

Electronic structure considerations for C₂ and O₂

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CONTENTS

I. Preface	1
II. Electronic Hamiltonian	2
III. Molecular Orbitals: C ₂	4
IV. Electronic States: $\sigma^2\pi^2$ electron occupancy	6
A. $^3\Sigma_g^-$ state	6
B. $^1\Sigma_g^+$ state	8
C. $^1\Delta_g$ state	9
V. Electronic States: $\sigma^1\pi^3$ electron occupancy	10
A. Energy ordering	11
B. Molecular potential curves	11
VI. Molecular oxygen	12
VII. “Missing” rotational levels	14

I. PREFACE

This is a little discussion of the electronic structure of a “simple” diatomic molecule, C₂. As you will see it’s hardly simple. The richness of chemistry lies in its complexity. As a physicist, you’ll probably throw up your hands in disgust, finding this complexity too impure.

Unexpectedly, O₂, although possessing more electrons, is actually simpler, from the viewpoint of molecular electronic structure.

Because both O and C have zero spin, the diatomic molecules are bosons. This prohibits either even (in the case of O₂) or odd (in the case of C₂) rotational levels.

II. ELECTRONIC HAMILTONIAN

Within the Born-Oppenheimer approximation, the N nuclei are assumed to be fixed positive charges. The Hamiltonian for the motion of the M electrons in the field of these fixed positive charges is

$$\hat{H}_{el}(q_1, \dots, q_M; \vec{R}) = -\frac{1}{2} \sum_{i=1}^M \nabla_i^2 - \sum_{n=1}^N \sum_{i=1}^M \frac{Z_n}{R_{ni}} + \sum_i \sum_j \frac{1}{r_{ij}} \quad (1)$$

Here we are assuming atomic units ($e = \hbar = m_e = 1$), q_i designates the coordinates of the electrons, R_{ni} is the relative position of electron i and nucleus n , and r_{ij} is the distance between electrons i and j . Note that the Hamiltonian is implicitly a function of the position of the fixed nuclei, which we designate by the single coordinate \vec{R} . This Hamiltonian can be simplified as a sum of one- and two-electron operators as follows

$$\hat{H}_{el}(q_1, \dots, q_M) = \sum_{i=1}^M \hat{h}(q_i) + \sum_{i=1}^M \sum_{j=1}^M \frac{1}{r_{ij}}$$

where the definition of the one-electron operators is the kinetic energy operator for the electron plus its electrostatic attraction with all nuclei.

The eigenfunctions of the electronic Hamiltonian of Eq. (1)

$$\hat{H}_{el}(q_1, \dots, q_M; \vec{R}) \Phi_{el}^{(k)}(q_1, \dots, q_M; \vec{R}) = \mathcal{E}_{el}^{(k)}(\vec{R}) \Phi_{el}^{(k)}(q_1, \dots, q_M; \vec{R})$$

are implicitly functions of the positions of the nuclei. Note that, just as in the atomic limit, there are more than one electronic eigenfunctions, which we designate by the index k . These are the electronic states of the molecule.

It is, of course, impossible to solve exactly this multidimensional Schrodinger equation. Chemists approximate the wavefunction for these electronic states as an antisymmetrized product of one-electron functions (which chemists call molecular orbitals). These are expressed as linear combinations of “atomic orbitals”, which are one-electron functions local-

ized on the individual nuclei. This comprises the so-called MO-LCAO (molecular orbital – linear combination of atomic orbitals). This wavefunction is a Slater determinant built of so-called spin-orbitals ϕ_i which are products of spatial functions multiplied by a dependence on the spin of the electron $\sigma \equiv |s = \frac{1}{2}, m_s = \pm \frac{1}{2}\rangle$.

$$\Phi_{el}(q_1, \dots, q_M; \sigma_1, \dots, \sigma_M) = |\phi_1, \dots, \phi_M|$$

Where the vertical bars indicate the determinant. Here, for simplicity, we have dropped the state index k .

If the one-electron orbitals are normalized, then so is Φ_{el} , provided we assume that the determinant is multiplied by $M!^{-1/2}$.

Chemists then use the variational principle to obtain approximate values of the electronic energies $\mathcal{E}_{el}^{(k)}(\vec{R})$.

