

# 14 Molecular structure

## Solutions to exercises

### Discussion questions

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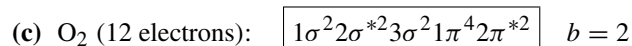
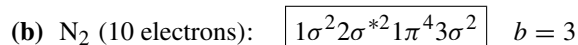
- E14.1(b)** Consider the case of the carbon atom. Mentally we break the process of hybridization into two major steps. The first is promotion, in which we imagine that one of the electrons in the  $2s$  orbital of carbon ( $2s^2 2p^2$ ) is promoted to the empty  $2p$  orbital giving the configuration  $2s 2p^3$ . In the second step we mathematically mix the four orbitals by way of the specific linear combinations in eqn 14.3 corresponding to the  $sp^3$  hybrid orbitals. There is a principle of conservation of orbitals that enters here. If we mix four unhybridized atomic orbitals we must end up four hybrid orbitals. In the construction of the  $sp^2$  hybrids we start with the  $2s$  orbital and two of the  $2p$  orbitals, and after mixing we end up with three  $sp^2$  hybrid orbitals. In the  $sp$  case we start with the  $2s$  orbital and one of the  $2p$  orbitals. The justification for all of this is in a sense the first law of thermodynamics. Energy is a property and therefore its value is determined only by the final state of the system, not by the path taken to achieve that state, and the path can even be imaginary.
- E14.2(b)** It can be proven that if an arbitrary wavefunction is used to calculate the energy of a system, the value calculated is never less than the true energy. This is the variation principle. This principle allows us an enormous amount of latitude in constructing wavefunctions. We can continue modifying the wavefunctions in any arbitrary manner until we find a set that we feel provide an energy close to the true minimum in energy. Thus we can construct wavefunctions containing many parameters and then minimize the energy with respect to those parameters. These parameters may or may not have some chemical or physical significance. Of course, we might strive to construct trial wavefunctions that provide some chemical and physical insight and interpretation that we can perhaps visualize, but that is not essential. Examples of the mathematical steps involved are illustrated in Sections 14.6(c) and (d), *Justification* 14.3, and Section 14.7.
- E14.3(b)** These are all terms originally associated with the Huckel approximation used in the treatment of conjugated  $\pi$ -electron molecules, in which the  $\pi$ -electrons are considered independent of the  $\sigma$ -electrons.  $\pi$ -electron binding energy is the sum the energies of each  $\pi$ -electron in the molecule. The delocalization energy is the difference in energy between the conjugated molecule with  $n$  double bonds and the energy of  $n$  ethene molecules, each of which has one double bond. The  $\pi$ -bond formation energy is the energy released when a  $\pi$  bond is formed. It is obtained from the total  $\pi$ -electron binding energy by subtracting the contribution from the Coulomb integrals,  $\alpha$ .
- E14.4(b)** In *ab initio* methods an attempt is made to evaluate all integrals that appear in the secular determinant. Approximations are still employed, but these are mainly associated with the construction of the wavefunctions involved in the integrals. In semi-empirical methods, many of the integrals are expressed in terms of spectroscopic data or physical properties. Semi-empirical methods exist at several levels. At some levels, in order to simplify the calculations, many of the integrals are set equal to zero.
- The Hartree-Fock and DFT methods are similar in that they are both regarded as *ab initio* methods. In HF the central focus is the wavefunction whereas in DFT it is the electron density. They are both iterative self consistent methods in that the process are repeated until the energy and wavefunctions (HF) or energy and electron density (DFT) are unchanged to within some acceptable tolerance.

### Numerical exercises

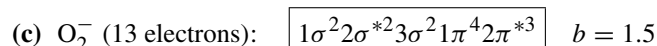
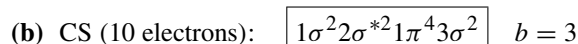
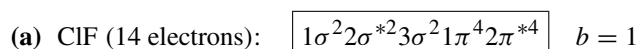
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- E14.5(b)** Use Fig. 14.23 for  $\text{H}_2^-$ , 14.30 for  $\text{N}_2$ , and 14.28 for  $\text{O}_2$ .

(a)  $\text{H}_2^-$  (3 electrons):  $\boxed{1\sigma^2 2\sigma^*1}$   $b = 0.5$



**E14.6(b)** CIF is isoelectronic with  $\text{F}_2$ , CS with  $\text{N}_2$ .



**E14.7(b)** Decide whether the electron added or removed increases or decreases the bond order. The simplest procedure is to decide whether the electron occupies or is removed from a bonding or antibonding orbital. We can draw up the following table, which denotes the orbital involved

	$\text{N}_2$	NO	$\text{O}_2$	$\text{C}_2$	$\text{F}_2$	CN
(a) $\text{AB}^-$	$2\pi^*$	$2\pi^*$	$2\pi^*$	$3\sigma$	$4\sigma^*$	$3\sigma$
Change in bond order	-1/2	-1/2	-1/2	+1/2	-1/2	+1/2
(b) $\text{AB}^+$	$3\sigma$	$2\pi^*$	$2\pi^*$	$1\pi$	$2\pi^*$	$3\sigma$
Change in bond order	-1/2	+1/2	+1/2	-1/2	+1/2	-1/2

(a) Therefore,  $\text{C}_2$  and CN are stabilized (have lower energy) by anion formation.

(b)  $\text{NO}$ ,  $\text{O}_2$  and  $\text{F}_2$  are stabilized by cation formation; in each of these cases the bond order increases.

**E14.8(b)** Figure 14.1 is based on Fig. 14.28 of the text but with Cl orbitals lower than Br orbitals. BrCl is likely to have a shorter bond length than  $\text{BrCl}^-$ ; it has a bond order of 1, while  $\text{BrCl}^-$  has a bond order of  $\frac{1}{2}$ .

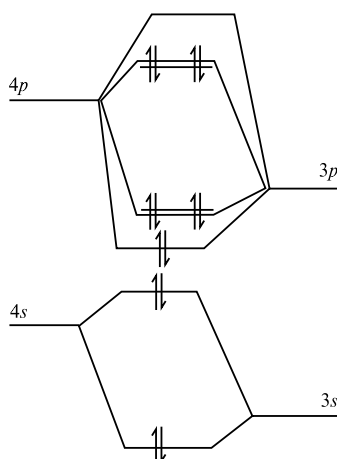
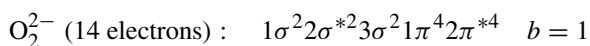
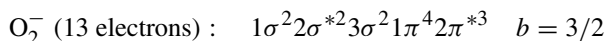
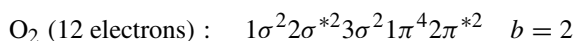
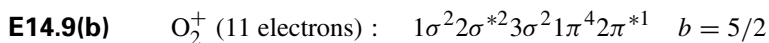


Figure 14.1

Each electron added to  $O_2^+$  is added to an antibonding orbital, thus increasing the length. So the sequence  $O_2^+, O_2, O_2^-, O_2^{2-}$  has progressively longer bonds.

$$\begin{aligned} \text{E14.10(b)} \quad \int \psi^2 d\tau &= N^2 \int (\psi_A + \lambda\psi_B)^2 d\tau = 1 = N^2 \int (\psi_A^2 + \lambda^2\psi_B^2 + 2\lambda\psi_A\psi_B) d\tau = 1 \\ &= N^2(1 + \lambda^2 + 2\lambda S) \quad \left[ \int \psi_A\psi_B d\tau = S \right] \end{aligned}$$

$$\text{Hence } N = \left( \frac{1}{1 + 2\lambda S + \lambda^2} \right)^{1/2}$$

**E14.11(b)** We seek an orbital of the form  $aA + bB$ , where  $a$  and  $b$  are constants, which is orthogonal to the orbital  $N(0.145A + 0.844B)$ . Orthogonality implies

$$\begin{aligned} \int (aA + bB)N(0.145A + 0.844B) d\tau &= 0 \\ 0 &= N \int [0.145aA^2 + (0.145b + 0.844a)AB + 0.844bB^2] d\tau \end{aligned}$$

The integrals of squares of orbitals are 1 and the integral  $\int AB d\tau$  is the overlap integral  $S$ , so

$$0 = (0.145 + 0.844S)a + (0.145S + 0.844)b \quad \text{so} \quad a = -\frac{0.145S + 0.844}{0.145 + 0.844S}b$$

This would make the orbitals orthogonal, but not necessarily normalized. If  $S = 0$ , the expression simplifies to

$$a = -\frac{0.844}{0.145}b$$

and the new orbital would be normalized if  $a = 0.844N$  and  $b = -0.145N$ . That is

$$N(0.844A - 0.145B)$$

**E14.12(b)** The trial function  $\psi = x^2(L - 2x)$  does not obey the boundary conditions of a particle in a box, so it is not appropriate. In particular, the function does not vanish at  $x = L$ .

