverse of the hardness) are not always proportional, and, consequently, there are vibrational modes that follow or disobey only one of the two principles.\(^10\) We have also discussed the relationship between the breakdown of the maximum hardness principle and the pseudo-Jahn-Teller effect, showing that vibrational modes that suffer a large pseudo-Jahn-Teller effect are good candidates for disobeying this principle.\(^11\) Finally, we have provided exhaustive evidence about the breakdown of the minimum polarizability principle as a tool to predict the most aromatic ring in a given polycyclic aromatic molecule.\(^12\)

![Figure 2](image-url)  
**FIGURE 2.** Schematic representation of the displacement vectors corresponding to the two \(b_{2u}\) studied normal vibrational modes of benzene (1\(b_{2u}\) and 2\(b_{2u}\)) and the postdiagonalization nuclear distortions of benzene (1\(b_{2u}'\) and 2\(b_{2u}'\)).
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Insight And Progress In Density Functional Theory

Weitao Yang, Paula Mori-Sanchez, and Aron J. Cohen

Abstract. Density functional theory of electronic structure is widely and successfully applied in simulations throughout engineering and sciences. However, there are spectacular failures for many predicted properties. The errors include underestimation of the barriers of chemical reactions, the band gaps of materials, the energies of dissociating molecular ions and charge transfer excitation energies. Typical DFT calculations also fail to describe degenerate or near degenerate systems, as arise in the breaking of chemical bonds, and strongly correlated materials. These errors can all be characterized and understood through the perspective of fractional charges and fractional spins introduced recently.

DELOCALIZATION ERROR

Standard approximations for the exchange-correlation functional have been found to give big errors for the linearity condition of fractional charges, leading to delocalization error. What are the consequences of the delocalization error? In chemical reactions, approximate functionals predict much too low transition state energies and hence reaction barriers, because the transition state resembles stretched H and has electrons delocalized over more than one center. In an applied electric field, approximate functionals give the system too low an energy and too high a polarizability because fractional charges appear at the edges of the molecule. Approximate DFT can also predict unphysical charge transfer between the molecule and the metal leads in molecular electronic devices, and cause a significant overestimation of electronic conductance. When adding or removing an electron from a system, approximate functionals produce an overly disperse distribution for the added electron or hole. This effect can be magnified in large systems because the delocalization error increases with system size. Thus, the delocalization error may be a particular concern for cluster calculations that attempt to approach the bulk limit.

For the exact functional, its straight line behavior means that the derivatives of the energy with respect to fractional charge give the ionization energy and the electron affinity. Functionals with delocalization error get these derivatives wrong because of incorrect convex behavior. This explains the well-known underestimation of the band-gap. Functionals with incorrect concave behavior, like the Hartree-Fock approximation (which is an orbital functional within DFT), have the opposite characteristic and suffer from a localization error that saturates with system size. Hybrid functionals contain both convex and concave components and may benefit from error cancelation in some cases, thus reproducing good band gaps for solids with mid-size gaps; however, they do not provide general solutions.

STATIC CORRELATION ERROR

Consider the apparently simple problem of stretching H₂. Approximate functionals describe the covalent bond well but the energy is severely overestimated upon dissociation. This well-known problem is attributed to static correlation that arises in situations with degeneracy or near-degeneracy, as in transition metal chemistry and strongly correlated systems. These are very complicated problems with no clear solution within DFT. To analyze the error, consider one half of the closed-shell H molecule at the dissociation limit: a H atom with half a spin-up electron and half a spin-down electron, which is an exotic system with fractional spins. The exact energy of this system should be the same as that of the normal H atom in an integer-spin state. More generally, the constancy condition for the exact functional requires that systems with fractional spins have an energy equal to the normal-spin states.
FRACTIONAL CHARGES AND SPINS COMBINED

The linearity conditions for fractional charges and constancy condition for fractional spins have been recently unified and extended to states with both fractional charges and fractional spins to give a much more stringent condition: the exact energy functional is a plane, linear along the fractional charge coordinate and constant along the fractional spin coordinate with a line of discontinuity at the integer. Violation of this condition underlies the failure of known approximate functionals to describe the gaps in strongly correlated systems. It is shown that explicitly discontinuous functionals of the density or orbitals that go beyond these currently used smooth approximations is the key for the application of density functional theory to strongly correlated systems. Understanding the errors of functionals in the simplest way possible --- as violations of exact conditions for fractional charges and fractional spins -- opens the path forward for reduction of the errors and for applications of density functional theory in new frontiers.

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