You can show the expectation value of the electronic Hamiltonian for a determinantal wavefunction is

$$\langle \Phi_{el} | \hat{H}_{el} | \Phi_{el} \rangle = \sum_{i=1}^M \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{i=1}^{M-1} \sum_{j=i+1}^M [\phi_i^2 | \phi_j^2] - \sum_{i=1}^{M-1} \sum_{j=i+1}^M \delta_{\sigma_i, \sigma_j} [\phi_i \phi_j | \phi_j \phi_i] \quad (2)$$

here

$$[\phi_i^2 | \phi_j^2] = \int \int |\phi_i(q_1)|^2 \frac{1}{r_{12}} |\phi_j(q_2)|^2 dq_1 dq_2$$

and

$$[\phi_i \phi_j | \phi_j \phi_i] = \int dq_1 \int dq_2 \phi_i^*(q_1) \phi_j(q_2) \frac{1}{r_{12}} \phi_j^*(q_1) \phi_i(q_2) dq_1 dq_2$$

The first term $\langle \phi_i | \hat{h} | \phi_i \rangle$ is the one-electron energy (kinetic plus attraction to the nuclei) of each one-electron orbital. The second term is the Coulomb repulsion between all pairs of electrons. The third term is a purely quantum term, arising from the antisymmetry of the fermion wavefunction. This is a so-called exchange term, the self repulsion of the overlap between all pairs of orbitals which have the same spin.

III. MOLECULAR ORBITALS: C_2

The one-electron functions can be taken to be eigenfunctions of any operator which commutes with the Hamiltonian, in particular the spatial symmetry point group of the molecule. For a linear molecule with inversion symmetry, these are labelled σ , π corresponding to the projection of the electronic angular momentum around the bond axis (\hat{l}_z) as well as g and u , which are the even and odd eigenfunctions of the inversion operator. The π orbitals are labelled π_λ where $\lambda = m_l = \pm 1$.

Typically each orbital is expanded in terms of a linear sum of exponential (or Gaussian) functions centered at each atom, multiplied by $\exp(\pm i\lambda\phi)$, where ϕ is the azimuthal angle around the bond axis. As mentioned above, chemists obtain the expansion coefficients by application of the variational principle. The coefficients are the iterated (self-consistent) solutions of the so-called Hartree-Fock equations, which minimize the energy of each orbital (kinetic plus attraction to the nuclei) and the average energy of interaction with all the $M - 1$ other electrons. Nowadays these calculations are very fast, taking advantage of an enormous number of man hours of development work on so-called “quantum chemistry” codes. A very good calculation on C_2 takes less than 10 s on a Macbook pro.

The lowest energy orbitals correspond to linear combinations of the $1s$ orbitals on each C atom. The lowest is nodeless, and hence is symmetric with respect to inversion. This is called the $1\sigma_g$ orbital. The next is the $1\sigma_u$ orbital.



FIG. 1. The $1\sigma_g$ (left panel) and $1\sigma_u$ (right panel) molecular orbitals of C_2

The next two molecular orbitals ($2\sigma_g$ and $2\sigma_u$) corresponds to the symmetric and, respectively, antisymmetric linear combinations of the $2s$ orbitals on each C atom. Note that the $2\sigma_u$ orbital also contains a substantial contribution from the $2p_z$ ($l = 0$) orbitals (the $2p$ atomic orbitals lying along the C–C bond).

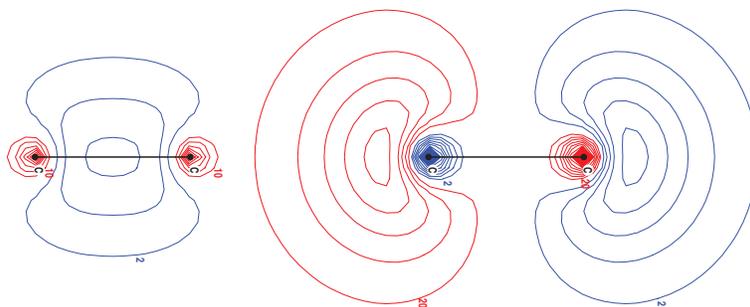


FIG. 2. The $2\sigma_g$ (left panel) and $2\sigma_u$ (right panel) molecular orbitals of C_2

The third (in terms of increasing energy) orbital of σ_g symmetry is shown below. This is also a linear combination of the $2s$ and $2p_z$ orbitals. There is a substantial buildup of electron density between the nuclei. It is this orbital that is partially responsible for the bonding between the two C atoms. Because this orbital is cylindrically symmetric, the bond so formed is called a “sigma” bond.