**E14.13(b)** The variational principle says that the minimum energy is obtained by taking the derivate of the trial energy with respect to adjustable parameters, setting it equal to zero, and solving for the parameters:

$$E_{\text{trial}} = \frac{3a\hbar^2}{2\mu} - \frac{e^2}{\epsilon_0} \left( \frac{a}{2\pi^3} \right)^{1/2} \quad \text{so} \quad \frac{dE_{\text{trial}}}{da} = \frac{3\hbar^2}{2\mu} - \frac{e^2}{2\epsilon_0} \left( \frac{1}{2\pi^3 a} \right)^{1/2} = 0.$$

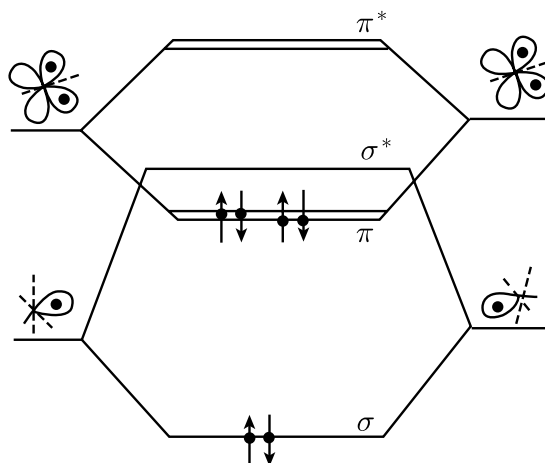
Solving for  $a$  yields:

$$\frac{3\hbar^2}{2\mu} = \frac{e^2}{2\epsilon_0} \left( \frac{1}{2\pi^3 a} \right)^{1/2} \quad \text{so} \quad a = \left( \frac{\mu e^2}{3\hbar^2 \epsilon_0} \right)^2 \left( \frac{1}{2\pi^3} \right) = \frac{\mu^2 e^4}{18\pi^3 \hbar^4 \epsilon_0^2}.$$

Substituting this back into the trial energy yields the minium energy:

$$E_{\text{trial}} = \frac{3\hbar^2}{2\mu} \left( \frac{\mu^2 e^4}{18\pi^3 \hbar^4 \epsilon_0^2} \right) - \frac{e^2}{\epsilon_0} \left( \frac{\mu^2 e^4}{18\pi^3 \hbar^4 \epsilon_0^2 \cdot 2\pi^3} \right)^{1/2} = \frac{-\mu e^4}{12\pi^3 \epsilon_0^2 \hbar^2}.$$

**E14.14(b)** The molecular orbitals of the fragments and the molecular orbitals that they form are shown in Fig. 14.2.



**Figure 14.2**

**E14.15(b)** We use the molecular orbital energy level diagram in Fig. 14.38. As usual, we fill the orbitals starting with the lowest energy orbital, obeying the Pauli principle and Hund's rule. We then write

(a)  $C_6H_6^-$  (7 electrons):  $a_{2u}^2 e_{1g}^4 e_{2u}^1$

$$E = 2(\alpha + 2\beta) + 4(\alpha + \beta) + (\alpha - \beta) = 7\alpha + 7\beta$$

(b)  $C_6H_6^+$  (5 electrons):  $a_{2u}^2 e_{1g}^3$

$$E = 2(\alpha + 2\beta) + 3(\alpha + \beta) = 5\alpha + 7\beta$$

**E14.16(b)** The secular determinants from E14.16(a) can be diagonalized with the assistance of general-purpose mathematical software. Alternatively, programs specifically designed of Hückel calculations (such as the one at Australia's Northern Territory University, <http://www.smeps.ntu.edu.au/modules/mod3/interface.html>) can be used. In both molecules, 14  $\pi$ -electrons fill seven orbitals.

(a) In anthracene, the energies of the filled orbitals are  $\alpha + 2.41421\beta$ ,  $\alpha + 2.00000\beta$ ,  $\alpha + 1.41421\beta$  (doubly degenerate),  $\alpha + 1.00000\beta$  (doubly degenerate), and  $\alpha + 0.41421\beta$ , so the total energy is  $14\alpha + 19.31368\beta$  and the  $\pi$  energy is  $19.31368\beta$ .

(b) For phenanthrene, the energies of the filled orbitals are  $\alpha + 2.43476\beta$ ,  $\alpha + 1.95063\beta$ ,  $\alpha + 1.51627\beta$ ,  $\alpha + 1.30580\beta$ ,  $\alpha + 1.14238\beta$ ,  $\alpha + 0.76905\beta$ ,  $\alpha + 0.60523$ , so the total energy is  $14\alpha + 19.44824\beta$  and the  $\pi$  energy is  $19.44824\beta$ .

## Solutions to problems

### Solutions to numerical problems

**P14.1**  $\psi_A = \cos kx$  measured from A,  $\psi_B = \cos k'(x - R)$  measuring  $x$  from A.

Then, with  $\psi = \psi_A + \psi_B$

$$\psi = \cos kx + \cos k'(x - R) = \cos kx + \cos k'R \cos k'x + \sin k'R \sin k'x$$

$$[\cos(a - b) = \cos a \cos b + \sin a \sin b]$$

$$(a) \quad k = k' = \frac{\pi}{2R}; \quad \cos k'R = \cos \frac{\pi}{2} = 0; \quad \sin k'R = \sin \frac{\pi}{2} = 1$$

$$\psi = \cos \frac{\pi x}{2R} + \sin \frac{\pi x}{2R}$$

For the midpoint,  $x = \frac{1}{2}R$ , so  $\psi\left(\frac{1}{2}R\right) = \cos \frac{1}{4}\pi + \sin \frac{1}{4}\pi = 2^{1/2}$  and there is constructive interference ( $\psi > \psi_A, \psi_B$ ).

$$(b) \quad k = \frac{\pi}{2R}, \quad k' = \frac{3\pi}{2R}; \quad \cos k'R = \cos \frac{3\pi}{2} = 0, \quad \sin k'R = -1.$$

$$\psi = \cos \frac{\pi x}{2R} - \sin \frac{3\pi x}{2R}$$

For the midpoint,  $x = \frac{1}{2}R$ , so  $\psi\left(\frac{1}{2}R\right) = \cos \frac{1}{4}\pi - \sin \frac{3}{4}\pi = 0$  and there is destructive interference ( $\psi < \psi_A, \psi_B$ ).

**P14.5** We obtain the electron densities from  $\rho_+ = \psi_+^2$  and  $\rho_- = \psi_-^2$  with  $\psi_+$  and  $\psi_-$  as given in Problem 14.4

$$\rho_{\pm} = N_{\pm}^2 \left( \frac{1}{\pi a_0^3} \right) \{e^{-|z|/a_0} \pm e^{-|z-R|/a_0}\}^2$$

We evaluate the factors preceding the exponentials in  $\psi_+$  and  $\psi_-$

$$N_+ \left( \frac{1}{\pi a_0^3} \right)^{1/2} = 0.561 \times \left( \frac{1}{\pi \times (52.9 \text{ pm})^3} \right)^{1/2} = \frac{1}{1216 \text{ pm}^{3/2}}$$

$$\text{Likewise, } N_- \left( \frac{1}{\pi a_0^3} \right)^{1/2} = \frac{1}{621 \text{ pm}^{3/2}}$$

$$\text{Then } \rho_+ = \frac{1}{(1216)^2 \text{ pm}^3} \{e^{-|z|/a_0} + e^{-|z-R|/a_0}\}^2$$

$$\text{and } \rho_- = \frac{1}{(622)^2 \text{ pm}^3} \{e^{-|z|/a_0} + e^{-|z-R|/a_0}\}^2$$

The "atomic" density is

$$\begin{aligned} \rho &= \frac{1}{2} \{ \psi_{1s}(A)^2 + \psi_{1s}(B)^2 \} = \frac{1}{2} \times \left( \frac{1}{\pi a_0^3} \right) \{e^{-2r_A/a_0} + e^{-2r_B/a_0}\} \\ &= \frac{e^{-(2r_A/a_0)} + e^{-(2r_B/a_0)}}{9.30 \times 10^5 \text{ pm}^3} = \frac{e^{-(2|z|/a_0)} + e^{-(2|z-R|/a_0)}}{9.30 \times 10^5 \text{ pm}^3} \end{aligned}$$

The difference density is  $\delta\rho_{\pm} = \rho_{\pm} - \rho$

Draw up the following table using the information in Problem 14.4

$z/\text{pm}$	-100	-80	-60	-40	-20	0	20	40
$\rho_+ \times 10^7/\text{pm}^{-3}$	0.20	0.42	0.90	1.92	4.09	8.72	5.27	3.88
$\rho_- \times 10^7/\text{pm}^{-3}$	0.44	0.94	2.01	4.27	9.11	19.40	6.17	0.85
$\rho \times 10^7/\text{pm}^{-3}$	0.25	0.53	1.13	2.41	5.15	10.93	5.47	3.26
$\delta\rho_+ \times 10^7/\text{pm}^{-3}$	-0.05	-0.11	-0.23	-0.49	-1.05	-2.20	-0.20	0.62
$\delta\rho_- \times 10^7/\text{pm}^{-3}$	0.19	0.41	0.87	1.86	3.96	8.47	0.70	-2.40

$z/\text{pm}$	60	80	100	120	140	160	180	200
$\rho_+ \times 10^7/\text{pm}^{-3}$	3.73	4.71	7.42	5.10	2.39	1.12	0.53	0.25
$\rho_- \times 10^7/\text{pm}^{-3}$	0.25	4.02	14.41	11.34	5.32	2.50	1.17	0.55
$\rho \times 10^7/\text{pm}^{-3}$	3.01	4.58	8.88	6.40	3.00	1.41	0.66	0.31
$\delta\rho_+ \times 10^7/\text{pm}^{-3}$	0.71	0.13	-1.46	-1.29	-0.61	-0.29	-0.14	-0.06
$\delta\rho_- \times 10^7/\text{pm}^{-3}$	-2.76	-0.56	5.54	4.95	2.33	1.09	0.51	0.24

The densities are plotted in Fig. 14.3(a) and the difference densities are plotted in Fig. 14.3(b).

