

Some Observations on Molecular Orbital Theory

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Few theories have had the impact that molecular orbital (MO) theory has had in chemistry. It is taught in various guises at all levels from introductory first-year to graduate level courses and rightly so for it is a remarkably powerful theory that provides considerable insight into the basic electronic structure of matter. MO theory traces its conceptual origins to Mulliken (1) and Hund (2) who developed it to understand, in a qualitative way, the role of quantum mechanics in the interpretation of molecular spectra. It was cast in a firm mathematical form by Hartree (3), Fock (4), and Slater (5) who derived the equations that have as their solutions the molecular orbitals envisioned by Mulliken and Hund. It became a practical molecular theory in the hands of Roothaan (6) and Hall (7) who, in 1951, showed how one could solve the Hartree–Fock equations for a general polyatomic molecule by expanding the molecular orbitals in terms of atomic-like functions. This was a monumental advance as it allows one to determine once and for all the molecular orbitals and their energies and to assess the quantitative accuracy of the MO concept and to begin the systematic development of theories that are more accurate and that now dominate the computational chemistry (8) landscape.

Since the MO theory is a well-defined quantitative theory (known commonly as the Hartree–Fock–Roothaan theory) it can make quantitative predictions that can be compared with experiment. However, since MO theory does not

treat electron correlation (9) completely it should come as no surprise that its predictions may be in error. We emphasize that calculations using more accurate theories (8) that include electron correlation (9) result in accurate dissociation energies. In a recent article in this *Journal*, Duke and O’Leary (10) discuss the inability of MO theory to predict the ESCA spectrum of N₂. In the following, we discuss a few additional flawed predictions in the context of homonuclear diatomic molecules since these are the systems we usually discuss in introducing our students to MO theory. First, however, we comment on a common misrepresentation of the relationship between the energy of an atomic orbital and the energy of the MO associated with the atomic orbital.

The Relationship between the Energy of a MO and the Atomic Orbital Energies of the Composite Atoms

When two identical atoms interact, the atomic orbitals give rise to molecular orbitals that frequently, but not always, have energies that are above and below the energies of the constituent atomic orbitals. We collect in Table 1 the molecular orbital energies for the first row homonuclear diatomics (11) at the ground-state equilibrium bond length and the energies of the constituent 1s, 2s, and 2p atomic orbitals (12). Note that the energies of the two lowest molecular orbitals (1σ_g and 1σ_u) in Li₂ are both above the 1s orbital energy of the Li atom and the highest MO in Li₂, the 2σ_g, is actually

Table 1. The Energy of the Molecular Orbitals in the Sequence H₂ through F₂ and the Corresponding Atomic Orbitals

Orbital	H ₂ (¹ Σ _g ⁺) R _e = 1.390 a ₀	Li ₂ (¹ Σ _g ⁺) R _e = 5.051 a ₀	B ₂ (³ Σ _g ⁻) R _e = 3.005 a ₀	C ₂ (¹ Σ _g ⁺) R _e = 2.3481 a ₀	N ₂ (¹ Σ _g ⁺) R _e = 2.068 a ₀	O ₂ (³ Σ _g ⁻) R _e = 2.282 a ₀	F ₂ (¹ Σ _g ⁺) R _e = 2.680 a ₀
1σ _g	-0.5969	-2.4523	-7.7040	-11.3598	-15.6820	-20.7296	-26.4289
1σ _u		-2.4520	-7.7032	-11.3575	-15.6783	-20.7286	-26.4286
1s	-0.5	-2.4778	-7.6953	-11.3255	-15.6289	-20.6686	-26.3829
2σ _g		-0.1816	-0.7057	-1.0613	-1.4736	-1.6488	-1.7620
2σ _u			-0.3637	-0.5172	-0.7780	-1.0987	-1.4997
2s		-0.1963	-0.4947	-0.7056	-0.9452	-1.2443	-1.5726
3σ _g					-0.6350	-0.7358	-0.7504
1π _u			-0.3594	-0.4579	-0.6154	-0.7052	-0.8097
1π _g						-0.5319	-0.6682
2p			-0.3099	-0.4333	-0.5677	-0.6319	-0.7300