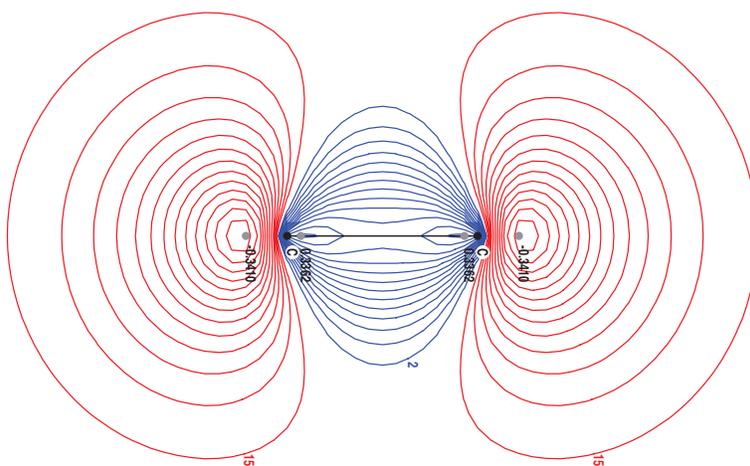


FIG. 3. The $3\sigma_g$ molecular orbital of C_2

Linear combinations of the $2p$ orbitals of the C with $m_l = \pm 1$ give rise to the so-called π molecular orbitals (nonzero m_l). The lowest is designated the 1π orbital, illustrated below. Note that this orbital is antisymmetric with respect to inversion, hence designated “u”. Here too there is a buildup of electron density between the nuclei. Thus this orbital is called a “bonding” orbital.

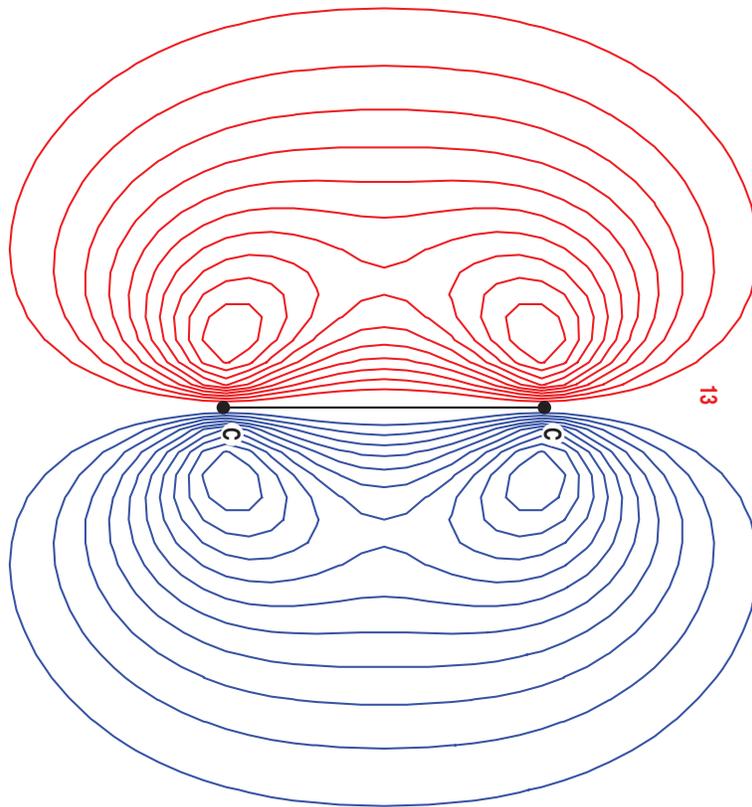


FIG. 4. The $1\pi_{ux}$ molecular orbital of C_2 . There is an equivalent degenerate molecular orbital in the yz plane.

