

LCAO Approximation for Diatomic Molecules

Kaito Takahashi

Born-Oppenheimer Approximation

Solve for the electron at a fixed nuclear geometry

$$\hat{H}^0(\mathbf{r}; \mathbf{R})\Psi_n^{el}(\mathbf{r}; \mathbf{R}) = \left[-\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + V(\mathbf{r}, \mathbf{R}) \right] \Psi_n^{el}(\mathbf{r}; \mathbf{R}) = E_n(\mathbf{R})\Psi_n^{el}(\mathbf{r}; \mathbf{R})$$

Calculate many nuclear geometries to obtain the potential energy surface

$$\hat{H}_{NU}(\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R}) = E_{el,NU}\chi_{n,v_n}^{NU}(\mathbf{R})$$

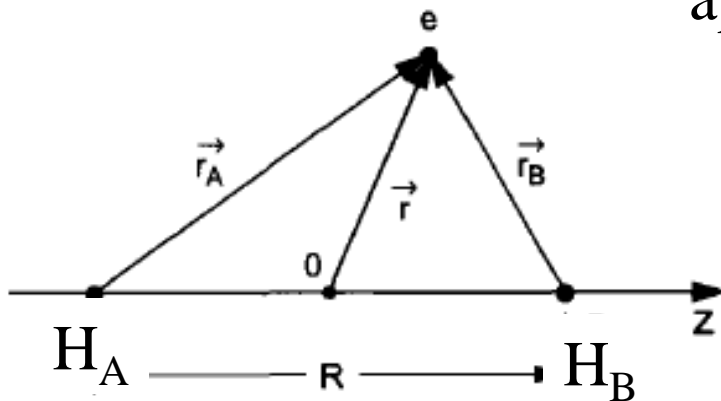
$$\hat{H}_{NU}(\mathbf{R}) = \left(-\frac{1}{2} \sum_{I=1}^N \frac{1}{M_I} \nabla_I^2 + V(\mathbf{R}) \right)$$

H_2^+ Most Simple Diatom

First find ways to solve the electronic wave function when given distance between to hydrogen nuclei

$$\left[-\frac{1}{2} \nabla^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_A|} - \frac{1}{|\mathbf{r}_B|} \right] \right] \Psi_n^{el}(\mathbf{r}; \mathbf{R}) = E_n(\mathbf{R}) \Psi_n^{el}(\mathbf{r}; \mathbf{R})$$

- Solve this problem:
1. Use exact solution
 2. Use **linear combination of atomic orbital** approximation



Atomic Orbital Review

TABLE 7.2

The Hydrogen-like Radial Wave Functions, $R_{nl}(r)$, for $n = 1, 2$, and 3 ^a

$$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\rho}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0} \right)^{3/2} (2 - \rho) e^{-\rho/2}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \rho e^{-\rho/2}$$

$$R_{30}(r) = \frac{2}{27} \left(\frac{Z}{3a_0} \right)^{3/2} (27 - 18\rho + 2\rho^2) e^{-\rho/3}$$

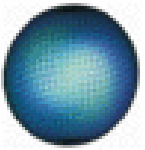
$$R_{31}(r) = \frac{1}{27} \left(\frac{2Z}{3a_0} \right)^{3/2} \rho(6 - \rho) e^{-\rho/3}$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}} \left(\frac{Z}{3a_0} \right)^{3/2} \rho^2 e^{-\rho/3}$$