NOTE: The energies are in units of a_u.

above the energy of the 2s orbital (Figure 1). As we see in Table 1 for the remaining diatomics, B₂ to F₂, the energies of the **two lowest** molecular orbitals are both always **lower** than the corresponding 1s atomic orbital while the remaining orbitals do indeed split as depicted in most textbooks. We show the splitting for the orbitals of N₂ in Figure 2. The difference in the energy of the 1σ_g and 1σ_u orbitals of the first row is small because it depends on the overlap of the in situ atomic orbitals, and these overlaps are very small. The difference between these molecular orbital energies and the corresponding atomic orbital energies, however, is relatively large. Some insight into this behavior may be obtained as follows.

The molecular orbitals and their energy are obtained (9) as solutions of the pseudo eigenvalue problem $\hat{F}\psi_i = \epsilon_i\psi_i$, where \hat{F} is the Fock operator for the molecule, ϵ_i is the en-

ergy of the *i*th MO, ψ_i . In a homonuclear diatomic, ψ_i is one of 1σ_g, 1σ_u, 2σ_g, and so forth, and, because of the high symmetry, may be written exactly as

$$\psi_i = \frac{\varphi_{iA} \pm \varphi_{iB}}{(2 \pm 2S_{iA,iB})^{1/2}}$$

where, φ_{iA} and φ_{iB} are the in situ atomic orbitals on centers A and B, respectively, and $S_{iA,iB} = \langle \varphi_{iA} | \varphi_{iB} \rangle$ is the overlap between them. For the 1σ_g and 1σ_u orbitals, φ_{iA} and φ_{iB} are essentially the 1s_A and 1s_B atomic orbitals, while for the valence MOs these are linear combinations of atomic orbitals that have been polarized, hybridized, and, in general, modified by the variation principle. If the 1σ_g and 1σ_u MOs are essentially linear combinations of unchanged 1s atomic or-

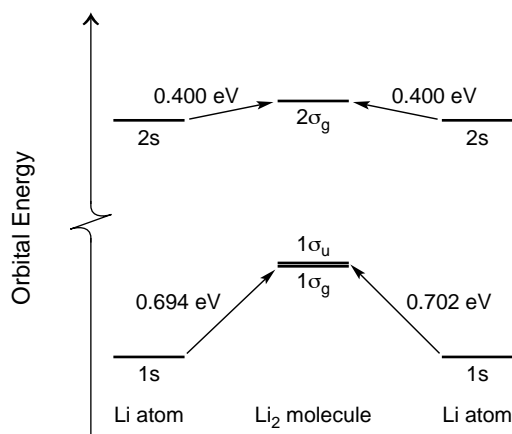


Figure 1. Relative energy of the Li atomic orbitals and the molecular orbitals of Li₂.

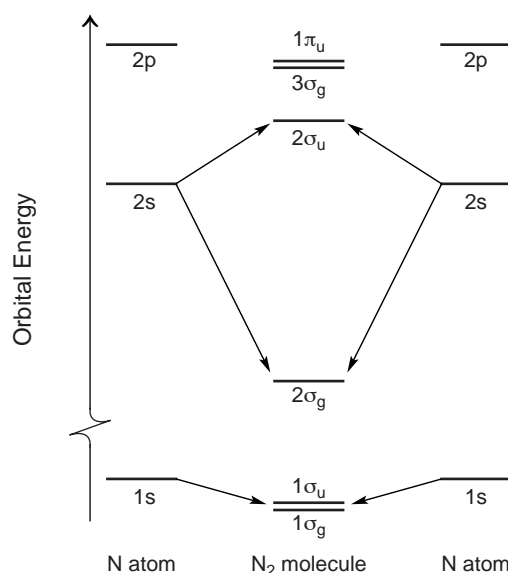


Figure 2. Molecular orbital energy levels of N₂.

