Quantum Chemistry

Corrections 11

1. *Predict the relative stability of the species* N_2^+*,* N_2*, and* N_2^-*.*

To predict the relative stability of different diatomic molecules, we compare the bond orders. We must first determine the electronic configuration of each species, then count the binding and anti-binding electrons
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Species	Electronic configuration	Bond order
N_2^+	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^1$	$\frac{4+1}{2}=2.5$
N_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2$	$\frac{4+2}{2}=3$
N_2^-	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^1$	$\frac{4+2-1}{2}=2.5$

The relative stability is therefore: $N_2 > N_2^+ \approx N_2^-$

2. *Determine the ground-state electron configurations of* NO^+ *and NO. Compare the bond order of these two species.*

Species	Electronic configuration	Bond order
NO^+	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2$	$\frac{4+2}{2}=3$
NO	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^1$	$\frac{4+2-1}{2}=2.5$

3. *Determine the bond order in a cyanide ion.*

Species	Electronic configuration	Bond order
CN^-	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2$	$\frac{4+2}{2}=3$

4. *Determine the ground-state molecular term symbols of* O_2 *and* O_2^+*.*

To determine the spectroscopic terms O_2 and O_2^+ in the ground state, it is first necessary to establish their electronic configuration.

Species	Electronic configuration
O_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p)^4(\pi^* 2p)^2$
O_2^+	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p)^4(\pi^* 2p)^1$

As we did for atoms, we only deal with incomplete molecular orbitals $(\pi^* 2p)$ in this case, because others have contributions to M_L and to M_S equal to zero. Let us then list the different possible states and calculate the value of M_L and M_S, to finally deduce the molecular terms.

For O_2:

m_L		M_L	M_S
-1	$+1$		
↑↓		-2	0
↑	↑	0	$+1$
↑	↓	0	0

m_L		M_L	M_S
-1	$+1$		
↓	↑	0	0
↓	↓	0	-1
	↑↓	$+2$	0

The values of $M_L = \pm 2$ with $M_S = 0$ indicate a term having $\Lambda = 2$ and $S = 0 \Rightarrow {}^1\Delta$.

After having crossed out the two corresponding states, all the remaining states have $M_L = 0$ and the maximum value of M_S is ± 1, which gives $\Lambda = 0$ and $S = 1 \Rightarrow {}^3\Sigma$.

We then eliminate from the table three states (three possible projections of $\vec{S}$: $M_S = 0, \pm 1$), and ultimately there is only one state with $M_L = 0$ and $M_S = 0$, that is to say $\Lambda = 0$ and $S = 0 \Rightarrow {}^1\Sigma$.

The term of the ground state (of lower energy) is determined by the rules of Hund: it is that of greater multiplicity of spin, namely ${}^3\Sigma$.

For O_2^+:

m_L		M_L	M_S
-1	$+1$		
↑		-1	$+\frac{1}{2}$
↓		-1	$-\frac{1}{2}$

m_L		M_L	M_S
-1	$+1$		
	↑	$+1$	$+\frac{1}{2}$
	↓	$+1$	$-\frac{1}{2}$

This time there is only one term with $\Lambda = 1$ and $S = \frac{1}{2} \Rightarrow {}^2\Pi$, which is therefore the term of the fundamental state of O_2^+.

5. *The highest occupied molecular orbitals for an excited electronic configuration of the oxygen molecule are*

$$[1\pi_g]^1[3\sigma_u]^1$$

What are the molecular term symbols for oxygen with this electronic configuration?

The list of possible states for this electronic configuration and the values of M_L and the corresponding M_S are given in the table below.