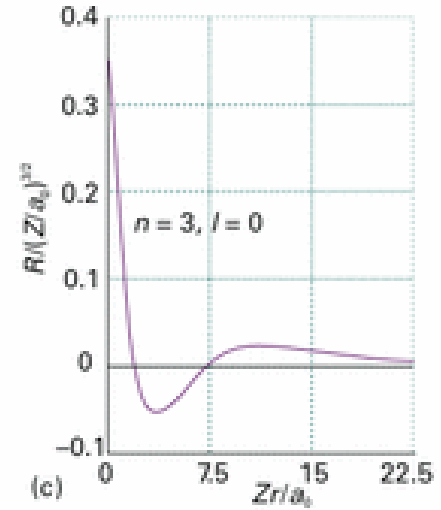
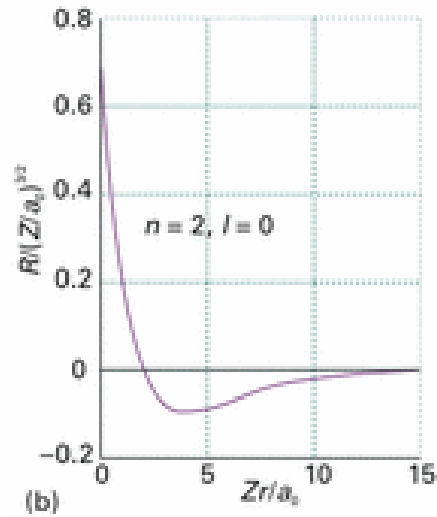
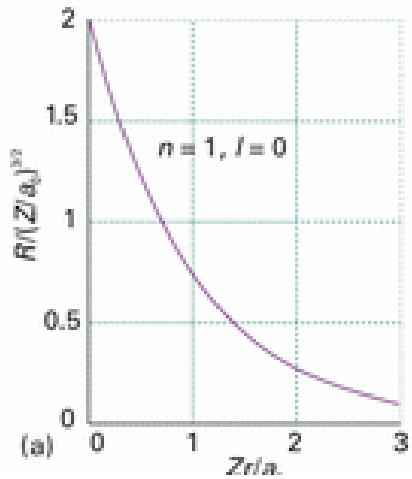
a. The quantity Z is the nuclear charge, and $\rho = Zr/a_0$, where a_0 is the Bohr radius.

Table 9.3 The spherical harmonics

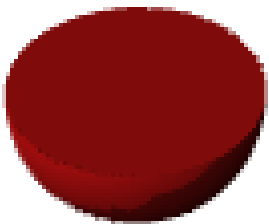
l	m_l	$Y_{lm_l}(\theta, \phi)$
0	0	$\left(\frac{1}{4\pi} \right)^{1/2}$
1	0	$\left(\frac{3}{4\pi} \right)^{1/2} \cos \theta$
	± 1	$\mp \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi} \right)^{1/2} (3 \cos^2 \theta - 1)$
	± 1	$\mp \left(\frac{15}{8\pi} \right)^{1/2} \cos \theta \sin \theta e^{\pm i\phi}$
	± 2	$\left(\frac{15}{32\pi} \right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi} \right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$
	± 1	$\mp \left(\frac{21}{64\pi} \right)^{1/2} (5 \cos^2 \theta - 1) \sin \theta e^{\pm i\phi}$
	± 2	$\left(\frac{105}{32\pi} \right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
	± 3	$\mp \left(\frac{35}{64\pi} \right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$



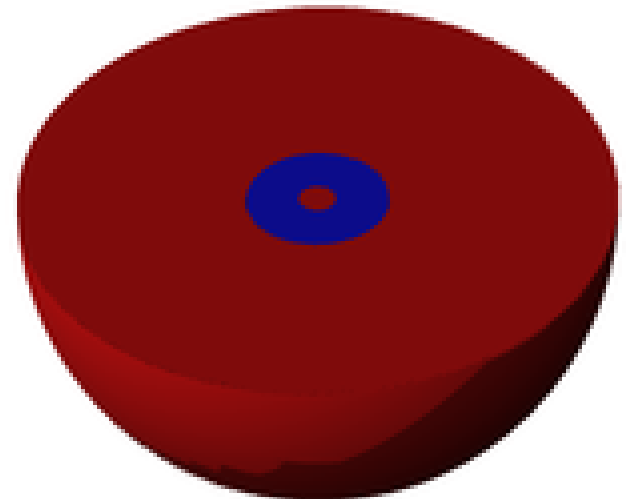
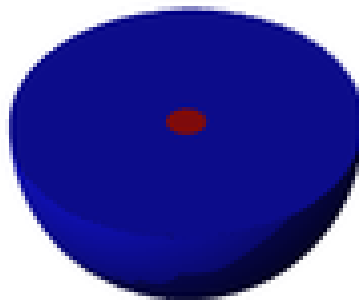
s Wavefunction