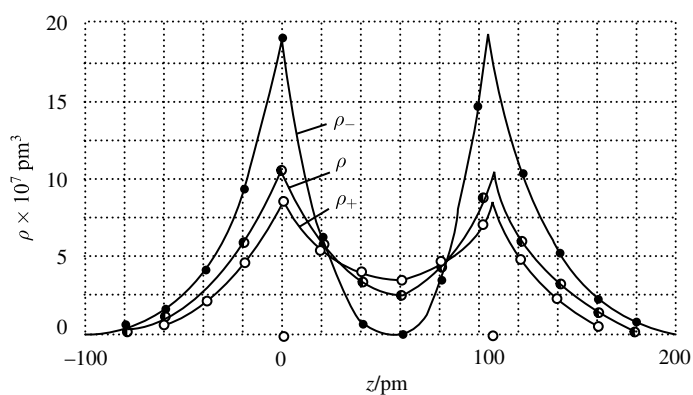


Figure 14.3(a)

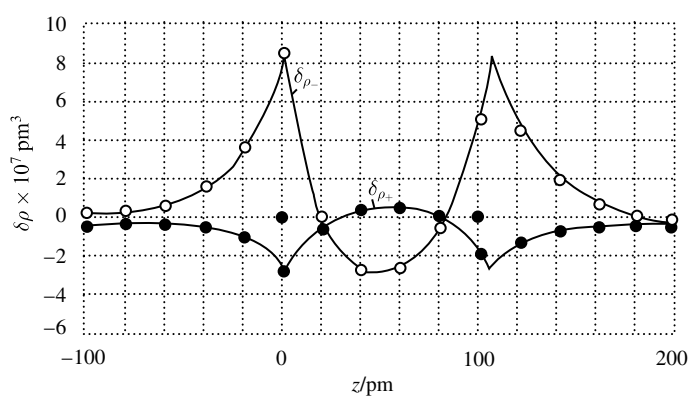
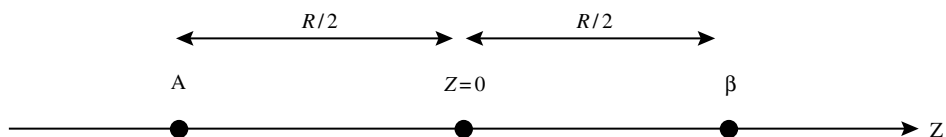


Figure 14.3(b)



- P14.6** (a) With spatial dimensions in units (multiples) of  $a_0$ , the atomic orbitals of atom A and atom B may be written in the form (eqn 13.24):

$$p_{z,A} = \frac{1}{4\sqrt{2\pi}}(z + R/2) e^{-[x^2+y^2+(z+R/2)^2]^{1/2}}/2$$

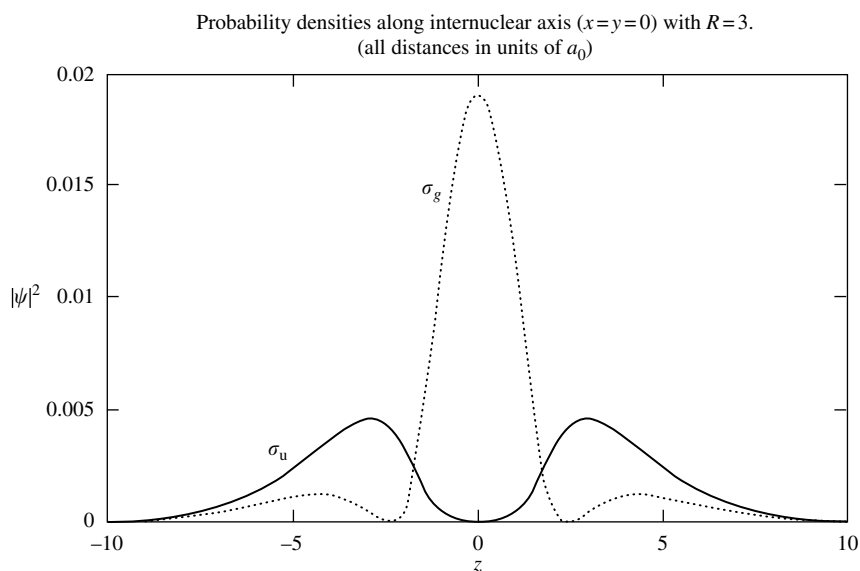
$$p_{z,B} = \frac{1}{4\sqrt{2\pi}}(z - R/2) e^{-[x^2+y^2+(z-R/2)^2]^{1/2}}/2$$

according to eqn 14.98, the LCAO-MO's have the form:

$$\psi_{\sigma_u} = \frac{p_{z,A} + p_{z,B}}{\sqrt{2(1+s)}} \quad \text{and} \quad \psi_{\sigma_g} = \frac{p_{z,A} - p_{z,B}}{\sqrt{2(1-s)}}$$

$$\text{where } s = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_{z,A} p_{z,B} dx dy dz \quad (\text{eqn 14.17})$$

computations and plots are readily prepared with mathematical software such as mathcad.



**Figure 14.4(a)**

- (b) With spatial dimensions in units of  $a_0$ , the atomic orbitals for the construction of  $\pi$  molecular orbitals are:

$$p_{x,A} = \frac{1}{4\sqrt{2\pi}} x e^{-[x^2+y^2+(z+R/2)^2]^{1/2}}/2$$

$R=3$

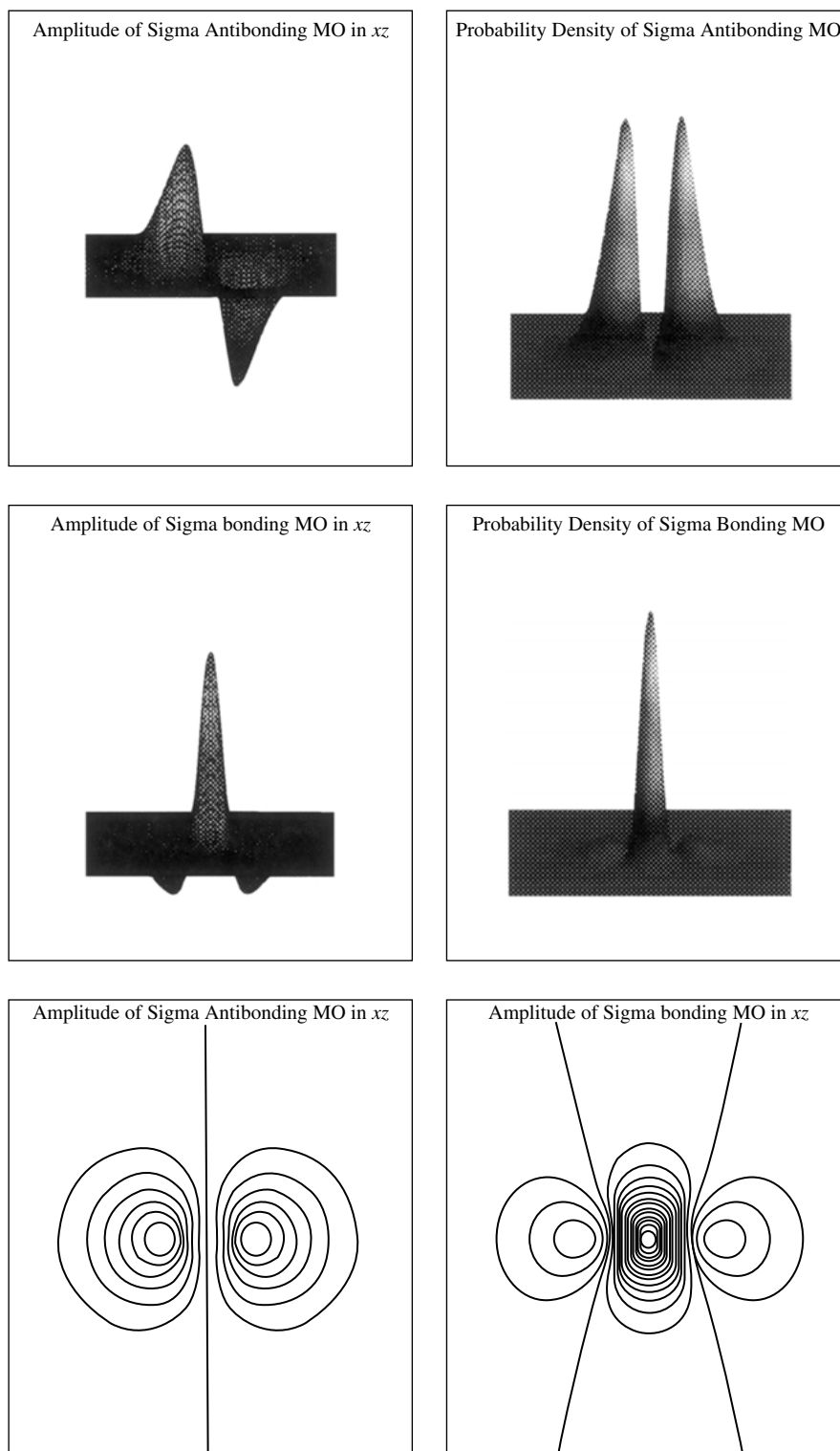


Figure 14.4(b)



