Theoretical Chemistry - Level II - Practical Class Molecular Orbitals in Diatomics

Problem 1

Draw molecular orbital diagrams for O_2 and O_2^+ .



Of these two molecules in their respective ground states, which would you expect to have the larger equilibrium bond length, and why?

 O_2 is expected to have a greater equilibrium bond length than O_2^+ , since the bond orders of O_2 and O_2^+ (predicted by the MO diagrams above) are 2 and 2.5, respectively. O_2 is predicted to have one more electron in antibonding orbitals than O_2^+ does, so O_2 should have a weaker, longer bond.

It is confirmed experimentally that the O-O distance in O₂ is about 7 to 8% longer than in O₂⁺, with $r_e({}^{16}O_2) = 120.752$ pm determined by microwave spectroscopy,¹ and $r(O_2^+)$ variously reported as 111.5 pm,² and 112.3 pm.³

Derive molecular term symbols for the ground states of O_2 and O_2^+ .

Molecular term symbols are of the form ${}^{2S+1}\Lambda_{(g/u)}$, where 2S + 1 is the multiplicity, Λ is the quantum number for the total orbital angular momentum about the internuclear axis. The (g/u) part is the parity label indicating whether the total molecular wavefunction is symmetric (g) or antisymmetric (u) with respect to inversion at the origin, and only applies to centrosymmetric molecules.⁴

The total spin angular momentum quantum number, *S*, can take on a range of integer values, given by a Clebsch-Gordan series of the corresponding quantum numbers of each electron, which all take the value $s = \frac{1}{2}$, since this is an intrinsic property of the electron.

$$S = s_1 + s_2, s_1 + s_2 - 1, s_1 + s_2 - 2, \dots, |s_1 - s_2|$$

³ N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth/Heinemann, 2nd edn., 1997, p. 616.

¹ D. R. Lide, ed., CRC Handbook of Chemistry and Physics, Taylor and Francis, 89th edn., 2009, ch. 9, p. 106.

² M. I. Winter, *Chemical Bonding*, Oxford University Press, 1994, p. 47.

⁴ Lecture handout from Prof. N. L. Allan's 2008-9 Level 2 course Understanding Structure and Reactivity 1, p 24.

Closed shell configurations (paired electrons) can be ignored since they contribute zero to S, so it is only necessary to consider the unpaired electrons in a molecule in order to derive its multiplicity.

For O₂ with two unpaired electrons, the possible multiplicities, (2S+1), are 3 (triplet, S = 1) or 1 (singlet, S = 0).



Hund's rules (if electrons occupy different degenerate orbitals they do so with their spins aligned parallel to one another)⁴ predict that the ground state is the triplet state.

The total orbital angular momentum (about the internuclear axis) quantum number, Λ , is given by the sum of the equivalent quantum numbers for each electron, λ_i .

$$\Lambda = \left| \sum_{i} \lambda_{i} \right|$$

So for O₂, consider only the partially filled orbitals.

$$2p_{x}\pi^{*} \stackrel{\checkmark}{\longrightarrow} 1 \qquad \stackrel{\checkmark}{\longrightarrow} 2p_{y}\pi^{*}$$
$$\lambda = 1 \qquad \lambda = -1$$
$$\Lambda = \left|+1 - 1\right| = 0$$

The notation used for $\Lambda = 0, 1, 2, 3$ in molecular term symbols is Σ , Π , Δ , Φ , by analogy with s, p, d, f from atomic spectroscopy. In the case of O₂, $\Lambda = 0$, represented by Σ .

The parity of the total wavefunction of a molecule is given by the product of the parities of the individual electron wavefunctions.



Combining the three results, the term symbol for the ground state of O_2 is ${}^{3}\Sigma_{g}$.

For O_2^+ , $S = s = \frac{1}{2}$ so (2S+1) = 2, $\lambda = 1$ so $\Lambda = 1$ (Π) and the unpaired electron occupies a π^* orbital of g parity, so the overall parity is g. The molecular term symbol for O_2^+ is therefore ${}^2\Pi_{\alpha}$.

Show that the value of the nuclear repulsion energy given by Gaussian is correct.

nuclear repulsion energy 23.7451311417 Hartrees.