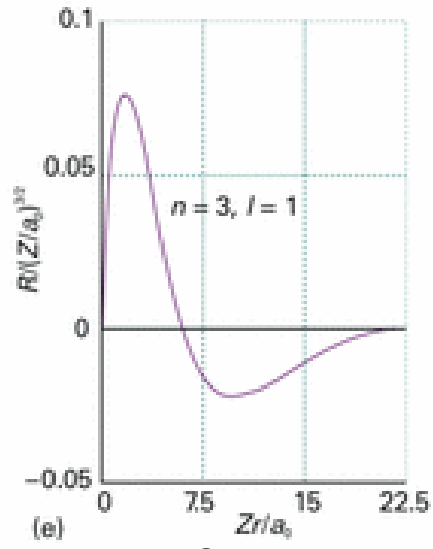
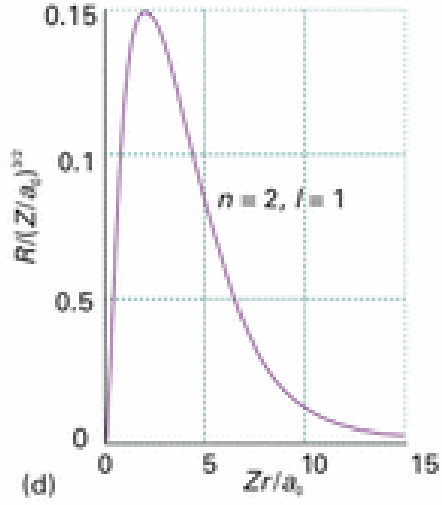
1s