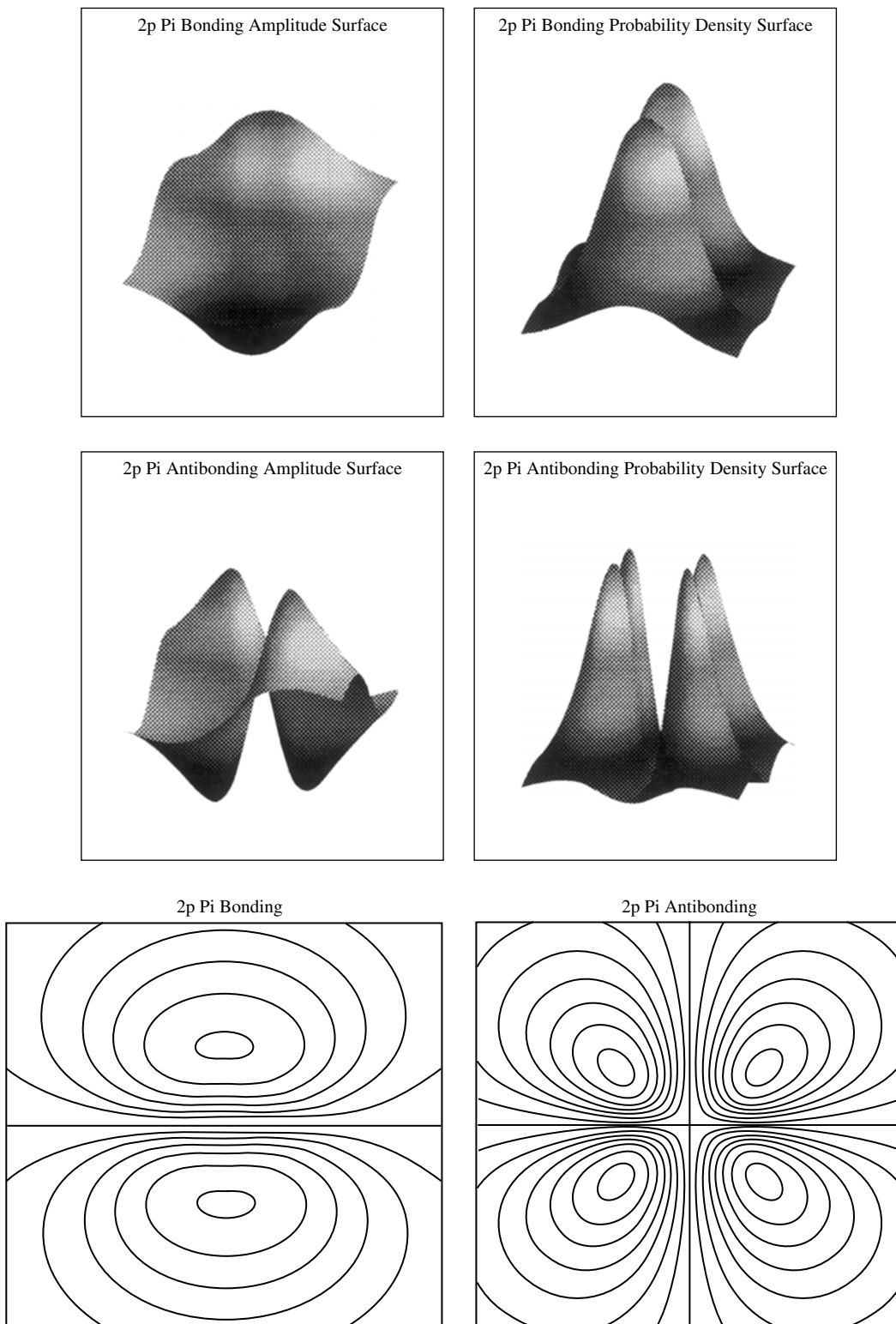
$R=3$ 

Figure 14.4(c)

$$p_{x,B} = \frac{1}{4\sqrt{2\pi}} x e^{-[x^2+y^2+(z-R/2)^2]^{1/2}/2}$$

The  $\pi$ -MO's are:

$$\psi_{\pi_u} = \frac{p_{x,A} + p_{x,B}}{\sqrt{2(1+s)}} \quad \text{and} \quad \psi_{\pi_g} = \frac{p_{x,A} - p_{x,B}}{\sqrt{2(1-s)}}$$

$$\text{where } s = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_{x,A} p_{x,B} dx dy dz$$

The various plot clearly show the constructive interference that makes a bonding molecular orbital. Nodal planes created by destructive interference are clearly seen in the antibonding molecular orbitals. When calculations and plots are produced for the  $R = 10$  case, constructive and destructive interference is seen to be much weaker because of the weak atomic orbital overlap.

**P14.7**  $P = |\psi|^2 d\tau \approx |\psi|^2 \delta\tau, \quad \delta\tau = 1.00 \text{ pm}^3$

(a) From Problem 14.5

$$\psi_+^2(z=0) = \rho_+(z=0) = 8.7 \times 10^{-7} \text{ pm}^{-3}$$

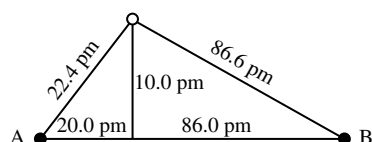
Therefore, the probability of finding the electron in the volume  $\delta\tau$  at nucleus A is

$$P = 8.6 \times 10^{-7} \text{ pm}^{-3} \times 1.00 \text{ pm}^3 = \boxed{8.6 \times 10^{-7}}$$

(b) By symmetry (or by taking  $z = 106 \text{ pm}$ )  $P = \boxed{8.6 \times 10^{-7}}$

(c) From Fig. 14.4(a),  $\psi_+^2\left(\frac{1}{2}R\right) = 3.7 \times 10^{-7} \text{ pm}^{-3}$ , so  $P = \boxed{3.7 \times 10^{-7}}$

(d) From Fig. 14.5, the point referred to lies at 22.4 pm from A and 86.6 pm from B.



**Figure 14.5**

$$\text{Therefore, } \psi = \frac{e^{-22.4/52.9} + e^{-86.6/52.9}}{1216 \text{ pm}^{3/2}} = \frac{0.65 + 0.19}{1216 \text{ pm}^{3/2}} = 6.98 \times 10^{-4} \text{ pm}^{-3/2}$$

$$\psi^2 = 4.9 \times 10^{-7} \text{ pm}^{-3}, \quad \text{so } P = \boxed{4.9 \times 10^{-7}}$$

For the antibonding orbital, we proceed similarly.

(a)  $\psi_-^2(z=0) = 19.6 \times 10^{-7} \text{ pm}^{-3}$  [Problem 14.5], so  $P = \boxed{2.0 \times 10^{-6}}$

(b) By symmetry,  $P = \boxed{2.0 \times 10^{-6}}$

(c)  $\psi_-^2\left(\frac{1}{2}R\right) = 0$ , so  $P = \boxed{0}$

(d) We evaluate  $\psi_-$  at the point specified in Fig. 14.5

$$\psi_- = \frac{0.65 - 0.19}{621 \text{ pm}^{3/2}} = 7.41 \times 10^{-4} \text{ pm}^{-3/2}$$

$$\psi_-^2 = 5.49 \times 10^{-7} \text{ pm}^{-3}, \quad \text{so } P = \boxed{5.5 \times 10^{-7}}$$

**P14.10** (a) To simplify the mathematical expressions, atomic units (a.u.) are used for which all distances are in units of  $a_0$  and  $e^2/(4\pi\epsilon_0 a_0)$  is the energy unit.

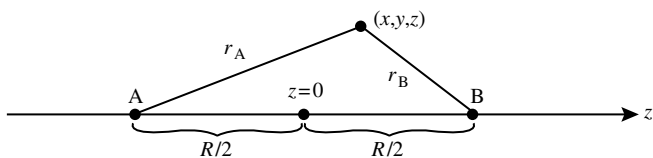


Figure 14.6(a)

$$A = \frac{1}{\sqrt{\pi}} e^{-r_A} = \frac{1}{\sqrt{\pi}} e^{-\sqrt{x^2+y^2+(z+R/2)^2}} \quad (\text{eqn 14.8})$$

$$B = \frac{1}{\sqrt{\pi}} e^{-r_B} = \frac{1}{\sqrt{\pi}} e^{-\sqrt{x^2+y^2+(z-R/2)^2}}$$

$$H = -\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \quad (\text{eqn 14.6})$$

$$\begin{aligned} \alpha &= \int AHA \, d\tau \quad (\text{coulomb integral, eqn 14.24}) \\ &= \int A \left( -\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) A \, d\tau \\ &= \underbrace{\int A \left( -\frac{\nabla^2}{2} - \frac{1}{r_A} \right) A \, d\tau}_{\substack{E_{1s} = -1/2 \\ (\text{eqns 13.13, 13.15})}} - \underbrace{\int \frac{A^2}{r_B} \, d\tau}_j + \underbrace{\frac{1}{R} \int A^2 \, d\tau}_{1/R} \quad (\text{Born-Oppenheimer approx.}) \end{aligned}$$

$$\alpha = \boxed{-\frac{1}{2} - j + \frac{1}{R}}$$

$$\begin{aligned} \beta &= \int AHB \, d\tau \quad (\text{Resonance integral, eqn 14.24}) \\ &= \int A \left( -\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) B \, d\tau \end{aligned}$$

$$\begin{aligned}
 &= \int A \underbrace{\left(-\frac{\nabla^2}{2} - \frac{1}{r_B}\right)}_{E_{1s}B = -\frac{1}{2}B} B \, d\tau - \underbrace{\int \frac{AB}{r_A} \, d\tau}_k + \frac{1}{R} \underbrace{\int AB \, d\tau}_S \\
 &= -\frac{1}{2} \underbrace{\int AB \, d\tau}_S - k + \frac{S}{R}
 \end{aligned}$$

$$\beta = \left(\frac{1}{R} - \frac{1}{2}\right) S - k$$

according to eqn 14.28,  $E_{1\sigma_g} = \frac{\alpha + \beta}{1 + S}$ . In order to numerically calculate  $E$  as a function of  $R$  we must devise a method by which  $S$ ,  $j$ , and  $k$  are evaluated with numerical integrations at specified  $R$  values. In the cartesian coordinate system drawn above,  $d\tau = dx \, dy \, dz$  and triple integrals are required. Numerical integration may proceed slowly with this coordinate system.