The nuclear repulsion energy of N₂ is given by $\frac{Z_N^2}{R_{_{NN}}}$. Gaussian reports the value in

hartrees (E_h), the atomic unit of energy, so atomic units for Z_N and R_{NN} need to be used.

(1) $Z_{\rm N}$ is the nuclear charge of nitrogen, so in atomic units, $Z_{\rm N} = 7e$, where *e* is the elementary charge (equal to 1.602×10^{-19} C).

(2) R_{NN} is the internuclear separation, given by Gaussian as 1.092 Å, or 2.064 Bohr radii, since one Bohr radius, $a_0 = 0.5292$ Å.

$$\frac{1.092000 \text{ Å}}{0.529177 \text{ Å } a_0^{-1}} = 2.06358 a_0$$

Combining the values of Z_{N} and R_{NN} from (1) and (2) gives the nuclear repulsion energy as:

$$\frac{Z_{\rm N}^2}{R_{\rm NN}} = \frac{\left(7e\right)^2}{2.06358 a_0} = 23.7451217949 E_{\rm h}$$

This value and the value returned by Gaussian are within 10^{-4} % of each other, and probably only differ because of slight differences in the values of a_0 and e used here and within Gaussian, respectively.

By considering the coefficients c_{ip} , describe the AO composition of the lowest energy MO of N_2 .

The lowest energy MO of N_2 is $1\sigma_g$. Although a simplistic treatment of MO theory would describe this orbital as an in-phase combination of two N 1s AOs, it is possible for all AOs of appropriate symmetry to contribute to the composition of this MO.

			1
			(SGG)0
EI	GENV	-15.51998	
11	N	1S	0.70306
2		2S	0.01284
3		2PX	0.00000
4		2PY	0.00000
5		2PZ	-0.00215
62	N	1S	0.70306
7		2S	0.01284
8		2PX	0.00000
9		2PY	0.00000
10		2PZ	0.00215

Gaussian calculates that the MO is composed mostly of the expected in-phase combination of nitrogen 1s AOs, with a small contribution from the two corresponding 2s AOs and a very small contribution from the two $2p_z$ AOs.



In the same way, identify a π bonding orbital and a π^* anti-bonding orbital.

MO5 of N₂ is a π bonding orbital. It is composed purely of the sum of two 2p_y AOs, overlapping orthogonally to the internuclear axis. MO8 of N₂ is a π^* anti-bonding orbital. It is composed purely of the difference of two 2p_y AOs, overlapping orthogonally to the internuclear axis.



Classify orbitals 5, 6, 7, 8 and 9 as bonding, non-bonding, or anti-bonding, based on the coefficients and the orbital energies generated by the calculation.

MOs 5 and 6 are degenerate and are identical except that they are orthogonal to one another - they are both valence-bonding orbitals. They have negative energies (both -0.57696 hartrees), so they are not virtual orbitals; they are bonding because there is no nodal plane bisecting the internuclear axis, so more electron density resides in the internuclear region than outside it (both coefficients have the same sign, so the AOs overlap in-phase); and they are valence MOs because they are composed of AOs (2p_x, 2p_y) belonging to the valence shell of nitrogen, namely the n = 2 shell.

MO 7 is a valence orbital, as it is composed mostly of valence AOs (2s and $2p_z$) and has a negative energy. Although it does not have a nodal plane bisecting the internuclear axis, much of the electron density appears concentrated outside the internuclear region, due to suboptimal overlap of the two $2p_z$ AOs (these have different signs, but they are not antibonding due to their alignment) so MO7 is high in energy and is probably best described as non-bonding.



MOs 8 and 9 are degenerate and are identical except that they are orthogonal to one another - they are both virtual anti-bonding orbitals. They have positive energies (both 0.28383 hartrees), so they are virtual orbitals; they are anti-bonding because there *is* a nodal plane bisecting the internuclear axis, so more electron density resides outside the internuclear region than inside it (the coefficients have opposite signs, so the AOs overlap in antiphase).

Draw a complete MO diagram for N_2 .



Determine the electronic configuration of an N_2 molecule in its ground state, and derive the corresponding molecular term symbol.