$m_L(1\pi_g)$		$m_L(3\sigma_u)$	M_L	M_S
-1	$+1$	0		
$\uparrow$		$\uparrow$	-1	$+1$
$\uparrow$		$\downarrow$	-1	0
$\downarrow$		$\uparrow$	-1	0
$\downarrow$		$\downarrow$	-1	-1

$m_L(1\pi_g)$		$m_L(3\sigma_u)$	M_L	M_S
-1	$+1$	0		
	$\uparrow$	$\uparrow$	$+1$	$+1$
	$\uparrow$	$\downarrow$	$+1$	0
	$\downarrow$	$\uparrow$	$+1$	0
	$\downarrow$	$\downarrow$	$+1$	-1

We deduce a term with $M_L = \pm 1$ and $M_S = 0, \pm 1$ (which corresponds to 6 states), that is to say $\Lambda = 1$ and $S = 1 \Rightarrow {}^3\Pi$.

The two remaining states have $M_L = \pm 1$ and $M_S = 0$, which gave $\Lambda = 1$ and $S = 0 \Rightarrow {}^1\Pi$.

6. *In class I derived the expressions for the three sp*^{2} *orbitals of carbon:*

$$\xi_1 = \frac{1}{\sqrt{3}}\,2s + \sqrt{\frac{2}{3}}\,2p_z$$

$$\xi_2 = \frac{1}{\sqrt{3}}\,2s - \frac{1}{\sqrt{6}}\,2p_z + \frac{1}{\sqrt{2}}\,2p_x$$

$$\xi_3 = \frac{1}{\sqrt{3}}\,2s - \frac{1}{\sqrt{6}}\,2p_z - \frac{1}{\sqrt{2}}\,2p_x$$

Using the angular parts of the p orbitals (i.e., the spherical harmonics), show that ξ_1 *and* ξ_2 *are directed 120° from each other.*

The 2s orbital has spherical symmetry and therefore does not contribute to the direction of hybrid orbitals. There is therefore no need to consider it.

The orbitals $2p_x$, $2p_y$ and $2p_z$ are oriented along the axes O*x*, O*y* and O*z* and they are the same 'size'. We can therefore consider their direction as equivalent to that of the basic vectors of space $\mathbb{R}^3$:

$$2p_x \rightarrow (1,0,0) \quad 2p_y \rightarrow (0,1,0) \quad 2p_z \rightarrow (0,0,1)$$

Therefore, the directions of the linear combinations ξ_1, ξ_2 and ξ_3 are those of the vectors $\vec{v}_1$, $\vec{v}_2$ and $\vec{v}_3$ obtained by taking the same linear combinations of $(1,0,0)$, $(0,1,0)$ and $(0,0,1)$.

So,

$$\xi_1 = \tfrac{1}{\sqrt{3}} 2s + \sqrt{\tfrac{2}{3}} 2p_z \quad \Rightarrow \quad \xi_1 \rightarrow \vec{v}_1 = \left(0,0,\sqrt{\tfrac{2}{3}}\right) \quad \text{(we don't take into account } 2s\text{)}$$

Likewise,

$$\xi_2 \rightarrow \vec{v}_2 = \left(\tfrac{1}{\sqrt{2}},0,-\tfrac{1}{\sqrt{6}}\right)$$

and

$$\xi_3 \rightarrow \vec{v}_3 = \left(-\tfrac{1}{\sqrt{2}},0,-\tfrac{1}{\sqrt{6}}\right)$$

Finally, to calculate the angle between ξ_1 and ξ_2, just calculate the angle of $\vec{v}_1$ and $\vec{v}_2$ using their dot product:

$$\vec{v}_1 \cdot \vec{v}_2 = x_1 x_2 + y_1 y_2 + z_1 z_2 = \|\vec{v}_1\| \cdot \|\vec{v}_2\| \cdot \cos\alpha_{12}$$

$$\Rightarrow \quad 0+0+\sqrt{\tfrac{2}{3}} \cdot \left(-\tfrac{1}{\sqrt{6}}\right) = \sqrt{\tfrac{2}{3}} \cdot \sqrt{\tfrac{1}{2}+\tfrac{1}{6}} \cdot \cos\alpha_{12} \quad \Rightarrow \quad \cos\alpha_{12} = -\tfrac{1}{2} \quad \Rightarrow \quad \alpha_{12} = 120°$$

We can calculate in the same way for α_{13} and α_{23} which are also 120°.