However, the symmetry of the wavefunction may be utilized to reduce the problem to double integrals by using the spherical coordinate system of Fig. 14.15 and eqn 14.9. The numerical integration will proceed more rapidly.

$$A = \frac{1}{\sqrt{\pi}} e^{-r} \quad \text{and} \quad B = \frac{1}{\sqrt{\pi}} e^{-r_B} = \frac{1}{\sqrt{\pi}} e^{-\sqrt{r^2 + R^2 - 2rR \cos\theta}} \quad (\text{eqn 14.9})$$

$$\begin{aligned}
 S(R) &= \int AB \, d\tau = \int_0^{2\pi} \int_{-\infty}^{\infty} \int_0^{\pi} A(r)B(r, \theta, R)r^2 \sin(\theta) \, d\theta \, dr \, d\phi \\
 &= 2\pi \int_{-\infty}^{\infty} \int_0^{\pi} A(r)B(r, \theta, R)r^2 \sin(\theta) \, d\theta \, dr
 \end{aligned}$$

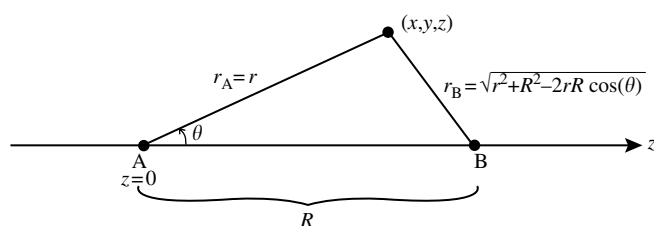


Figure 14.6(b)

The numerical integration,  $S_{\text{numerical}}(R)$ , may be performed with mathematical software (mathcad, TOL=0.001) and compared with the exact analytic solution (eqn 14.12),  $S_{\text{exact}}(R)$ . As shown in the following plot, the percentage deviation of the numerical integration is never more than 0.01% below  $R = L/a_0$ . This is satisfactory.

The numerical integrals of  $j$  and  $k$  are setup in the same way.

$$j(R) = 2\pi \int_{-\infty}^{\infty} \int_0^{\pi} \frac{A(r)^2 r^2 \sin(\theta)}{r_B(r, \theta, R)} \, d\theta \, dr$$

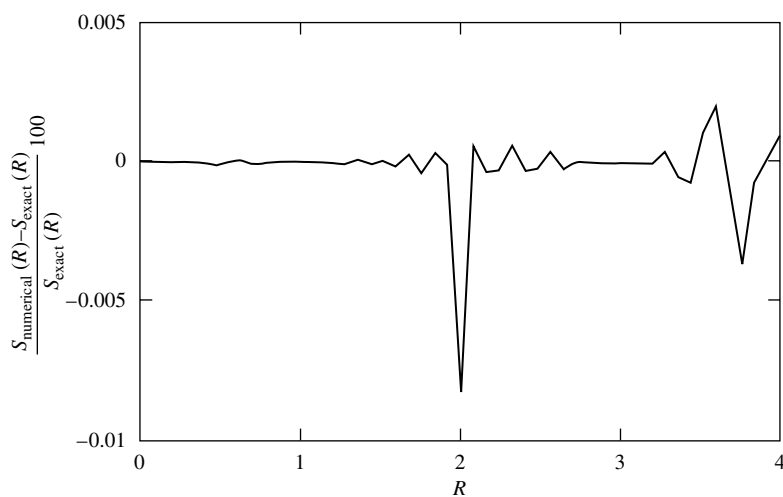


Figure 14.7(a)

$$k(R) = 2\pi \int_{-\infty}^{\infty} \int_0^{\pi} A(r)B(r, \theta, R)r \sin(\theta) d\theta dr$$

The coulomb and resonance integrals are:

$$\alpha(R) = -\frac{1}{2} - j(R) + \frac{1}{R} \quad \text{and} \quad \beta(R) = \left(\frac{1}{R} - \frac{1}{2}\right) S(R) - k(R)$$

$$\text{This orbital energy is: } E_{1\sigma_g}(R) = \frac{\alpha(R) + \beta(R)}{1 + S(R)}$$

This numerical calculation of the energy,  $E_{\text{numerical}}(R)$ , may be performed and compared with the exact analytic solution (eqns 14.11 and 14.12),  $E_{\text{exact}}(R)$ . The following plot shows that the numerical integration method correctly gives energy values within about 0.06% of the exact value in the range  $a_0 \leq R \leq 4a_0$ .

- (b) The minimum energy, as determined by a numerical computation, may be evaluated with several techniques. When the computations do not consume excessive lengths of time,  $E(R)$

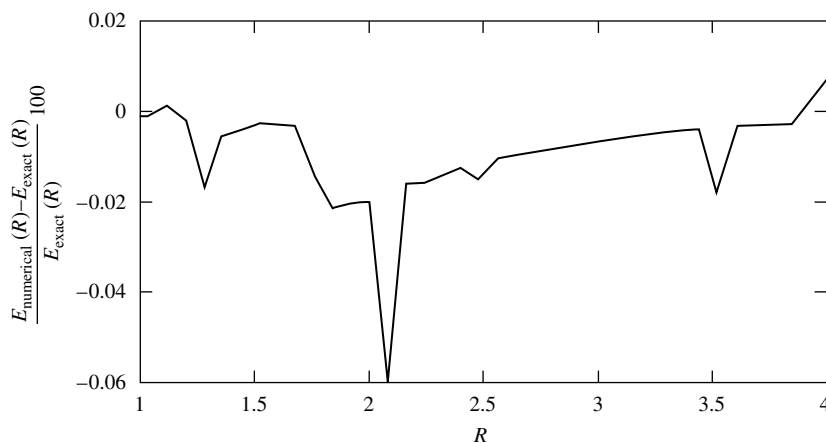


Figure 14.7(b)

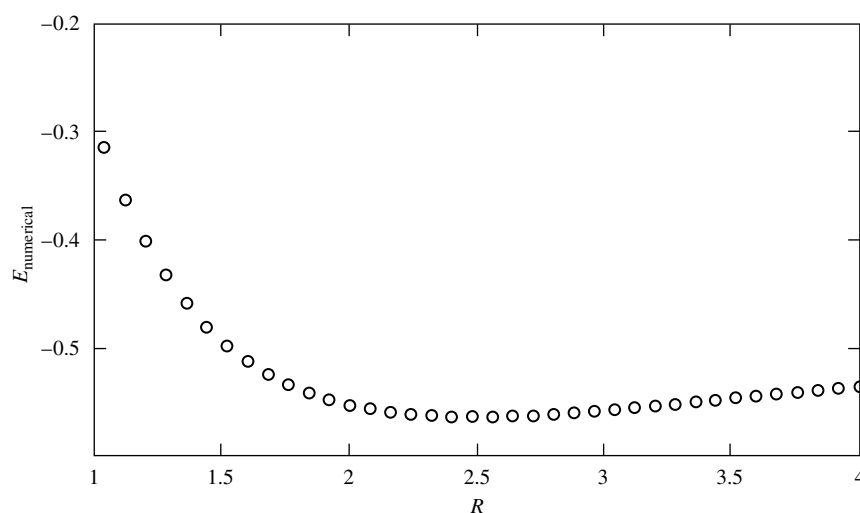


Figure 14.7(c)

may be calculated at many  $R$  values as is done in the above figure. The minimum energy and corresponding  $R$  may be read from a table of calculated values. Values of the figure give:  $E_{\min} = -0.5647(\text{a.u.}) = -15.367\text{e}$  and  $R_e = 2.4801(\text{a.u.}) = 131.24\text{ pm}$ . Alternatively, lengthy computations necessitate a small number of numerical calculations near the minimum after which an interpolation equation is devised for calculating  $E$  at any value of  $R$ . The minimum is determined by the criteria that  $\frac{d}{dR}E_{\text{interpolation}}(R) = 0$ .

The spectroscopic dissociation constant,  $D_e$ , for  $\text{H}_2^+$  is referenced to a zero electronic energy when a hydrogen atom and a proton are at infinite separation.

$$D_e = E_{\min} - (E_{\text{H}} + E_{\text{proton}}) = \left[ -0.5647 - \left( -\frac{1}{2} + 0 \right) \right] (\text{a.u.})$$

$$D_e = -0.0647 (\text{a.u.}) = 1.76 \text{ eV}$$

**P14.12** The internuclear distance  $\langle r \rangle_n \approx n^2 a_0$ , would be about twice the average distance ( $\approx 1.06 \times 10^6 \text{ pm}$ ) of a hydrogenic electron from the nucleus when in the state  $n = 100$ . This distance is so large that each of the following estimates are applicable.

Resonance integral,  $\beta \approx -\delta$  (where  $\delta \approx 0$ )

Overlap integral,  $S \approx \varepsilon$  (where  $\varepsilon \approx 0$ )

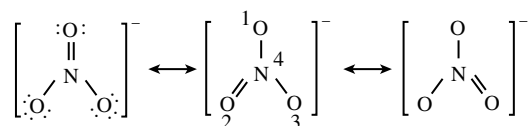
Coulomb integral,  $\alpha \approx E_{n=100}$  for atomic hydrogen

$$\begin{aligned} \text{Binding energy} &= 2\{E_+ - E_{n=100}\} \\ &= 2 \left\{ \frac{\alpha + \beta}{1 - S} - E_{n=100} \right\} \\ &= 2\{\alpha - E_{n=100}\} \\ &\approx 0 \end{aligned}$$

Vibrational force constant,  $k \approx 0$  because of the weak binding energy. Rotational constant,  $B = \frac{\hbar^2}{2hcl} = \frac{\hbar^2}{2hc\mu r_{\text{AB}}^2} \approx 0$  because  $r_{\text{AB}}^2$  is so large.

The binding energy is so small that thermal energies would easily cause the Rydberg molecule to break apart. It is not likely to exist for much longer than a vibrational period.

