Why the Lower-Energy Term of Singlet Dioxygen Has a Doubly Occupied $\pi^*$ Orbital

Terry S. Carlton
Department of Chemistry, Oberlin College, Oberlin, OH 44074; terry.carlton@oberlin.edu

Introductory treatments of molecular orbitals draw special attention to the ground state of dioxygen, which is unusual in being a triplet state and hence paramagnetic. Those treatments explain these properties in terms of the numbers and spins of electrons in two degenerate orbitals. Dioxygen’s first two excited states, known collectively as singlet oxygen, also deserve special pedagogical attention (though probably not until an inorganic or physical chemistry course). The relative energies of these two spin-paired singlet terms are surprising: the term with a pair of singly occupied degenerate orbitals is higher in energy than the term in which one of those orbitals is doubly occupied and the other is vacant.

Ground states (both atomic and molecular) behave quite differently: electrons occupy singly as many degenerate orbitals as possible. One might erroneously conclude that a pair of electrons always have lower energy in separate degenerate orbitals than when they are in the same orbital. Brief consideration of the three lowest terms of dioxygen can show students that the actual cause of the ground-state pattern is the energy advantage of groups of electrons with the same spin.

This article will present a simple physical explanation for the relative energies of the lowest two singlet terms of O$_2$. The explanation invokes $\pi_+$ and $\pi_-$ molecular orbitals, which are eigenfunctions of orbital angular momentum about the molecular axis.

$$\pi_+ = \frac{1}{\sqrt{2}} \left( \pi_x + i\pi_y \right); \quad \pi_- = \frac{1}{\sqrt{2}} \left( \pi_x - i\pi_y \right)$$

Though $\pi_+$ and $\pi_-$ orbitals are much more commonly used than $\pi_+^*$ and $\pi_-^*$ orbitals in discussions of diatomic molecules, the former are inappropriate for situations (such as the present one) in which orbital angular momentum is under consideration. Fortunately, we may ignore the fact that $\pi_+$ and $\pi_-$ wave functions involve complex numbers, since the present explanation will depend only on their probability densities, which are real.

Background

Singlet oxygen, which can be formed chemically or by photosensitization, is highly reactive. It causes desirable and undesirable biological damage (1) and has applications in synthesis and photodynamic therapy (2). It is a mixture of two electronic states, the $1\Sigma$ and $1\Lambda$ terms. The latter term is regarded as the more important reactant because of its longer lifetime.

Dioxygen’s first two excited electronic states and its ground state all have the electronic configuration [Be$_2$] $3\alpha^2 \pi^2 1\pi^1 \sigma^2$. The electronic structures of these three states differ in the occupancies of the two antibonding $1\pi^\pi$ orbitals (referred to subsequently as $\pi^*$ orbitals) and in the relative spins of the two electrons in this pair of orbitals (Figure 1). The electronic energies of the $1\Sigma$ term and the $1\Lambda$ term are 158 and 95 kJ/mol higher respectively than that of the $1\Sigma$ ground-state term (3).

Because oxygen is a linear molecule, the component of orbital angular momentum about the molecular axis (the $z$ axis) is quantized. The quantum number $\Lambda$ is the absolute value of this $z$ component in units of $\hbar$. In the three terms under consideration, orbitals other than $\pi^*$ make a net contribution of zero to $\Lambda$. The two $\pi^*$ orbitals are $\pi^*_+$ and $\pi^*_-$, where the subscript indicates whether each electron in that orbital has an orbital angular momentum of $\hbar$ or $-\hbar$. Thus the $1\Lambda$ term, for which $\Lambda$ is 2 (hence the $\Lambda$), has both electrons in the same $\pi^*$ orbital (either $\pi^*_+$ or $\pi^*_-$), whereas $\Lambda$ is zero in the $1\Sigma$ term (and in the $1\Sigma$ term) because the orbital angular momentum of the $\pi^*$ electron cancels that of the $\pi^*$ electron.