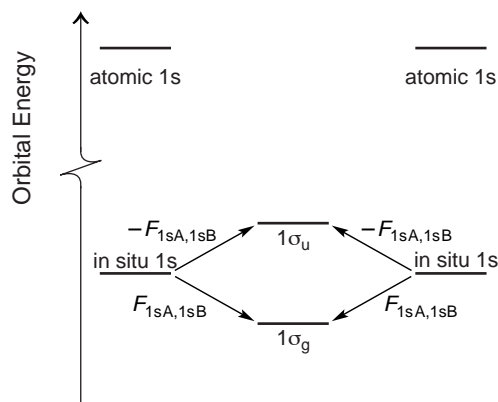


Figure 3. Schematic relationship between the atomic 1s energy levels and the in situ levels about which the 1σ_g and 1σ_u split.

bitals, why are their energies different from the free atom energies? We believe the basic answer is that while the orbitals are essentially the same; their environment is different in the molecule than in the atom. One can rationalize this as follows. Since $\hat{F}\psi_i = \epsilon_i\psi_i$ we may write

$$\epsilon_i = \langle \psi_i | \hat{F} | \psi_i \rangle = \frac{F_{iA,iA} + F_{iB,iB} \pm 2F_{iA,iB}}{2 \pm 2S_{iA,iB}}$$

where $F_{iA,iA} = \langle \varphi_{iA} | \hat{F} | \varphi_{iA} \rangle = e_{iA}$. Because we are dealing with a homonuclear diatomic, $F_{iA,iA} = F_{iB,iB}$, and $e_{iA} = e_{iB} = e_i$, so

$$\epsilon_i = \frac{e_i \pm F_{iA,iB}}{1 \pm S_{iA,iB}}$$

The energies of the $1\sigma_g$ and $1\sigma_u$ orbitals are therefore

$$\epsilon_{1\sigma_g} = \frac{e_{1s} + F_{1sA,1sB}}{1 + S_{1sA,1sB}} \quad \text{and} \quad \epsilon_{1\sigma_u} = \frac{e_{1s} - F_{1sA,1sB}}{1 - S_{1sA,1sB}}$$

where $e_{1s} = \langle 1s_A | \hat{F} | 1s_A \rangle$ and $F_{1sA,1sB} = \langle 1s_A | \hat{F} | 1s_B \rangle$. Since $S_{1sA,1sB} \approx 0$ the above equations become

$$\epsilon_{1\sigma_g} = e_{1s} + F_{1sA,1sB} \quad \text{and} \quad \epsilon_{1\sigma_u} = e_{1s} - F_{1sA,1sB}$$

which show that the energies of the $1\sigma_g$ and $1\sigma_u$ orbitals are above and below e_{1s} . However since \hat{F} is the molecular Fock operator, e_{1s} is an in situ 1s orbital energy and not the free-atom 1s orbital energy. This situation is shown schematically in Figure 3 for the case where the in situ energy e_{1s} is below the free-atom energy. For the special case of the $1\sigma_g$ and $1\sigma_u$ orbitals, where the overlap between the $1s_A$ and $1s_B$ is negligible, we may evaluate e_{1s} and $F_{1sA,1sB}$ as follows. Since

$$1\sigma_g = \frac{1s_A + 1s_B}{\sqrt{2}} \quad \text{and} \quad 1\sigma_u = \frac{1s_A - 1s_B}{\sqrt{2}}$$

we may write

$$1s_A = \frac{1\sigma_g + 1\sigma_u}{\sqrt{2}} \quad \text{and} \quad 1s_B = \frac{1\sigma_g - 1\sigma_u}{\sqrt{2}}$$

and so

$$\begin{aligned} e_{1s} &= \langle 1s_A | \hat{F} | 1s_A \rangle = \left\langle \frac{1\sigma_g + 1\sigma_u}{\sqrt{2}} \left| \hat{F} \right| \frac{1\sigma_g + 1\sigma_u}{\sqrt{2}} \right\rangle \\ &= \frac{\epsilon_{1\sigma_g} + \epsilon_{1\sigma_u}}{2} \end{aligned}$$

and

$$\begin{aligned} F_{1sA,1sB} &= \langle 1s_A | \hat{F} | 1s_B \rangle = \left\langle \frac{1\sigma_g + 1\sigma_u}{\sqrt{2}} \left| \hat{F} \right| \frac{1\sigma_g - 1\sigma_u}{\sqrt{2}} \right\rangle \\ &= \frac{\epsilon_{1\sigma_g} - \epsilon_{1\sigma_u}}{2} \end{aligned}$$