**P14.13** In the simple Hückel approximation



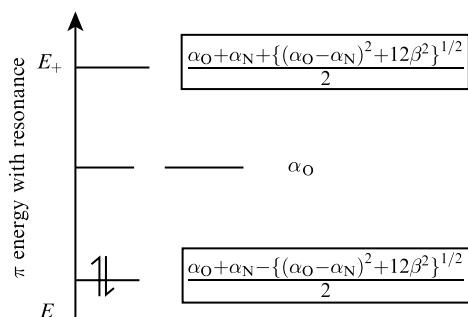
$$\begin{vmatrix} \alpha_{\text{O}} - E & 0 & 0 & \beta \\ 0 & \alpha_{\text{O}} - E & 0 & \beta \\ 0 & 0 & \alpha_{\text{O}} - E & \beta \\ \beta & \beta & \beta & \alpha_{\text{N}} - E \end{vmatrix} = 0$$

$$(E - \alpha_{\text{O}})^2 \times \left\{ (E - \alpha_{\text{O}}) \times (E - \alpha_{\text{N}}) - 3\beta^2 \right\} = 0$$

Therefore, the roots are

$$E - \alpha_{\text{O}} = 0 \text{ (twice)} \quad \text{and} \quad (E - \alpha_{\text{O}}) \times (E - \alpha_{\text{N}}) - 3\beta^2 = 0$$

Each equation is easily solved (Fig. 14.8(a)) for the permitted values of  $E$  in terms of  $\alpha_{\text{O}}$ ,  $\alpha_{\text{N}}$ , and  $\beta$ . The quadratic equation is applicable in the second case.



**Figure 14.8(a)**

In contrast, the  $\pi$  energies in the absence of resonance are derived for  $\text{N}=\text{O}$ , that is, just one of the three

$$\begin{vmatrix} \alpha_{\text{O}} - E & \beta \\ \beta & \alpha_{\text{N}} - E \end{vmatrix} = 0$$

Expanding the determinant and solving for  $E$  gives the result in Fig. 14.8(b).

$$\text{Delocalization energy} = 2 \{ E_- \text{ (with resonance)} - E_- \text{ (without resonance)} \}$$

$$= \left\{ (\alpha_{\text{O}} - \alpha_{\text{N}})^2 + 12\beta^2 \right\}^{1/2} - \left\{ (\alpha_{\text{O}} - \alpha_{\text{N}})^2 + 4\beta^2 \right\}^{1/2}$$

If  $\beta^2 \ll (\alpha_{\text{O}} - \alpha_{\text{N}})^2$ , then

$$\text{Delocalization energy} \approx \frac{4\beta^2}{(\alpha_{\text{O}} - \alpha_{\text{N}})}$$

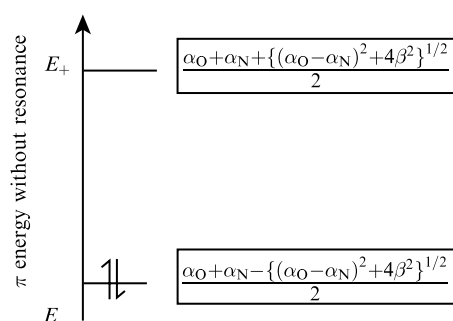


Figure 14.8(b)

- P14.17** In all of the molecules considered in P14.16, the HOMO was bonding with respect to the carbon atoms connected by double bonds, but antibonding with respect to the carbon atoms connected by single bonds. (The bond lengths returned by the modeling software suggest that it makes sense to talk about double bonds and single bonds. Despite the electron delocalization, the nominal double bonds are consistently shorter than the nominal single bonds.) The LUMO had just the opposite character, tending to weaken the C=C bonds but strengthen the C—C bonds. To arrive at this conclusion, examine the nodal surfaces of the orbitals. An orbital has an antibonding effect on atoms between which nodes occur, and it has a binding effect on atoms that lie within regions in which the orbital does not change sign. The  $\pi^* \leftarrow \pi$  transition, then, would lengthen and weaken the double bonds and shorten and strengthen the single bonds, bringing the different kinds of polyene bonds closer to each other in length and strength. Since each molecule has more double bonds than single bonds, there is an overall weakening of bonds.

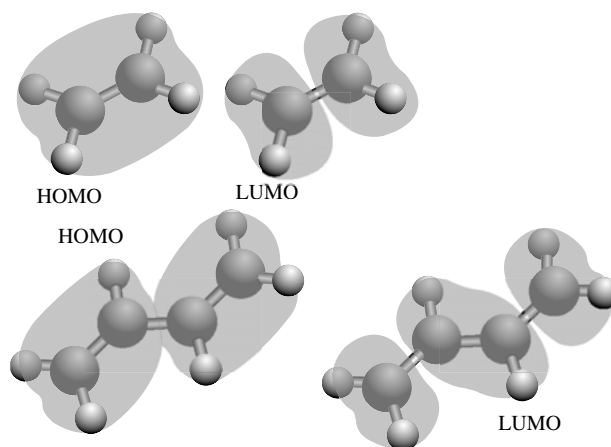


Figure 14.9(a)

### Solutions to theoretical problems

- P14.19** Since

$$\begin{aligned}\psi_{2s} &= R_{20}Y_{00} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} \times \left(2 - \frac{\rho}{2}\right) e^{-\rho/4} \times \left(\frac{1}{4\pi}\right)^{1/2} \quad [\text{Tables 13.1, 12.3}] \\ &= \frac{1}{4} \left(\frac{1}{2\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \times \left(2 - \frac{\rho}{2}\right) e^{-\rho/4}\end{aligned}$$



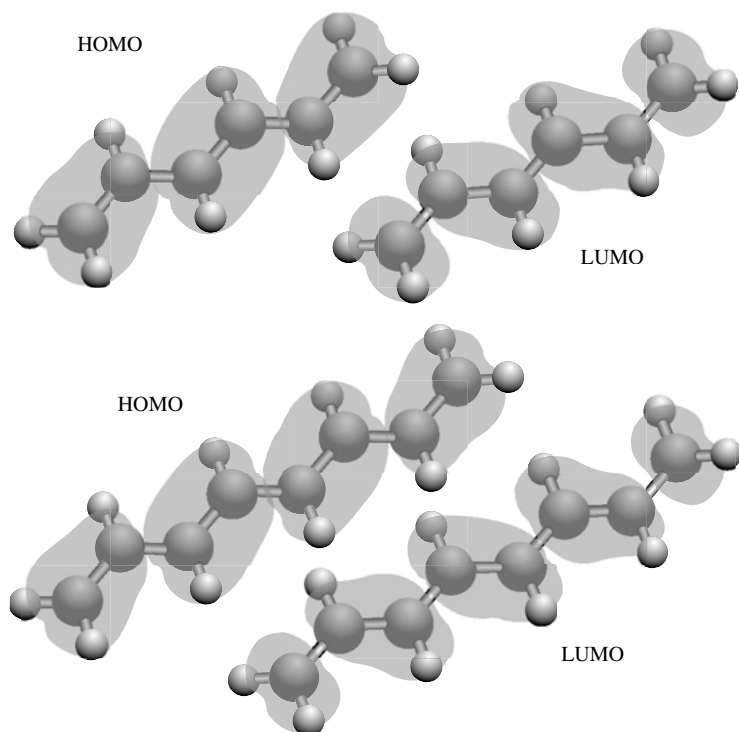


Figure 14.9(b)

$$\begin{aligned}
 \psi_{2p_x} &= \frac{1}{\sqrt{2}} R_{21}(Y_{1,1} - Y_{1,-1}) \text{ [Section 13.2]} \\
 &= \frac{1}{\sqrt{12}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{\rho}{2} e^{-\rho/4} \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta (e^{i\phi} + e^{-i\phi}) \text{ [Tables 13.1, 12.3]} \\
 &= \frac{1}{\sqrt{12}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{\rho}{2} e^{-\rho/4} \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta \cos \phi \\
 &= \frac{1}{4} \left(\frac{1}{2\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \frac{\rho}{2} e^{-\rho/4} \sin \theta \cos \phi \\
 \psi_{2p_y} &= \frac{1}{2i} R_{21}(Y_{1,1} + Y_{1,-1}) \text{ [Section 13.2]} \\
 &= \frac{1}{4} \left(\frac{1}{2\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \frac{\rho}{2} e^{-\rho/4} \sin \theta \sin \phi \text{ [Tables 13.1, 12.3]}
 \end{aligned}$$

Therefore,

$$\begin{aligned}
 \psi &= \frac{1}{\sqrt{3}} \times \frac{1}{4} \times \left(\frac{1}{\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \\
 &\quad \times \left(\frac{1}{\sqrt{2}} \left(2 - \frac{\rho}{2}\right) - \frac{1}{2} \frac{\rho}{2} \sin \theta \cos \phi + \frac{\sqrt{3}}{2} \frac{\rho}{2} \sin \theta \sin \phi\right) e^{-\rho/4} \\
 &= \frac{1}{4} \left(\frac{1}{6\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \times \left\{2 - \frac{\rho}{2} - \frac{1}{\sqrt{2}} \frac{\rho}{2} \sin \theta \cos \phi + \sqrt{\frac{3}{2}} \frac{\rho}{2} \sin \theta \sin \phi\right\} e^{-\rho/4}
 \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{4} \left( \frac{1}{6\pi} \right)^{1/2} \times \left( \frac{Z}{a_0} \right)^{3/2} \times \left\{ 2 - \frac{\rho}{2} \left( 1 + \frac{1}{\sqrt{2}} \sin \theta \cos \phi - \sqrt{\frac{3}{2}} \sin \theta \sin \phi \right) \right\} e^{-\rho/4} \\
&= \frac{1}{4} \left( \frac{1}{6\pi} \right)^{1/2} \times \left( \frac{Z}{a_0} \right)^{3/2} \times \left\{ 2 - \frac{\rho}{2} \left( 1 + \frac{[\cos \phi - \sqrt{3} \sin \phi]}{\sqrt{2}} \sin \theta \right) \right\} e^{-\rho/4}
\end{aligned}$$

The maximum value of  $\psi$  occurs when  $\sin \theta$  has its maximum value (+1), and the term multiplying  $\rho/2$  has its maximum negative value, which is  $-1$ , when  $\phi = 120^\circ$ .