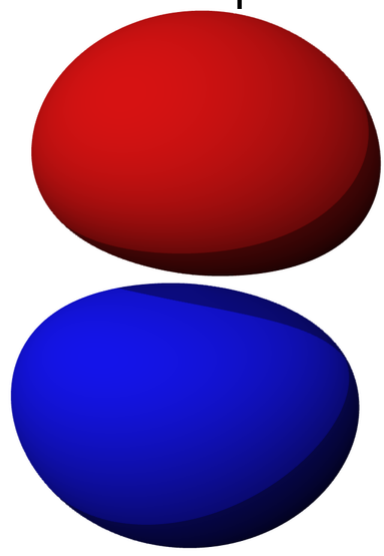
2s



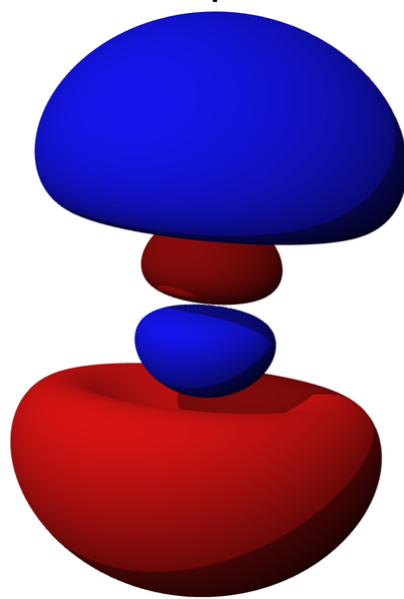
p Wavefunction



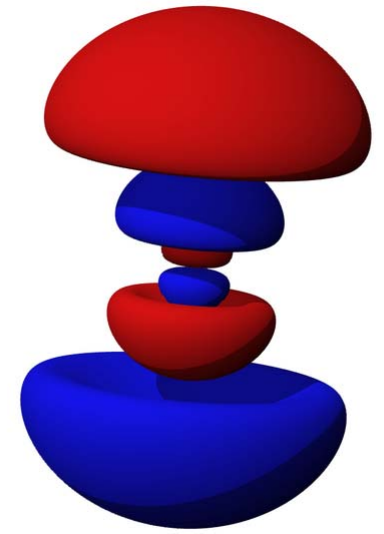
2p



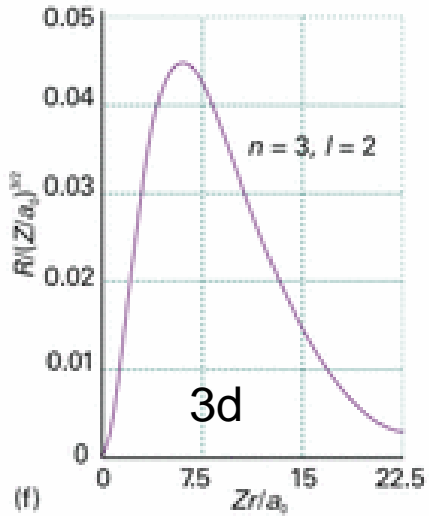
3p



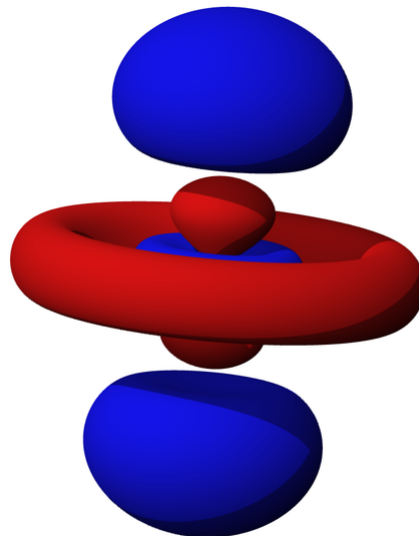
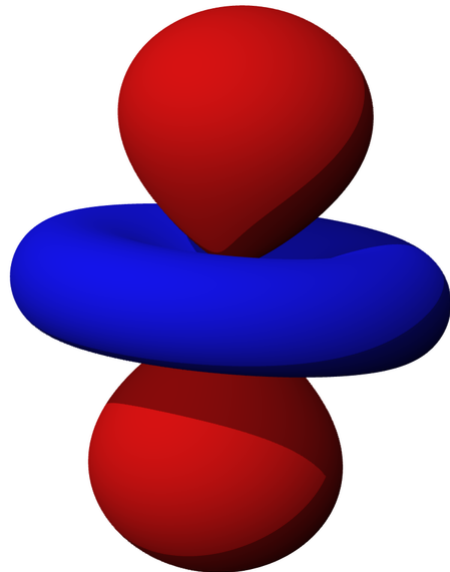
4p