The ground state of N₂ is a closed shell configuration, so $\Lambda = 0$, S = 0 and so the multiplicity is 1 (singlet). There is the same number of electrons in g orbitals as in u orbitals, $u \times u = g$ and $g \times g = g$, so the overall parity is g. The term symbol is thus ${}^{1}\Sigma_{\sigma}$.

View the following MOs on the screen, and answer the questions: MO1: Is this consistent with the coefficients deduced in Problem 3?



The boundary surface plot for MO1 of N_2 is indeed consistent with the coefficients from Problem 3. It largely resembles two 1s AOs, one on each nucleus, added in phase. There is little overlap of the AOs, and thus little electron density in the internuclear region, as expected for core electrons.

MOs 5 and 8: Are these what you expect?



Yes, these look exactly like the π and π^* MOs expected for the sum and difference of two $2p_x$ or $2p_y$ AOs.

MO7 (the HOMO): Where is the bulk of the electron density in this orbital? How might this relate to the energy of this MO?



Most of the electron density is located outside the internuclear region, leading to a high energy. Better overlap could be attained by increasing the internuclear separation, but this would simultaneously reduce the overlap of the $2p_x$ and $2p_y$ pairs of AOs - one sigma bond would strengthen at the expense of two pi bonds, so the change is unfavourable.

Write out the LCAO-MO description of the HOMO of N₂.

 $\Psi_{7} = -0.06889\phi_{1_{S(N1)}} + 0.40939\phi_{2_{S(N1)}} + 0.60377\phi_{2_{p_{2}(N1)}} - 0.06889\phi_{1_{S(N2)}} + 0.40939\phi_{2_{S(N2)}} - 0.60377\phi_{2_{p_{2}(N2)}} - 0.00377\phi_{2_{p_{2}(N2)}} - 0.0037\phi_{2_{p_{2}(N2)}} - 0.0037\phi_{2_{p_{2}(N2$

By considering the coefficients c_{ip} describe the AO composition of the two MOs of CO with lowest energies, and identify a π bonding orbital and a π^* anti-bonding orbital.

As for N₂, MO5 of CO is a π bonding orbital. It is composed purely of the weighted sum of C 2p_y and O 2p_y AOs, overlapping orthogonally to the internuclear axis. MO8 of CO is a π^* anti-bonding orbital. It is composed purely of the weighted difference of C 2p_y and O 2p_y AOs, overlapping orthogonally to the internuclear axis.

Classify orbitals 5, 6, 8 and 9 as bonding, non-bonding, or anti-bonding.

MOs 5 and 6 are degenerate and are both bonding, since they have negative energies and are composed solely of valence AOs. MOs 8 and 9 are degenerate and are both anti-bonding, since they have positive energies - both contain a nodal plane that bisects the internuclear axis.

What is the symmetry of the HOMO?

The HOMO is MO 7 and has sigma symmetry (it has cylindrical symmetrical about the internuclear axis), and exhibits significant $s-p_z$ mixing.

Draw a complete MO diagram for CO, marking the energies of the various occupied MOs on your diagram.



Determine the electronic configuration of a CO molecule in its ground state, and derive the corresponding molecular term symbol.

Electron configuration from MO diagram above: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$, isoelectronic with N₂.

CO has a closed shell configuration, so $\Lambda = 0$ (Σ), S = 0 (2S + 1 = 1, singlet) and the molecule is non-centrosymmetric so parity (g/u) labels do not apply. Its molecular term symbol is therefore ${}^{1}\Sigma$.

Problem 6

Use the answer to Problem 5 to explain why the band arising from orbitals 5 and 6 in the photoelectron spectrum of CO consists of several peaks. What does the magnitude of the separation between the peaks in this band tell us?

PES measures the energy of the incident photon and the ejected electron for the process $CO + hv \rightarrow CO^+ + e^-$. The difference between the two is the ionization energy of the orbital from which the electron was ejected. Koopman's theorem equates this with the orbital energy, which while not strictly true (neglects rearrangement of electronic structure as the cation forms) is a useful guide.

MOs 5 and 6 of CO are degenerate, so we might expect to see just one peak in the PES of CO corresponding to ionization energy of these MOs. The existence of several peaks is vibrational fine structure. All the peaks correspond to the formation of CO^+ from CO (in its vibrational ground state, v = 0, at room temperature), but each peak corresponds to the formation of CO^+ in a different vibrational state, which each have a different energy.