Table 2. Comparison of the Energies of the Free Atom 1s Atomic Orbital and the in situ 1s Atomic Orbital in the Molecule

Molecule	e_{1s}/au	$F_{1sA,1sB}/\text{au}$	$\epsilon_{\text{atomic},1s}/\text{au}$
Li ₂	-2.4522	-0.0002	-2.4778
B ₂	-7.7036	-0.0004	-7.6953
C ₂	-11.3587	-0.0012	-11.3255
N ₂	-15.6802	-0.0019	-15.6289
O ₂	-20.7291	-0.0005	-20.6686
F ₂	-26.4288	-0.0002	-26.3829

We collect the intrinsic 1s energies, e_{1s} and $F_{1sA,1sB}$, along with the atomic 1s energies for the first row diatomics in Table 2. With the above interpretation of the MO energies, Li₂ is the only first-row diatomic whose intrinsic 1s energy is greater than the 1s energy of the free atom. The reason for this is beyond the scope of this article.

These ideas are applicable to the valence MOs as well. Consider, for example, the $2\sigma_g$ and $2\sigma_u$ orbitals. We may write their energies as

$$\epsilon_{2\sigma_g} = \frac{e_{2s} + F_{2sA,2sB}}{1 + S_{2sA,2sB}} \quad \text{and} \quad \epsilon_{2\sigma_u} = \frac{e_{2s} - F_{2sA,2sB}}{1 - S_{2sA,2sB}}$$

or rearranging slightly

$$\epsilon_{2\sigma_g} = e_{2s} + \frac{F_{2sA,2sB} - S_{2sA,2sB} e_{2s}}{1 + S_{2sA,2sB}}$$

and

$$\epsilon_{2\sigma_u} = e_{2s} - \frac{F_{2sA,2sB} - S_{2sA,2sB} e_{2s}}{1 - S_{2sA,2sB}}$$

The quantity $F_{2sA,2sB} - S_{2sA,2sB} e_{2s}$ is negative and so $\epsilon_{2\sigma_g} < e_{2sA}$ and $\epsilon_{2\sigma_u} > e_{2sA}$. Indeed, because of the finite overlap $\epsilon_{2\sigma_u}$ is farther above the in situ e_{2s} energy than $\epsilon_{2\sigma_g}$ is below. If the in situ atomic energies are only slightly different from the free-atom orbital energies then these equations are consistent with the observed splitting of both the valence and core orbitals. It seems to be the zero overlap between the atomic 1s orbitals that keeps the $1\sigma_u$ below the energy of the in situ 1s in the sequence B₂ through F₂.

Note also that in Table 1 there is no energy given for MOs that are not occupied because in ab initio MO theory (9) the energy of an empty orbital corresponds approximately to the energy of an electron in the negative ion and not to an electron in that orbital in the neutral ground state. For homonuclear diatomics these empty orbital energies are positive and bear no direct relation to the occupied orbital energies. The practice of plotting the empty orbital energies as a function of the atomic number of the atom in the diatomic (13) and showing them merge with the occupied orbital energies has meaning in Huckel-like theories where the energy of an orbital is independent of its occupation, but not in ab initio MO theory.