IV. ELECTRONIC STATES: $\sigma^2\pi^2$ ELECTRON OCCUPANCY

The C_2 molecule has 12 electrons. They are assigned (in pairs, with opposite values of m_s) to the energetically lowest orbitals. 10 electrons are accounted for, then, by the three σ_g orbitals and the two σ_u orbitals depicted in Figs. 1–3. The $3\sigma_g$ orbital lies only slightly lower in energy than the $1\pi_u$ orbital. This ordering changes (a) as a function of bond length and, (b) as a function of the total charge (neutral molecule vs. positive or negative ion). This leads to considerable complexity in the assignment of the electronic spectrum of the first- and second-row diatomic molecules.

A. ${}^3\Sigma_g^-$ state

The possible electronic states of the C_2 molecule correspond to the different assignments of the 12 electrons. The assignment of the previous paragraph is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^3 1\pi_u^2$. Because of the degeneracy of the $1\pi_u$ orbital, different electronic states are possible. If we

use the definite m ($\pi_{\pm 1}$) orbitals, then one possibility is $1\pi_1 1\pi_{-1}$ both with $m_s = +1/2$. Ignoring the first 10 electrons, which are spin-paired and in orbitals with $m_l = 0$, then the electronic wavefunction for this state can be written as

$$|M_L = 0 M_S = 1\rangle = 2^{-1/2} |\pi_1 \pi_{-1}| \quad (3)$$

The left-hand ket indicates the projection of the total electronic angular momentum (which is a good quantum number) as well as the projection of the total spin (also a good quantum number). The right-hand side is the Slater determinantal representation in terms of single-particle orbitals

$$|M_L = 0, M_S = 1\rangle = 2^{-1/2} [1\pi_1(1)1\pi_{-1}(2) - 1\pi_1(2)1\pi_{-1}(1)] \times 2^{-1/2} |m_s(1) = 1/2, m_s(2) = -1/2\rangle \quad (4)$$

The spin wavefunction (the second term on the right) can be combined in a simple way by defining “spin-orbitals”

$$\pi_{\pm 1} \equiv 1\pi_{\pm 1}(1)|m_s = 1/2\rangle$$

and

$$\bar{\pi}_{\pm 1} \equiv 1\pi_{\pm 1}(1)|m_s = -1/2\rangle$$

The superscript bar denotes $m_s = -1/2$.

This compact notation is used in defining the electronic wavefunction for the two π electrons contained in Eq. (3). This is a state then with $M_L = 0$ and $M_S = 1$. Since $M_S = 1$, S (which is a good quantum number) has to be 1. The spin degeneracy of this state is then 3, a triplet. The two other components are obtained by operating with the lowering operator $\hat{S}_- = \hat{s}_{1-} + \hat{s}_{2-}$ on the state of Eq. (3). The projection of the orbital electronic angular momentum ($M_L = 0$) doesn't change with application of \hat{S}_- . Thus the three M_S components of this triplet state all have $M_L = 0$. Just as orbitals with $m_l = 0$ are designated σ orbitals, so electronic states with $M_L = 0$ are designated Σ states. Thus, one of the possible $1\pi_u^2$ states of C_2 corresponds to a so-called ${}^3\Sigma$ state (the multiplicity precedes as a superscript).

Now, the overall M -electron wavefunction must also be symmetric or antisymmetric with respect to inversion (of the coordinates of all the electrons). The electronic configuration is

a product of two π_u orbitals, each of which is antisymmetric. Thus the total wavefunction is symmetric. Hence, the electronic state is designated “g”, or ${}^3\Sigma_g$.

There is one more symmetry which must be considered: Reflection in a plane containing the molecular axis. Without loss of generality, we can take this to be the xz plane (remember, the bond axis defines the z axis). Since $\hat{\sigma}_{xz}Y_{1,\pm 1}(\theta, \phi) = -Y_{1,\mp 1}(\theta, \phi)$ (where Y_{lm} is a spherical harmonic), operating on the determinantal wavefunction of Eq. (4) with $\hat{\sigma}_{xz} = \hat{\sigma}_{xz}(1)\hat{\sigma}_{xz}(2)$, reverses the order of the columns in the determinant and hence changes the sign of the determinant. Thus, the ${}^3\Sigma_g$ state will be *antisymmetric* with respect to reflection in the xz -plane (and, you can show, with respect to reflection in any plane containing the z axis). This is added to the state notation as a superscript minus, namely ${}^3\Sigma_g^-$. This designator is called by molecular spectroscopists the *term symbol*.

