Chapter 11. Exercises

1. After separation of variables in the H_2^+ problem, the function $\Xi(\xi)$ obeys the differential equation

$$\frac{d}{d\xi}\left[(\xi^2-1)\frac{d\Xi}{d\xi}\right] + \left(A + 2R\xi + \tfrac{1}{4}R^2 E\xi^2 - \frac{\lambda^2}{\xi^2-1}\right)\Xi(\xi) = 0$$

where A is a constant, R is the internuclear distance, λ is the angular momentum quantum number, an integer, and E is the energy, a negative number for bound states. Find the asymptotic solution of the above equation as $\xi \to \infty$.

2. Write out the two-electron orbital function for the H_2 molecule

$$\psi(1,2) = \psi_{1\sigma g}(1)\,\psi_{1\sigma g}(2)$$

assuming the LCAO approximation for each MO. Expand this result and show how it relates to the corresponding valence-bond wavefunction. What is the meaning of the left-over terms?

3. Give the electron configuration, term symbol and bond order for the ground state of each of the following species: N_2^+, N_2 and N_2^-

4. Predict the electronic configuration and term symbol for the ground state of the superoxide ion O_2^- and of the peroxide ion O_2^{-2}.

5. Propose electron configurations and term symbols for the two lowest singlet excited states of O_2.

6. Rationalize why the Be_2 molecule, unlike He_2, is weakly bound ($D_2 \approx 0.1$ eV). Hint: 2s-2p hybridization is involved.

7. The overlap integral between a $1s$ and a $2p\sigma$ orbital on nuclei separated by a distance R (in bohr) is given by

$$S = \left(R + R^2 + \frac{R^3}{3}\right)e^{-R}$$

Determine the value of R which gives the maximum overlap. (It may be of interest that the internuclear distance in HF equals 0.916Å.)

8. Carry out a Hückel calculation on the allyl radical

$$CH_2 = CH - CH_2°$$

Determine, in terms of the empirical parameters α and β, the energies of the π-molecular orbitals, the resonance stabilization energy and the wavelength of the lowest-energy electronic transition.

9. The species H_3 occurs as an intermediate in the hydrogen exchange reaction

$$H_2 + H \rightleftharpoons H_3 \rightleftharpoons H + H_2$$
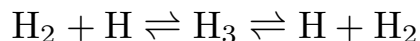
Is H_3 a linear or a triangular molecule? For both the linear and equilateral triangular configurations, apply a variant of the Hückel theory based on hydrogen 1s orbitals (rather than carbon $2p$) to predict which has the lower energy. Also predict the shapes of the ions H_3^+ and H_3^-.

Chapter 11. Solutions

1. As $\xi \to \infty$, the equation reduces approximatly to

$$\xi^2 \frac{d^2\Xi}{d\xi^2} - \frac{R^2|E|\xi^2}{4}\Xi \approx 0$$

Cancelling the ξ^2 and noting that E is negative for bound states,

$$\Xi(\xi) \approx \exp\left(-\frac{R}{2}\sqrt{|E|}\,\xi\right)$$

2.
$$\psi_{1\sigma g} = 1s_A + 1s_B$$

Thus
$$\psi(1,2) = \left(1s_A(1) + 1s_B(1)\right)\left(1s_A(2) + 1s_B(2)\right) =$$

$$\left\{1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)\right\} + 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)$$

Term in brackets is the valence bond function for the bond. The remaining terms represent ionic structures H^+H^- and H^-H^+ with both electrons on the same hydrogen atom.

3. N_2 $\ldots 1\pi_u^4 3\sigma_g^2$ $^1\Sigma_g^+$ BO=3

N_2^+ $\ldots 1\pi_u^4 3\sigma_g$ $^2\Sigma_g^+$ BO=2.5

N_2^- $\ldots 1\pi_u^4 3\sigma_g^2 1\pi_g$ $^2\Pi_g$ BO= 2.5

4. O_2 $\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$ $^3\Sigma_g^-$

O_2^- $\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^3$ $^2\Pi_g$

O_2^{-2} $\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^4$ $^1\Sigma_g^+$

5.   Both excited states have same configuration as ground state, $\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$, but with the following occupancy of $1\pi_g$ orbitals:

$$\uparrow\downarrow \qquad {}^1\Sigma_g^+ \qquad \text{and} \qquad \mathbb{\uparrow\downarrow}\ \_\!\_ \qquad {}^1\Delta_g$$

The plus superscript in the first term symbol is rather tricky. Don't worry about it. But if you insist … two-electron singlet spin state has anti-symmetric spin function, thus must have *symmetric* orbital function like $\pi_x(1)\pi_y(2) + \pi_y(1)\pi_x(2)$ which *doesn't* change sign upon transformation $\phi \to -\phi$. Singlet oxygen and other active oxygen species are involved in lipid metabolism.

6. Be_2 has configuration $\ldots 2\sigma_g^2 2\sigma_u^2 \quad {}^1\Sigma_g^+$

The 2σ orbitals are LCAO's made from hybrids of $2s$ and $2p\sigma$. The $2\sigma_g$ MO probably becomes more strongly bonding while the $2\sigma_u$ becomes more weakly antibonding, with the net effect being weak bonding.

7. Setting $dS/dR = 0$ find maximum at $R = 2.1038$ bohrs or $2.1038 \times .593 = 1.115$ Å.

8. Secular determinant

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x^3 - 2x = 0$$

where $x = (\alpha - E)/\beta$. Roots $x = 0, \pm\sqrt{2}$, thus $E = \alpha - \sqrt{2}\beta$, α, $\alpha + \sqrt{2}\beta$. Remember both α and β are negative. Ground state energy (3 electrons) $= 2(\alpha + \sqrt{2}\beta) + \alpha = 3\alpha + 2\sqrt{2}\beta$. One localized π-orbital plus one unpaired electron would have energy $= 2(\alpha + \beta) + \alpha = 3\alpha + 2\beta$. Resonance stabilization energy $= (2 - 2\sqrt{2})\beta = -.828\,\beta = .828|\beta|$. Lowest energy electronic transition given by

$$\frac{hc}{\lambda} = \sqrt{2}|\beta|$$

9. For linear H_3, the secular equation is

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x^3 - 2x = 0$$

with roots $x = 0, \pm\sqrt{2}$. Thus the three MO energies are $\alpha - \sqrt{2}\beta$, α, $\alpha + \sqrt{2}\beta$. The energy of the three-electron ground state is $3\alpha + 2\sqrt{2}\beta \approx 3\alpha + 2.828\beta$.

For triangular H_3,

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = x^3 - 3x + 2 = 0$$

One obvious root is $x = 1$. Division of $x^3 - 3x + 2$ by $x - 1$ gives $x^2 + x - 2$, with roots $x = 1$ and -2. The three MO's are $\alpha + 2\beta, \alpha - \beta, \alpha - \beta$. The energy of the ground state is $3\alpha + 3\beta$.

Apparently the triangular form of H_3 has a slightly lower energy.