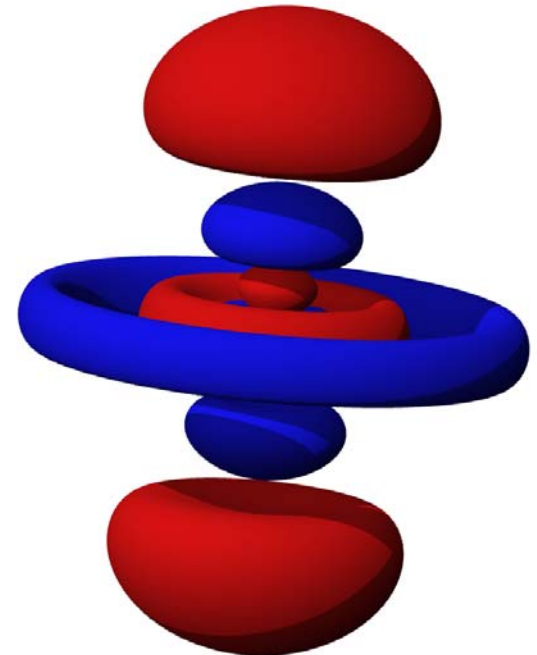
d Wavefunction



4d



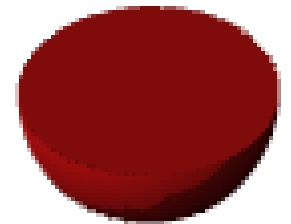
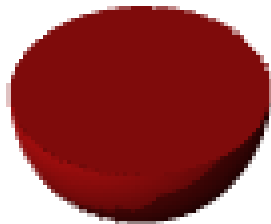
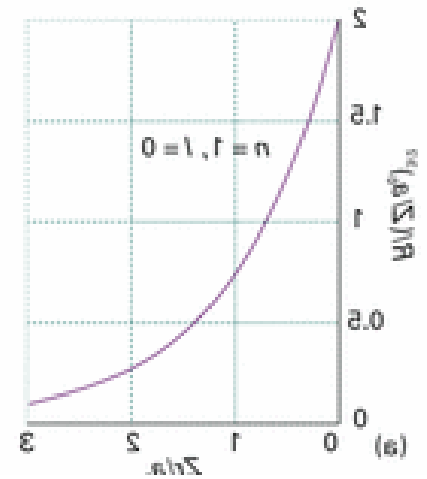
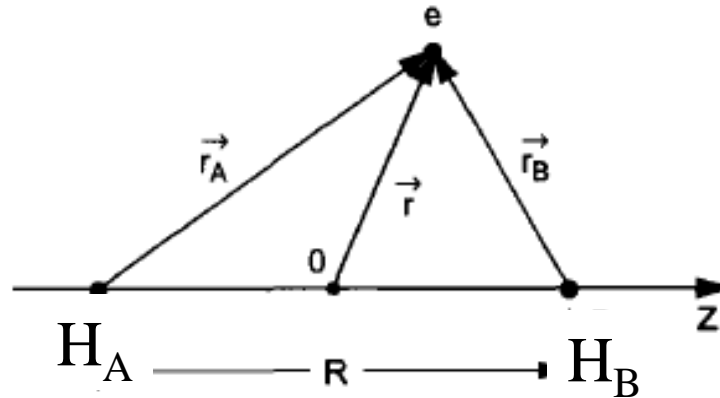
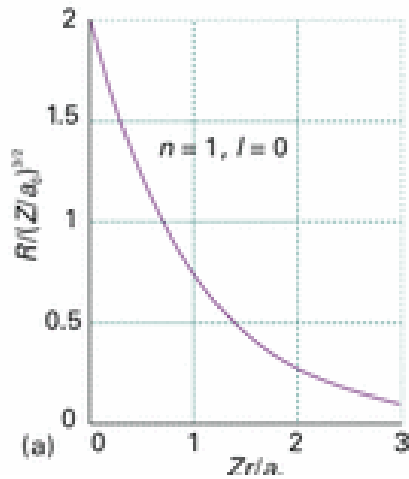
5d



LCAO

To make the molecular orbital (the electronic wavefunction for the molecule) let just add up each atomic orbital (electronic wavefunction for the atoms making the molecule)

$$\Psi_n^{el}(\mathbf{r}) = C_A \psi_{1S,A}(\mathbf{r}) + C_B \psi_{1S,B}(\mathbf{r})$$