The probability densities of the $\pi^*_+$ and $\pi^*_-$ orbitals are figures of revolution about the $z$ axis (4–6). These two probability–density functions are identical, whereas $\pi^*_+$ and $\pi^*_-$ orbitals are rotated from each other by 90° about the $x$ axis. (The sign of angular momentum is unspecified for $\pi^*_+$ and $\pi^*_-$ orbitals, making them unsuitable for describing singlet or triplet oxygen.)

Explanation

Two $\pi^*$ electrons of O$_2$ do not avoid each other any better merely by being in different $\pi^*$ orbitals instead of the same one. Because the $\pi^*_+$ and $\pi^*_-$ orbitals have identical one-electron probability-density distributions in space, the energy of electrostatic repulsion between one electron’s charge distribution and that of the other is unaffected by whether the two electrons are in the same $\pi^*$ orbital or different ones.

Yet the $1\Lambda$ term, in which both $\pi^*$ electrons occupy the same orbital, is more stable than the $1\Sigma$ term, in which one electron occupies the $\pi^*_+$ orbital and the other occupies the

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**Figure 1.** Occupancy of $\pi^*$ orbitals in the three lowest-energy terms of O$_2$. 

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Contrast with Ground States

In the aufbau of atomic or molecular ground states, double occupancy of an orbital in a degenerate set occurs only when unavoidable. Why does single occupancy have priority? Not because electrons in different orbitals must occupy different regions of space. Degenerate pairs of atomic orbitals with opposite values of \( l_z \) have identical probability-density distributions, like the \( \pi^* \) and \( \pi \), orbitals of dioxygen.

Instead, only by occupying different orbitals can two electrons have the same spin, and electrons with the same spin are never at the same position and rarely in close proximity (on the atomic scale). This strong avoidance is a consequence of the Pauli principle, which guarantees that under exchange of spatial coordinates for any pair of electrons with the same spin, the wave function is antisymmetric and hence tends toward zero as the electrons approach each other. This strong avoidance by electrons with unpaired spins enables orbitals to shift toward the nucleus (compared to the same orbitals when the corresponding electrons have paired spins), thereby lowering both the electron–nuclear energy and the total energy (7).

Thus the ground state of dioxygen is the \( ^3\Sigma^+ \) term not because of but in spite of the fact that its two \( \pi^* \) electrons occupy different orbitals. Energy lowering due to high spin more than offsets the energy cost of having the \( \pi^* \) electrons in orbitals with opposite orbital angular momenta. In contrast, because the \( \pi^* \) electrons of singlet terms are paired, they are not restricted to different orbitals, nor does antisymmetry prevent their close approach. Only relative orbital angular momentum causes the \( ^1\Delta \) term to be lower in energy than the \( ^1\Sigma^+ \).

Pedagogical Considerations

I suggest beginning with a quick review of the molecular orbitals that are occupied in the ground state of dioxygen. As the last step of this review, write on the board two horizontal lines representing the degenerate \( 2p\pi^* \) orbitals, and ask the class to specify their occupancy and the spin of each electron. After obtaining the correct answer, write the remaining two diagrams (unlabeled) from Figure 1, but beside, not above, the first one. Then label each diagram with the word singlet or triplet, possibly with advice from the class.

State that the two singlet states are the first two excited states of dioxygen. Ask the students to predict which of the two is lower in energy. I suspect that they will be surprised by the correct answer and that this surprise will enhance their interest in your explanation based on angular momentum and Figure 2. You can then explain the term symbols (omitting \( +, –, \text{and } g \)) in a diagram like Figure 1.

Point out that for atomic and molecular configurations, the energy effect of spin is typically greater than that of orbital angular momentum. This is why the ground term has the largest spin compatible with the ground configuration, even though other terms may have larger angular momenta. Statement of Hund’s spin rule follows naturally, as would an explanation of its basis in the Pauli principle.