The Dissociation Energy and Bond Length in the Homonuclear Diatomics H₂ through Cl₂

The dissociation energy, D_e , or bond energy in the MO theory is calculated as

$$D_e = 2E_{\text{atoms}} - E(R_e)_{\text{molecule}}$$

where E_{atoms} is the calculated Hartree–Fock energy of the isolated atom and $E(R_e)_{\text{molecule}}$ is the Hartree–Fock or MO energy of the molecule at the calculated equilibrium internuclear separation, R_e . If D_e is positive, the diatomic is stable with respect to dissociation into its constituent atoms and is thermodynamically bound. If D_e is less than zero the molecule is thermodynamically unbound. The calculated (14, 15) and experimental (16) values of D_e are shown in Figure 4 and Table 3. Note that the calculated dissociation energies are often in poor agreement with experimental values and in particular in the MO theory F₂ and Na₂ are both predicted to be unbound and should not exist, while Li₂ is predicted to be marginally stable. Most textbooks do not discuss the direct predictions of MO theory as reflected in Table 3 but focus on the correlation between the bond order and the experimental D_e . How well the theory is doing should be gauged by comparison between the predicted and experimental D_e values, not surrogate quantities like bond orders. Table 3 also compares the predicted bond lengths, R_e , with experimental values and, in contrast to the D_e , these are in reasonable agreement. It is a characteristic of MO theory for

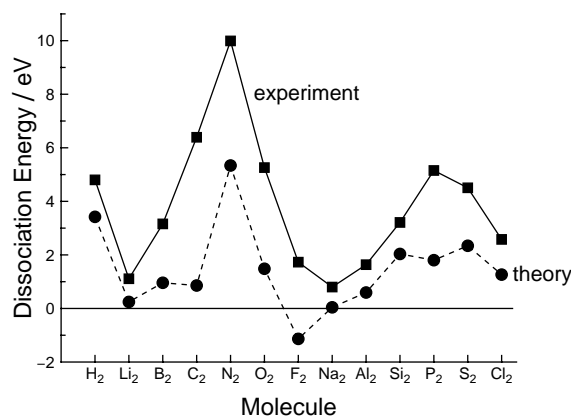


Figure 4. Comparison of MO-predicted dissociation energies with experimental values.

molecules composed of main-group elements that geometric parameters such as bond lengths and bond angles are predicted more accurately (8) than energetic quantities like bond energies or ionization potentials. It is especially interesting that the computed bond length of F₂ is reasonable while the computed bond energy is poor. It turns out that correlation between the lone pairs in the π system of F₂ is crucial to obtaining the correct bond energy but not the correct bond length (17).

Table 3. Comparison of the MO-Predicted (Hartree–Fock) Bond Length and Dissociation Energy with Experimental Values

Molecule	Configuration	State	Bond Length/ a_0		Dissociation Energy/eV	
			H–F	Exp	H–F	Exp
H ₂	1 σ_g^2	1 Σ_g^+	1.390	1.401	3.364	4.751
Li ₂	(He)2 σ_g^2	1 Σ_g^+	5.260	5.051	0.170	1.068
B ₂	(He)2 σ_g^2 2 σ_u^2 1 π_u^2	3 Σ_g^-	3.092	3.005	0.910	3.09
C ₂	(He ₂)2 σ_g^2 2 σ_u^2 1 π_u^4	1 Σ_g^+	2.341	2.348	0.788	6.32
C ₂	(He ₂)2 σ_g^2 2 σ_u^2 3 σ_g^2 1 π_u^2	3 Σ_g^-	2.526	2.588	3.791	5.52
N ₂	(He ₂)2 σ_g^2 2 σ_u^2 3 σ_g^2 1 π_u^4	1 Σ_g^+	2.013	2.074	5.280	9.906
O ₂	(He ₂)2 σ_g^2 2 σ_u^2 3 σ_g^2 1 π_u^4 1 π_g^2	3 Σ_g^-	2.175	2.282	1.410	5.214
F ₂	(He ₂)2 σ_g^2 2 σ_u^2 3 σ_g^2 1 π_u^4 1 π_g^4	1 Σ_g^+	2.509	2.668	-1.190	1.659
Na ₂	(Ne ₂)4 σ_g^2	1 Σ_g^+	6.043	5.818	-0.020	0.730
Al ₂	(Ne ₂)4 σ_g^2 4 σ_u^2 2 π_u^2	3 Σ_g^-	4.800	4.660	0.530	1.570
Si ₂	(Ne ₂)4 σ_g^2 4 σ_u^2 5 σ_g^2 2 π_u^2	3 Σ_g^-	4.188	4.244	1.970	3.15
P ₂	(Ne ₂)4 σ_g^2 4 σ_u^2 5 σ_g^2 2 π_u^4	1 Σ_g^+	3.496	3.578	1.720	5.081
S ₂	(Ne ₂)4 σ_g^2 4 σ_u^2 5 σ_g^2 2 π_u^4 2 π_g^2	3 Σ_g^-	3.513	3.570	2.270	4.414
Cl ₂	(Ne ₂)4 σ_g^2 4 σ_u^2 5 σ_g^2 2 π_u^4 2 π_g^4	1 Σ_g^+	3.732	3.757	1.230	2.514