**P14.21** The normalization constants are obtained from

$$\begin{aligned}
\int \psi^2 d\tau &= 1, \quad \psi = N(\psi_A \pm \psi_B) \\
N^2 \int (\psi_A \pm \psi_B)^2 d\tau &= N^2 \int (\psi_A^2 + \psi_B^2 \pm 2\psi_A\psi_B) d\tau = N^2(1 + 1 \pm 2S) = 1
\end{aligned}$$

$$\text{Therefore, } N^2 = \frac{1}{2(1 \pm S)}$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_A} - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_B} + \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{R}$$

$H\psi = E\psi$  implies that

$$-\frac{\hbar^2}{2m} \nabla^2 \psi - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_A} \psi - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_B} \psi + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} \psi = E\psi$$

Multiply through by  $\psi^*$  ( $= \psi$ ) and integrate using

$$\begin{aligned}
-\frac{\hbar^2}{2m} \nabla^2 \psi_A - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_A} \psi_A &= E_H \psi_A \\
-\frac{\hbar^2}{2m} \nabla^2 \psi_B - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_B} \psi_B &= E_H \psi_B
\end{aligned}$$

Then for  $\psi = N(\psi_A + \psi_B)$

$$N \int \psi \left( E_H \psi_A + E_H \psi_B - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_A} \psi_B - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_B} \psi_A + \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{R} (\psi_A + \psi_B) \right) d\tau = E$$

$$\text{hence } E_H \int \psi^2 d\tau + \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{R} \int \psi^2 d\tau - \frac{e^2}{4\pi\epsilon_0} N \int \psi \left( \frac{\psi_B}{r_A} + \frac{\psi_A}{r_B} \right) d\tau = E$$

$$\text{and so } E_H + \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{R} - \frac{e^2}{4\pi\epsilon_0} N^2 \int \left( \psi_A \frac{1}{r_A} \psi_B + \psi_B \frac{1}{r_B} \psi_A + \psi_A \frac{1}{r_B} \psi_A + \psi_B \frac{1}{r_A} \psi_B \right) d\tau = E$$

$$\text{Then use } \int \psi_A \frac{1}{r_A} \psi_B d\tau = \int \psi_B \frac{1}{r_B} \psi_A d\tau \text{ [by symmetry]} = V_2 / (e^2 / 4\pi\epsilon_0)$$

$$\int \psi_A \frac{1}{r_B} \psi_A d\tau = \int \psi_B \frac{1}{r_A} \psi_B d\tau \text{ [by symmetry]} = V_1 / (e^2 / 4\pi\epsilon_0)$$

$$\text{which gives } E_H + \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{R} - \left( \frac{1}{1+S} \right) \times (V_1 + V_2) = E$$

$$\text{or } E = \boxed{E_H - \frac{V_1 + V_2}{1 + S} + \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{R}} = E_+$$

as in Problem 14.8.

The analogous expression for  $E_-$  is obtained by starting from

$$\psi = N(\psi_A - \psi_B)$$

$$\text{with } N^2 = \frac{1}{2(1 - S)}$$

and the following through the step-wise procedure above. The result is

$$E = E_H - \frac{V_1 - V_2}{1 - S} + \frac{e^2}{4\pi\epsilon_0 R} = E_-$$

as in Problem 14.9.

**P14.22** (a)  $\psi = e^{-kr}$   $H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$

$$\int \psi^2 d\tau = \int_0^\infty r^2 e^{-2kr} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{\pi}{k^3}$$

$$\int \psi \frac{1}{r} \psi d\tau = \int_0^\infty r e^{-2kr} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{\pi}{k^2}$$

$$\int \psi \nabla^2 \psi d\tau = \int \psi \frac{1}{r} \frac{d^2}{dr^2} (r e^{-kr}) d\tau = \int \psi \left( k^2 - \frac{2k}{r} \right) \psi d\tau$$

$$= \frac{\pi}{k} - \frac{2\pi}{k} = -\frac{\pi}{k}$$

Therefore

$$\int \psi H \psi d\tau = \frac{\hbar^2}{2\mu} \times \frac{\pi}{k} - \frac{e^2}{4\pi\epsilon_0} \times \frac{\pi}{k^2}$$

and

$$E = \frac{\left(\frac{\hbar^2\pi}{2\mu k}\right) - \left(\frac{e^2\pi}{4\pi\epsilon_0 k^2}\right)}{\pi/k^3} = \frac{\hbar^2 k^2}{2\mu} - \frac{e^2 k}{4\pi\epsilon_0}$$

$$\frac{dE}{dk} = 2\left(\frac{\hbar^2}{2\mu}\right)k - \frac{e^2}{4\pi\epsilon_0} = 0 \quad \text{when } k = \frac{e^2\mu}{4\pi\epsilon_0\hbar^2}$$

The optimum energy is therefore

$$E = -\frac{e^4\mu}{32\pi^2\epsilon_0^2\hbar^2} = \boxed{-hc\mathcal{R}_H} \text{ the exact value}$$

(b)  $\psi = e^{-kr^2}$ ,  $H$  as before.

$$\int \psi^2 d\tau = \int_0^\infty e^{-2kr^2} r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{\pi}{2} \left(\frac{\pi}{2k^3}\right)^{1/2}$$

$$\int \psi \frac{1}{r} \psi d\tau = \int_0^\infty r e^{-2kr^2} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{\pi}{k}$$

$$\begin{aligned} \int \psi \nabla^2 \psi \, d\tau &= -2 \int \psi (3k - 2k^2 r^2) \psi \, d\tau \\ &= -2 \int_0^\infty (3kr^2 - 2k^2 r^4) e^{-2kr^2} \, dr \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi \\ &= -8\pi \left\{ \left( \frac{3k}{8} \right) \times \left( \frac{\pi}{2k^3} \right)^{1/2} - \frac{3k^2}{16} \left( \frac{\pi}{2k^5} \right)^{1/2} \right\} \end{aligned}$$

Therefore

$$E = \frac{3\hbar^2 k}{2\mu} - \frac{e^2 k^{1/2}}{\epsilon_0 (2\pi)^{1/2}}$$

$$\frac{dE}{dk} = 0 \quad \text{when} \quad k = \frac{e^4 \mu^2}{18\pi^3 \epsilon_0^2 \hbar^4}$$

and the optimum energy is therefore

$$E = -\frac{e^4 \mu}{12\pi^3 \epsilon_0^2 \hbar^2} = \boxed{-\frac{8}{3\pi} \times hc\mathcal{R}_H}$$

Since  $8/3\pi < 1$ , the energy in (a) is lower than in (b), and so the exponential wavefunction is better than the Gaussian.

- P14.23** (a) The variation principle selects parameters so that energy is minimized. We begin by finding the criteria for selecting  $\eta_{\text{best}}$  at constant  $R$  ( $\omega = \eta R$ )

$$\begin{aligned} \frac{dE_{\text{el}}(\eta_{\text{best}})}{d\eta} &= 0 \\ &= 2\eta F_1 + \eta^2 \frac{d\omega}{d\eta} \frac{dF_1}{d\omega} + F_2 + \eta \frac{d\omega}{d\eta} \frac{dF_2}{d\omega} \\ &= 2\eta F_1 + \eta^2 R \frac{dF_1}{d\omega} + F_2 + \eta R \frac{dF_2}{d\omega} \\ \eta_{\text{best}}(\omega) &= \frac{-F_2(\omega) - \omega \frac{dF_2(\omega)}{d\omega}}{2F_1(\omega) - \omega \frac{dF_1(\omega)}{d\omega}} \end{aligned}$$

We must now select  $R$  so as to minimize the total energy,  $E$ . Using Hartree atomic units for which length is in units of  $a_0$  and energy is in units of  $e^2/4\pi\epsilon_0 a_0$ , the total energy equation is:

$$E(\omega) = E_{\text{el}}(\omega) + \frac{1}{R(\omega)} = \eta_{\text{best}}^2 F_1(\omega) + \eta_{\text{best}}(\omega) F_2(\omega) + \frac{\eta_{\text{best}}(\omega)}{\omega}$$

where  $R(\omega) = \omega/\eta_{\text{best}}(\omega)$ . Mathematical software provides numerical methods for easy evaluation of derivatives within  $\eta_{\text{best}}(\omega)$ . We need only setup the software to calculate  $E(\omega)$  and  $R(\omega)$  over a range of  $\omega$  values. The value of  $R$  for which  $E$  is a minimum is the solution.

The following plot is generated with  $1.5 \leq \omega \leq 8.0$

The plots indicates an energy minimum at about  $-0.58$  au and an  $R_e$  value of about 2.0 au. More precise values can be determined by generating a plot over a more restricted  $\omega$  range, say,  $2.478 \leq \omega \leq 2.481$ . A table of  $\omega$ ,  $R(\omega)$ , and  $E(\omega)$  may be examined for the minimum energy and corresponding  $\omega$  and  $R$  values.