Kauzmann (9) and Atkins and Friedman (10) have used an angular-momentum rationale like the present one to justify Hund’s angular-momentum rule for atoms. This rule states that for a given configuration consisting of closed shells plus degenerate electrons, the lowest-energy term from among those with the largest spin is the one with the largest angular-momentum quantum number \( L \) (8).

Nevertheless, it is not feasible to extend to atoms the classroom presentation of the angular-momentum rationale. Many atomic orbital diagrams do not represent eigenfunctions of \( L^2 \) and hence may not be labeled with a value of \( L \). Any atomic configuration for which Hund’s angular-momentum rule is relevant has so few orbital diagrams with well-defined \( L \) that one cannot use them persuasively to justify the angular-momentum rationale.
An Alternative Treatment of Angular Correlation

Hückel (11), recapitulated by Kasha and Brabham (5), also uses angular correlation about the z axis to explain relative energies of the \(1\Sigma\) and \(1\Delta\) and even the \(3\Sigma\) terms. Hückel compares for these terms the probability density’s explicit dependence on angles \(\phi_1\) and \(\phi_2\), where 1 and 2 refer to the \(\pi^*\) electrons. Each term’s probability density includes the same function of \(r_1\), \(r_2\), \(z_1\), and \(z_2\). After removing this common factor, the normalized angular probability densities are

\[
\left(\frac{1}{2\pi^2}\right)\cos^2(\phi_1 - \phi_2) \text{ for } 1\Sigma^+
\]

\[
\left(\frac{1}{4\pi^2}\right) \text{ for } 1\Delta_g
\]

\[
\left(\frac{1}{2\pi^2}\right)\sin^2(\phi_1 - \phi_2) \text{ for } 3\Sigma^-
\]

The \(1\Delta\) probability density is independent of \(\phi_1\) and \(\phi_2\). The \(1\Sigma\) density is much higher than the \(1\Delta\) when the two electrons are approximately 0° or 180° from one another, but much lower than the \(1\Delta\) at approximately ±90°. Because the interelectronic potential \(\varepsilon/r_{12}\) is highly nonlinear, densities at small angles dominate the repulsion energy. Therefore the energy of the \(1\Sigma\) term is higher than that of the \(1\Delta\) term. However, the \(\sin^2(\phi_1 - \phi_2)\) behavior of \(3\Sigma\) strongly depletes the density for small values of \(\phi_1 - \phi_2\), causing the \(3\Sigma\) energy to be lower than the \(1\Delta\). Indeed, Hückel proves that to first order in energy (with \(\varepsilon/r_{12}\) as the energy perturbation), the \(1\Delta\) energy is midway between the \(1\Sigma\) and \(3\Sigma\) energies.

Both the Hückel explanation and the present one based on Figure 2 attribute the higher energy of the \(1\Sigma\) term to the increased likelihood (compared to \(1\Delta\)) that both electrons are near the same angle. The present explanation has two advantages. It can be presented quickly to students who have minimal acquaintance with wave functions. Secondly, the physical principal on which it is based—cancellation of two electrons’ orbital angular momenta—applies just as well to the exact wave function as to the orbital approximation on which the Hückel explanation depends.

Notes

1. The reader might object that the orbital diagram labeled \(1\Sigma^+\) in Figure 1 could belong to either a singlet or a triplet term (12). This is because it is compatible with either of these two (unnormalized) wave functions:

\[
(\pi_+\pi_- + \pi_-\pi_+)(\alpha\beta - \beta\alpha)
\]

\[
(\pi_+\pi_- - \pi_-\pi_+)(\alpha\beta + \beta\alpha)
\]

However, this consideration is unlikely to occur to students in the present context. This orbital diagram is the natural one for representing an oxygen molecule in which two electrons with paired spins occupy singly both \(\pi^*\) orbitals. Indeed, this is the only orbital diagram for the \(1\Sigma^+\) term that I have found in published discussions of singlet oxygen.

Literature Cited