Since the complex definite- m spherical harmonics can be converted, by a 2×2 rotation, to real Cartesian functions, you can write equivalent real representations of the ${}^3\Sigma_g^-$ electronic states in terms of the π_x (depicted in Fig. 3) and the π_y orbitals. We have

$$|{}^3xy, M_S = 1\rangle = |\pi_x\pi_y| \quad (5)$$

The two other components of the triplet can be obtained, as before, by use of the \hat{S}_- lowering operator.

The Cartesian representation of Eq. (5) reveals clearly the antisymmetry with respect to reflection, since

$$\hat{\sigma}_{xz}\pi_x = -\pi_x$$

and

$$\hat{\sigma}_{xz}\pi_y = +\pi_y$$

B. ${}^1\Sigma_g^+$ state

The component of the triplet state with $M_S = 0$ is, in determinantal notation,

$$|M_L = 0, M_S = 0\rangle = \hat{S}_-|\pi_1\pi_{-1}\rangle = 2^{-1/2} [|\bar{\pi}_1\pi_{-1}\rangle + |\pi_1\bar{\pi}_{-1}\rangle]$$

There is a state which is orthogonal to this one (corresponding to the singleton $S = 0$, $M_S = 0$ Clebsch-Gordan coupled state), namely (to within an overall phase factor, of course)

$$2^{-1/2} [|\bar{\pi}_1\pi_{-1}| - |\pi_1\bar{\pi}_{-1}|]$$

This determinant still corresponds to a Σ state, since $M_L = 0$, but is a singlet state ($S = 0$). It is still symmetric with respect to inversion, thus “g”. Also, because the relative sign of the two determinants is changed, you can show that the wavefunction is now symmetric with respect to reflection, in the xz or yz planes. Thus, the overall term symbol for the singlet state is ${}^1\Sigma_g^+$. You can show that the Cartesian representation is

$$|{}^1\Sigma_g^+\rangle = 2^{-1/2} [|\pi_x\bar{\pi}_x| + |\pi_y\bar{\pi}_y|]$$

C. ${}^1\Delta_g$ state

There is yet another way of assigning the two π electrons, namely

$$|M_L = 2, M_S = 0\rangle = |\pi_1\bar{\pi}_1|$$

This is a singlet-state, but with $M_L = 2$. There is an equivalent state with $M_L = -2$, namely

$$|M_L = -2, M_S = 0\rangle = |\pi_{-1}\bar{\pi}_{-1}|$$

Note that there are components of this state only for $M_L = \pm 2$. This is consistent with the fact that L is not a good quantum number for a system of cylindrical symmetry.

Just as Σ designates a state with $M_L = 0$, so Δ designates a state with $M_L = \pm 2$. The term symbol then for the C_2 state arising from a $1\pi^2$ electronic configuration with $M_L = \pm 2$ is then ${}^1\Delta_g$ (no “+” and “-” reflection symmetry label!).

You can show that

$$\hat{\sigma}_{xy} |M_L = 2, M_S = 0\rangle = |M_L = -2, M_S = 0\rangle$$

As you might anticipate the $M_L = \pm 2$ states, which are eigenfunctions of rotation around the z axis, are not eigenfunctions of reflection (since rotation and reflection don’t in general

commute). However, you can take positive and negative linear combinations of the $M_L = \pm 2$ functions to form eigenfunctions of reflection. In general for $M_L \geq 1$, the positive and negative linear combinations are symmetric and antisymmetry eigenfunctions of reflection. Since both are possible, the term symbols for the states with $M_L > 0$ are not labelled with the “+” and “-” reflection symmetry.