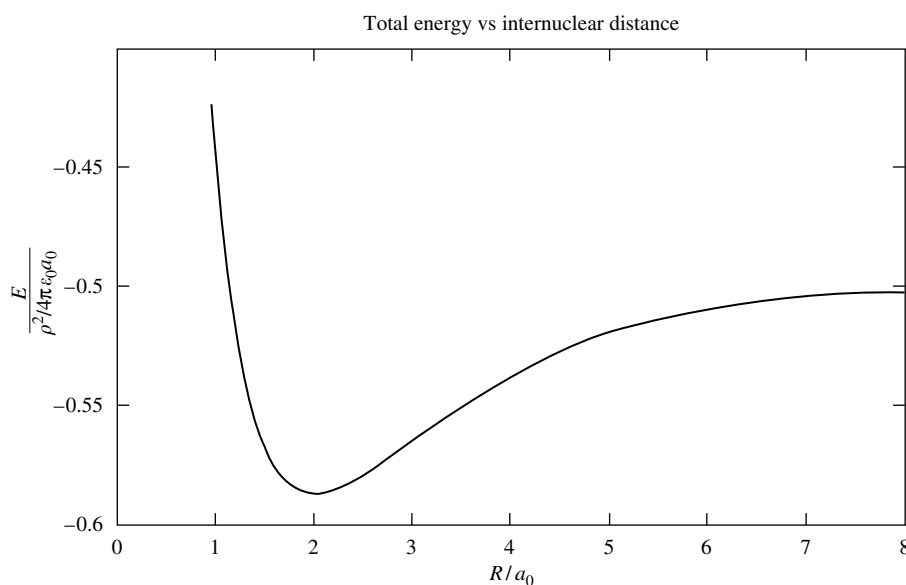


Figure 14.10

$$\omega_{\text{best}} = 2.4802a_0$$

$R_e = 2.0033a_0 = 106.011 \text{ pm}$ $E(R_e) = -0.5865 \text{ au} = -15.960 \text{ eV}$ $\eta_{\text{best}} = 1.2380$
---

$D_e$  for  $\text{H}^+$  is referenced to a zero electronic energy when a hydrogen atom and a proton are at rest at infinite separation.

$$\begin{aligned} D_e &= -[E(R_e) - E_{\text{H}}^+ - E_{\text{proton}}] \\ &= -[-0.5865 \text{ au} + 0.5 \text{ au} - 0 \text{ au}] \end{aligned}$$

$D_e = 0.0865 \text{ au} = 2.35 \text{ eV}$
---

The experimental value of  $D_e$  is 2.78 eV and that of  $R_e$  is  $2.00a_0$ . The equilibrium internuclear distance is in excellent agreement with the experimental value but the spectroscopic dissociation energy is off by 15.3%.

- (b) The virial theorem (Atkins Eq. 12.46) states that the potential energy is twice the negative of the kinetic energy. In the electronic energy equation,

$$E_{\text{el}} = \eta^2 F_1(\omega) + \eta F_2(\omega)$$

the term  $\eta^2 F_1(\omega)$  is the electron kinetic energy and, consequently, the total kinetic energy because the nuclei do not move the Born-Oppenheimer approximation. The term  $\eta F_2(\omega)$  is the electron potential energy only so the nuclear potential ( $1/R_e$  in au) must be added to get the total potential energy. The wavefunction approximation satisfies the virial theorem when

$$f = \eta_{\text{best}} F_2(\omega_{\text{best}}) + 1/R_e + 2\eta_{\text{best}}^2 F_1(\omega_{\text{best}}) = 0$$

Since numerology has been used, we will calculate the fraction  $|f/E(R_e)|$ . If the fraction is very small the virial theorem is satisfied.

$$\left| \frac{2\eta_{\text{best}}^2 F_1(\omega_{\text{best}}) + \eta_{\text{best}} F_2(\omega_{\text{best}}) + \frac{1}{R_e}}{E(R_e)} \right| = 4.996 \times 10^{-6}$$

The fraction is so small that we conclude that the virial theorem is satisfied.

$$(c) \quad \psi_A = \sqrt{\frac{\eta^3}{\pi a_0^3}} e^{-\eta r_A/a_0}; \quad \psi_B = \sqrt{\frac{\eta^2}{\pi a_0^3}} e^{-\eta r_B/a_0}$$

$$\begin{aligned} S &= \int \psi_A \psi_B d\tau = \frac{\eta^3}{\pi a_0^3} \int e^{-\eta(r_A+r_B)/a_0} d\tau \\ &= \frac{\eta^3}{\pi a_0^3} \int_0^{2\pi} \int_{-1}^1 \int_1^\infty e^{-\eta R\mu/a_0} \left\{ \frac{R^3}{8} (\mu^2 - \nu^2) \right\} d\mu d\nu d\phi \\ &= \frac{1}{\pi} \left( \frac{\eta R}{2a_0} \right)^3 \left\{ \begin{array}{l} \int_0^{2\pi} d\phi \int_{-1}^1 d\nu \int_1^\infty \mu^2 e^{-\eta R\mu/a_0} d\mu \\ - \int_0^{2\pi} d\phi \int_{-1}^1 \nu^2 d\nu \int_1^\infty e^{-\eta R\mu/a_0} d\mu \end{array} \right\} \\ &= \frac{1}{\pi} \left( \frac{\eta R}{2a_0} \right)^3 \left\{ \begin{array}{l} \left( \frac{4\pi a_0}{\eta^3 R^3} \right) (2a_0^2 + 2\eta R a_0 + \eta^2 R^2) e^{-\eta R/a_0} \\ - 2\pi \left( \frac{2}{3} \right) \left( \frac{a_0}{\eta R} \right) e^{-\eta R/a_0} \end{array} \right\} \\ &= \frac{1}{\pi} \left( \frac{\eta R}{2a_0} \right)^3 \left( \frac{2\pi a_0^3}{\eta^3 R^3} \right) \left\{ \begin{array}{l} \left( 4 + \frac{4\eta R}{a_0} + \frac{\eta^2 R^2}{a_0^2} \right) e^{-\eta R/a_0} \\ - \frac{2}{3} \left( \frac{\eta^2 R^2}{a_0^2} \right) e^{-\eta R/a_0} \end{array} \right\} \\ &= \frac{1}{4} \left( 4 + 4\omega + \frac{4}{3}\omega^2 \right) e^{-\omega} \quad \text{where } \omega = \eta R/a_0 \\ S &= \left( 1 + \omega + \frac{1}{3}\omega^2 \right) e^{-\omega} \end{aligned}$$

**P14.25** The secular determinant for a cyclic species  $H_N^m$  has the form

$$\begin{array}{ccccccccc} 1 & 2 & 3 & \dots & \dots & \dots & N-1 & N \\ \hline x & 1 & 0 & \dots & \dots & \dots & 0 & 1 \\ 1 & x & 1 & \dots & \dots & \dots & 0 & 0 \\ 0 & 1 & x & 1 & \dots & \dots & 0 & 0 \\ 0 & 0 & 1 & x & 1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & 1 \\ 1 & 0 & 0 & 0 & 0 & \dots & 1 & x \end{array}$$

where  $x = \frac{\alpha - E}{\beta}$  or  $E = \alpha - \beta x$

Expanding the determinant, finding the roots of the polynomial, and solving for the total binding energy yields the following table. Note that  $\alpha < 0$  and  $\beta < 0$ .

Species	Number of e <sup>-</sup>	Permitted x	Total binding energy
H <sub>4</sub>	4	-2,0,0,2	4 $\alpha$ + 4 $\beta$
H <sub>5</sub> <sup>+</sup>	4	$-2, \frac{1}{2}(1 - \sqrt{5}), \frac{1}{2}(1 - \sqrt{5}), \frac{1}{2}(1 + \sqrt{5}), \frac{1}{2}(1 + \sqrt{5})$	4 $\alpha$ + (3 + $\sqrt{5}$ ) $\beta$
H <sub>5</sub>	5	$-2, \frac{1}{2}(1 - \sqrt{5}), \frac{1}{2}(1 - \sqrt{5}), \frac{1}{2}(1 + \sqrt{5}), \frac{1}{2}(1 + \sqrt{5})$	5 $\alpha$ + $\frac{1}{2}(5 + 3\sqrt{5})\beta$
H <sub>5</sub> <sup>-</sup>	6	$-2, \frac{1}{2}(1 - \sqrt{5}), \frac{1}{2}(1 - \sqrt{5}), \frac{1}{2}(1 + \sqrt{5}), \frac{1}{2}(1 + \sqrt{5})$	6 $\alpha$ + (2 + 2 $\sqrt{5}$ ) $\beta$
H <sub>6</sub>	6	-2,-1,-1,1,1,2	6 $\alpha$ + 8 $\beta$
H <sub>7</sub> <sup>+</sup>	6	-2,-1.248,-1.248,-1.248,-1.248,0.445,0.445,0.445	6 $\alpha$ + 8.992 $\beta$

$$\text{H}_4 \rightarrow 2\text{H}_2 \quad \Delta_r U = 4(\alpha + \beta) - (4\alpha + 4\beta) = 0$$

$$\begin{aligned} \text{H}_5^+ \rightarrow \text{H}_2\text{H}_3^+ \quad \Delta_r U &= 2(\alpha + \beta) + (2\alpha + 4\beta) - (4\alpha + 5.236\beta) \\ &= 0.764\beta < 0 \end{aligned}$$

The above  $\Delta_r U$  values indicate that H<sub>4</sub> and H<sub>5</sub><sup>+</sup> are unstable.

$$\begin{aligned} \text{H}_5^- \rightarrow \text{H}_2 + \text{H}_3^- \quad \Delta_r U &= 2(\alpha + \beta) - (4\alpha + 2\beta) - (6\alpha + 6.472\beta) \\ &= -2.472\beta > 0 \end{aligned}$$

$$\begin{aligned} \text{H}_6 \rightarrow 3\text{H}_2 \quad \Delta_r U &= 6(\alpha + \beta) - (6\alpha + 8\beta) \\ &= -2\beta > 0 \end{aligned}$$

$$\begin{aligned} \text{H}_7^+ \rightarrow 2\text{H}_2 + \text{H}_3^+ \quad \Delta_r U &= 4(\alpha + \beta) + (2\alpha + 4\beta) - (6\alpha + 8.992\beta) \\ &= -0.992\beta > 0 \end{aligned}$$

The  $\Delta_r U$  values for H<sub>5</sub><sup>-</sup>, H<sub>6</sub>, and H<sub>7</sub><sup>+</sup> indicate that they are stable.

Species	Satisfies Hückel's 4n + 2 low energy rule	
	Correct number of e <sup>-</sup>	Stable
H <sub>4</sub> , 4e <sup>-</sup>	No	No
H <sub>5</sub> <sup>+</sup> , 4e <sup>-</sup>	No	No
H <sub>5</sub> <sup>-</sup> , 6e <sup>-</sup>	Yes	Yes
H <sub>6</sub> , 6e <sup>-</sup>	Yes	Yes
H <sub>7</sub> <sup>+</sup> , 6e <sup>-</sup>	Yes	Yes

Hückel's 4n + 2 rule successfully predicts the stability of hydrogen rings.