Wrong MO Prediction of the C₂ Molecule Ground State

MO theory predicts the wrong ground state for the C₂ molecule. Experimentally C₂ has a ${}^1\Sigma_g^+$ ground state corresponding to the electron configuration (18)

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$$

that, according to MO theory, has the energy -75.40602 au (11). However, in MO theory, the ${}^3\Sigma_g^-$, Δ_g , and ${}^1\Sigma_g^+$ states, derived from the configuration

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2$$

have the energies -75.51522, -75.47665, and -75.43850 au (11), all three being lower than the configuration corresponding to the experimental ground state. While much significance is made of the prediction that O₂ has a triplet ground state, this flawed prediction about C₂ is rarely mentioned. This error is due to the omission of electron correlation in MO theory and is easily traced to the concept of near degeneracy (19).

The concept of near degeneracy is best approached from an atomic perspective. Basically, it is recognition that the description of an atom in terms of one electron configuration is an approximation that is better for some atoms than for others. In the carbon atom, for example, while the electronic configuration $1s^2 2s^2 2p^2$ (where two different p orbitals are occupied) is dominant in the ground 3P state, the inclusion of the configuration $1s^2 2p^4$ (where we excite the 2s pair into the empty p orbital) is important for a quantitative description of the atom. This comes about because the 2s and 2p orbitals are nearly degenerate. Exciting the 2s pair into a 2p pair does not require excessive energy and results in a more accurate description of the atom. If one goes to the next atom in the table, N with the electronic configuration $1s^2 2s^2 2p^3$ (where all p orbitals are singly occupied) we cannot excite the N 2s pair into a p orbital because they are all occupied with one electron. If however we went back in the table to Be with the electron configuration $1s^2 2s^2$ we have three empty 2p orbitals that can be excited into. The resulting wavefunction would be a mixture of the aufbau configuration $1s^2 2s^2$ as well as the three near degeneracy configurations, $1s^2 2p_x^2$, $1s^2 2p_y^2$, and $1s^2 2p_z^2$. Clearly for B we have two empty p orbitals to accommodate the 2s pair. So, as one goes across the first row of the periodic table, the near degeneracy effect is not important for Li since we have a single 2s electron (and exciting it into a 2p orbital changes the electronic symmetry), it is important for Be, B, and C and not important for the remaining first row atoms. This concept applies to C₂ in the following way. The electron configuration associated with the $X^1\Sigma_g^+$ state of C₂ is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$$

where the $2\sigma_g$ orbital is formally

$$\frac{2s_A + 2s_B}{\sqrt{2 + 2S_{2s_A, 2s_B}}}$$

The empty $3\sigma_g$ orbital is formally the bonding combination of the carbon $2p_z$ orbitals, or

$$\frac{2p_{\sigma A} + 2p_{\sigma B}}{\sqrt{2 + 2S_{2p_{\sigma A}, 2p_{\sigma B}}}}$$

and therefore exciting from the $2\sigma_g$ to the $3\sigma_g$ is a near degeneracy excitation (2s to 2p). When this is done (20) the resulting orbital occupations are

$$1\sigma_g^2 1\sigma_u^2 (2\sigma_g^{1.575} + 3\sigma_g^{0.425}) 2\sigma_u^2 1\pi_u^4$$

showing that the single configuration for C₂ is a very poor approximation.

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