The Franck-Condon principle applies here - the ionization process is much faster than the movement of nuclei - so the most intense peaks correspond to transitions with the greatest overlap of CO and CO^+ vibrational wavefunctions. The magnitude of separation of the peaks is equal to the separation of vibrational energy levels in CO^+ .

Problem 7

Plot MOs 5, 7 and 8 of CO. Where is (or would be) the bulk of the electron density in these orbitals? Compare and contrast the forms of these orbitals with their counterparts in N_2 . What do you notice about the symmetry of the electron densities of orbitals 7 and 8?



In MO 5 of CO, the bulk of the electron density lies between the nuclei, as befits a bonding orbital - it is difficult to discern any asymmetry in the electron density from the plot, but the coefficient on oxygen is much bigger due to its greater electronegativity, so the electron density lies more on oxygen:

$$\Psi_5 = 0.44547\phi_{2p_x(C)} + 0.78850\phi_{2p_x(O)}$$

 $\Psi_5^2 = \left(0.44547\phi_{2p_x(C)} + 0.78850\phi_{2p_x(O)}\right)^2 \approx 0.199\phi_{2p_x(C)}^2 + 0.622\phi_{2p_x(O)}^2 + 0.703\phi_{2p_x(C)}\phi_{2p_x(O)}\right)$

By contrast, MO 5 of N_2 has equal coefficients for each AO, and the bond is completely non-polarised, reflecting the equal electronegativity of the two nitrogen atoms.

In MO 7 of CO most of the electron density is localised on carbon, making this orbital effectively non-bonding, and leading to its approximate description as a carbon lone pair. The equivalent MO in dinitrogen, on the other hand, has equal electron density on each atom.

In MO 8 of CO, the opposite polarity to that of MO 5 is seen, with the bulk of the electron density on C this time - a natural consequence of the asymmetry of MO 5, since MOs 5 and 8 are the sum and difference of the C and O $2p_x$ AOs, respectively.

MO 7 for both CO and N₂ has σ symmetry and can thus act as a σ donor, while MO 8 has π symmetry and can act as a π acceptor - see below for details.

Problem 8

Discuss the relevance of your results for the HOMO and LUMO of these molecules to the bonding in transition-metal carbonyls and the bonding of N_2 to transition metals.

Both CO and N₂ are known to bond to transition metals, but unlike simple ligands like H⁻, the nature of the bonding can involve both donation of electron density from highlying ligand σ MOs into vacant metal d orbitals <u>and</u> acceptance of electron density from filled metal d orbitals into vacant ligand π MOs. This is synergic bonding, or π back-bonding.



For strong bonding to occur the HOMO of CO or N_2 has to be a good size, energy and symmetry match for the vacant metal d orbital it is donating into, and the LUMO has to match the size, energy and symmetry of the occupied donor metal d orbital.

It turns out that the HOMOs of of CO and N₂ have high ionization energies, hold on to their electrons relatively strongly and are thus poor σ donors, as evidenced by the weak complexes these ligands form with simple σ acceptors such as BF₃. When π

back-donation from an electron rich metal centre is possible, the σ bond becomes more favourable, hence the term synergic bonding.

The fact that both atoms in the diatomic N_2 have the same electronegativity leads to better orbital overlap than in CO, resulting in a higher energy HOMO and lower energy LUMO for N_2 , making both components of synergic bonding with transition metals less favourable. Consequently, N_2 forms much weaker bonds with transition metals because it is both a weaker σ donor and a weaker π acceptor than CO.

Molecular Orbitals of Dinitrogen				
MO number	MO symmetry	Surface plot		
10	$3\sigma_{u}$			
8, 9	$1\pi_{ m g}$			
7	$3\sigma_{g}$			
5, 6	$1\pi_{u}$			
4	$2\sigma_u$			
3	$2\sigma_{g}$			
2	$1\sigma_u$			
1	lσ _g			

Molecular Orbitals of Carbon Monoxide				
MO number	MO symmetry	Surface plot		
10	6σ			
8, 9	2π			
7	5σ			
5, 6	1π			
4	4σ			
3	3σ			
2	2σ			
1	1σ			