The Cartesian representation of the ${}^1\Delta$ states is, for the state of positive reflection symmetry,

$$|{}^1\Delta_{x^2-y^2}\rangle = 2^{-1/2} [|\pi_x\bar{\pi}_x| - |\pi_y\bar{\pi}_y|]$$

and, for the state of negative reflection symmetry,

$$|{}^1\Delta_{xy}\rangle = 2^{-1/2} [|\pi_x\bar{\pi}_y| - |\bar{\pi}_x\pi_y|]$$

The minus sign of the second determinant implies that this state is orthogonal to the $M_S = 0$ component of the ${}^3\Sigma$ state, namely

$$|{}^3\Sigma(M_S = 0)\rangle = 2^{-1/2} [|\pi_x\bar{\pi}_y| + |\bar{\pi}_x\pi_y|]$$

V. ELECTRONIC STATES: $\sigma^1\pi^3$ ELECTRON OCCUPANCY

Since both the $3\sigma_g$ and the ${}^1\pi_u$ orbitals are bonding (with a buildup of electron density between the nuclei), another possible electron occupancy for C_2 is $3\sigma_g^1\pi_u^3$. This is a degenerate state, with the π orbital triply filled: either two electrons in π_1 and one in π_{-1} or vice versa. The total projection of the orbital angular momentum M_L can be either +1 or -1. Thus, the electronic state is a Π_u state, u because there are an odd number of electrons in an orbital of antisymmetric inversion symmetry.

The third π electron can be either singlet- or triplet-coupled with the singleton electron in the $3\sigma_g$ orbital. The net result is that a $\sigma^1\pi^3$ electron occupancy for C_2 will give rise to both ${}^3\Pi_u$ and ${}^1\Pi_u$ electronic states.

A. Energy ordering

The exchange terms in Eq. (2) lead to a lowering in energy for states with higher multiplicity. Thus, we would expect the $^3\Sigma^-$ state of C_2 to have the lowest energy. Considerations based on the size of the Coulomb repulsion — we expect the repulsion between two electrons in the same Cartesian π orbital to be greater than between one electron in the π_x and another in a π_y orbital — lead to the prediction that the $^3\Sigma^-$ state is the lowest, the $^1\Delta$ state next, and then the $^1\Sigma^+$ state.

Similarly, for the Π_u states arising from the $\sigma^1\pi^3$ electron occupancy, the $^3\Pi$ state will lie below the $^1\Pi$ state.

B. Molecular potential curves

The eigenfunctions of the electronic Hamiltonian of Eq. (1)

$$\hat{H}_{el}(q_1, \dots, q_M; \vec{R})\Phi_{el}^{(k)}(q_1, \dots, q_M; \vec{R}) = \mathcal{E}_{el}^{(k)}(\vec{R})\Phi_{el}^{(k)}(q_1, \dots, q_M; R)$$

are implicitly functions of the positions of the nuclei. Note that, just as in the atomic limit, there are more than one electronic eigenfunctions, which we designate by the index k . These are the electronic states of the molecule.

In the Born-Oppenheimer approximation, the potential for motion of the nuclei is the sum of the electronic energy plus the Coulomb repulsion between the nuclei. For a diatomic molecule, this central potential is a function only of the scalar distance between the nuclei, namely

$$V^{(k)}(R) = \mathcal{E}^{(k)}(R) + \frac{Z_1 Z_2}{R}$$

This defines the molecular potential energy curve(s), shown below.

In this figure we note that the energy ordering discussed in the previous section is roughly correct, **except that the lowest electronic state of C_2 is seen to be the $^1\Sigma^+$ state**, in stark contrast to the prediction.

This is a unique, and interesting feature of C_2 . It arises because there are three possible electron occupancies which all have overall $^1\Sigma_g^+$ symmetry, namely $|\dots 2\sigma_u^2 3\sigma_g^2 1\pi_u^2|$,

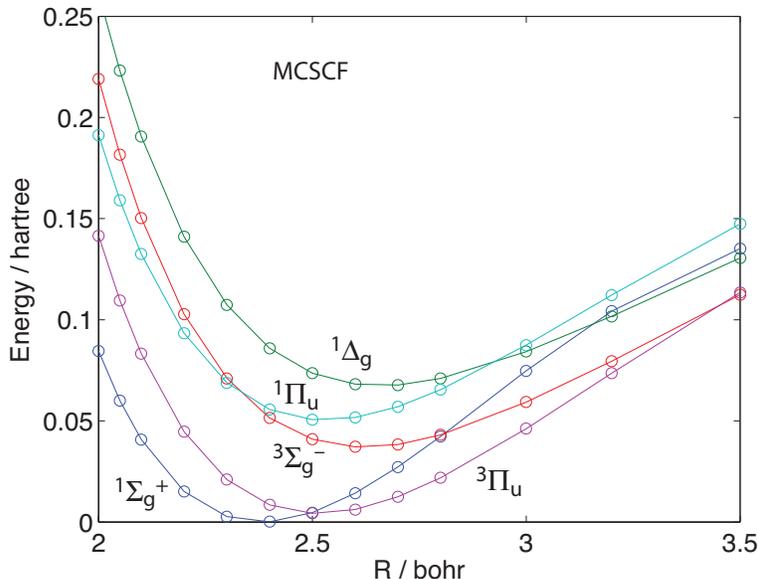


FIG. 5. Potential energy curves of the low-lying electronic states of C_2 . Energies in Hartree atomic units (1 h = 27 eV).

$|\dots 2\sigma_u^2 3\sigma_g^0 1\pi_u^4|$, and $|\dots 2\sigma_u^0 3\sigma_g^2 1\pi_u^4|$. It is this *multireference* character of the $^1\Sigma_g^+$ state which explains the anomaly.

The blue color you see in the flame of a gas stove is the electronic absorption of C_2 from the $^3\Pi_u$ state to the $^3\Sigma_g^-$ state. These are called the “Swann bands” and are a characteristic of the spectra of carbon stars, comets, and burning hydrocarbon fuels.

The C_2 molecule also possesses another curious anomaly. The lowest state ($^1\Sigma_g^+$) is singly degenerate. The first excited state ($^3\Pi_u$) is 6-fold degenerate ($M_S = +1, 0, -1$ and $M_L = +1$ or -1). Because of this 6-fold degeneracy, even at modest temperatures, the relative Boltzmann weight of this state can exceed that of the ground electronic state.

VI. MOLECULAR OXYGEN

If you think C_2 is too complicated, you will be consoled by O_2 , a diatomic molecule with four more (16) electrons. The molecular orbitals are entirely similar. The $1\pi_u$ orbital, shown below for O_2 , is now quadruply filled, with the remaining two electrons going into the first “antibonding” orbital $1\pi_g$, also shown below. You can see the antibonding node between the nuclei very clearly.

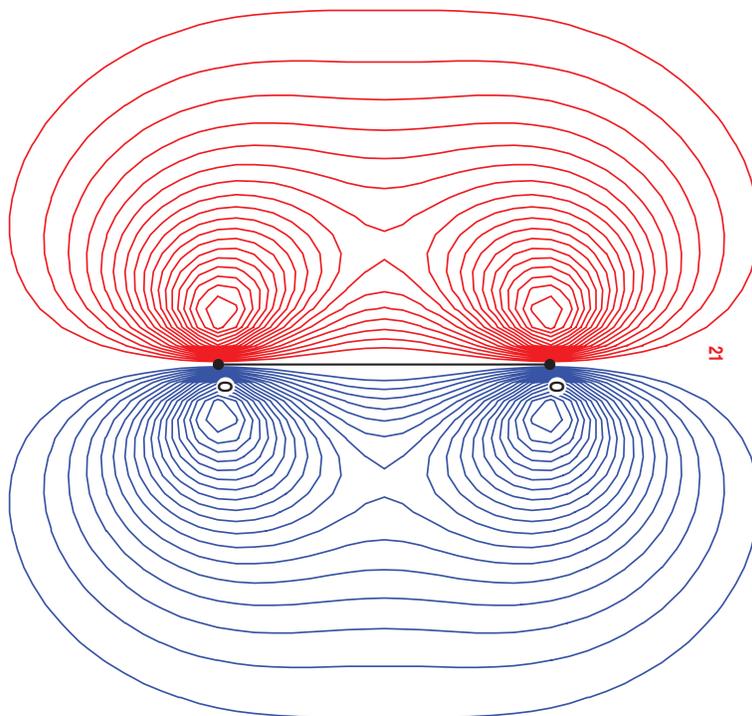


FIG. 6. The $1\pi_{ux}$ molecular orbital of O_2 . There is an equivalent degenerate molecular orbital in the yz plane.

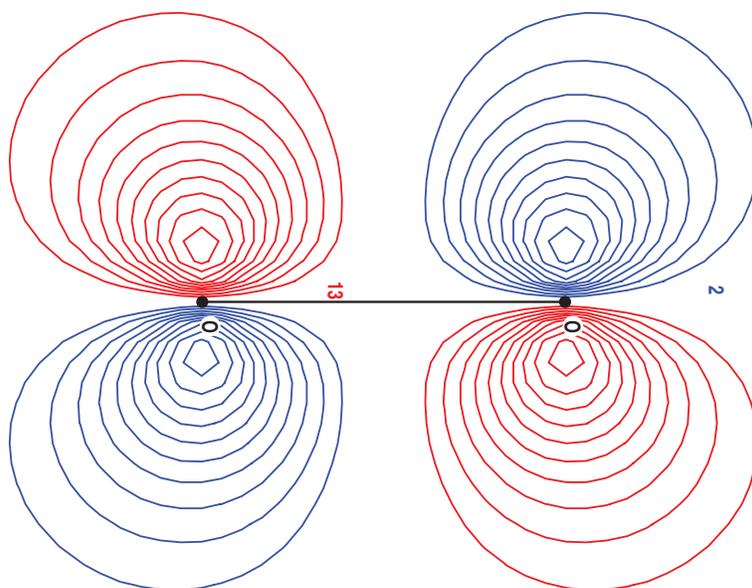


FIG. 7. The $1\pi_{gx}$ molecular orbital of O_2 . There is an equivalent degenerate molecular orbital in the yz plane.

Because the $3\sigma_g$ and $1\pi_u$ bonding orbitals are completely filled, there is only one way of adding the two additional electrons, in the case of O_2 ; no multireference possibility. The

lowest energy state is the triplet, with one electron in $1\pi_{gx}$ and the other in $1\pi_{gy}$. The overall electronic state has then g inversion symmetry, and is antisymmetric with respect to reflection in a plane containing the O–O axis. Thus, the term symbol of the ground electronic state is ${}^3\Sigma_g^-$. Molecular oxygen in its ground electronic state has a magnetic moment. This paramagnetism can be [seen clearly](#) in an experiment where you flow liquid O₂ between the poles of a strong magnet.

VII. “MISSING” ROTATIONAL LEVELS

The ${}^{16}\text{O}$ atom has spin zero, and is hence a boson. Thus, the overall wavefunction for the O₂ molecule must be symmetric with respect to interchange of the two nuclei. This wavefunction is a product of the electronic wavefunction, multiplied by vibrational and rotational wavefunctions for the relative motion of the two O nuclei. Because of the antisymmetry of the $1\pi_g$ orbital, the ground electronic state is antisymmetric with respect to interchange of the two nuclei. [Correctly, the operator for nuclear exchange is](#)

$$\hat{\pi} = \hat{\sigma}_v \times \hat{i}$$

[where \$\hat{i}\$ is the inversion operator and \$\hat{\sigma}_v\$ is the operator for reflection in a plane containing the nuclei. Thus, a \$\Sigma_g^-\$ state \(symmetric with respect to inversion, antisymmetric with respect to reflection\) is antisymmetric with respect to interchange of the two nuclei.](#)

The ground vibrational wavefunction is obviously symmetric with respect to interchange of the two nuclei. Thus, to ensure bosonic character for the overall molecule, the rotational wavefunction must also be antisymmetric with respect to exchange of the two nuclei. This antisymmetry occurs only for odd values of the rotational quantum number (the overall rotation of the molecule). Thus, only *odd* rotational levels of the O₂ molecule will occur.

The ${}^{12}\text{C}$ atom also has spin zero. But, for C₂ we have seen that the ground electronic wavefunction (with term symbol ${}^1\Sigma_g^+$, is symmetric with respect to both reflection in a plane containing the molecular axis and inversion. Thus, to ensure bosonic character for the ${}^{12}\text{C}_2$ molecule, only *even* rotational levels will occur.