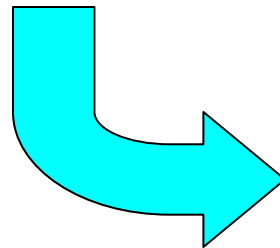
Variational Theory 1

$$E_{exact} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} < E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle}$$

$$\psi_{trial} = \sum_{i=1}^n c_i \phi_i \quad E_{trial} = \frac{\int \sum_{i=1}^n c_i^* \phi_i^* \hat{H} \sum_{j=1}^n c_j \phi_j d\tau}{\int \sum_{i=1}^n c_i^* \phi_i^* \sum_{j=1}^n c_j \phi_j d\tau} = \frac{\sum_i \sum_j c_i^* H_{ij} c_j}{\sum_i \sum_j c_i^* S_{ij} c_j}$$

$$H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau$$

$$S_{ij} = \int \phi_i^* \phi_j d\tau$$



$$\sum_i \sum_j c_i^* c_j (H_{ij} - E_{trial} S_{ij}) = 0$$

Variational Theory 2

$$\sum_i \sum_j c_i^* c_j (H_{ij} - E_{trial} S_{ij}) = 0$$

Take derivative with c_i^*

$$\sum_j c_j (H_{ij} - E_{trial} S_{ij}) + \sum_i \sum_j c_i^* c_j \left(-\frac{\partial E_{trial}}{\partial c_i^*} S_{ij} \right) = 0$$

Take derivative with c_j

$$\sum_i c_i^* (H_{ij} - E_{trial} S_{ij}) + \sum_i \sum_j c_i^* c_j \left(-\frac{\partial E_{trial}}{\partial c_j} S_{ij} \right) = 0$$

Due to stationary condition of the solution

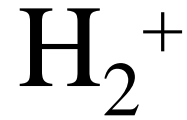
$$\frac{\partial E_{trial}}{\partial c_j} = 0; \quad \frac{\partial E_{trial}}{\partial c_i^*} = 0$$

Variational Theory

$$\sum_j c_j (H_{ij} - E_{trial} S_{ij}) = 0$$

$$\sum_i c_i^* (H_{ij} - E_{trial} S_{ij}) = 0$$

$$\begin{vmatrix} H_{11} - E_{trial} S_{11} & H_{12} - E_{trial} S_{12} & \dots & H_{1n} - E_{trial} S_{1n} \\ H_{21} - E_{trial} S_{21} & H_{22} - E_{trial} S_{22} & \dots & H_{2n} - E_{trial} S_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} - E_{trial} S_{n1} & H_{n2} - E_{trial} S_{n2} & \dots & H_{nn} - E_{trial} S_{nn} \end{vmatrix} = 0$$



$$\hat{H}\Psi_n^{el}(\mathbf{r}; \mathbf{R}) = \left[-\frac{1}{2}\nabla^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_A|} - \frac{1}{|\mathbf{r}_B|} \right] \right] \Psi_n^{el}(\mathbf{r}; \mathbf{R}) = E_n(\mathbf{R})\Psi_n^{el}(\mathbf{r}; \mathbf{R})$$

$$\Psi_n^{el}(\mathbf{r}; R) = C_A \psi_{1S,A}(\mathbf{r}; R) + C_B \psi_{1S,B}(\mathbf{r}; R) = C_A |A\rangle + C_B |B\rangle$$

$$\begin{vmatrix} H(R)_{AA} - E(R) & H(R)_{AB} - E(R)S(R) \\ H(R)_{BA} - E(R)S(R) & H(R)_{BB} - E(R) \end{vmatrix} = 0$$

$$H(R)_{AA} = \langle A | \hat{H} | A \rangle = \langle B | \hat{H} | B \rangle = H(R)_{BB}$$

$$H(R)_{AB} = \langle A | \hat{H} | B \rangle = \langle B | \hat{H} | A \rangle = H(R)_{BA}$$

$$S = \langle A | B \rangle = \langle B | A \rangle$$

$$\langle A | A \rangle = \langle B | B \rangle = 1$$

Overlap Integral

$$S(R) = \langle A | B \rangle = \langle B | A \rangle \text{ Overlap Integral (R dependent)}$$

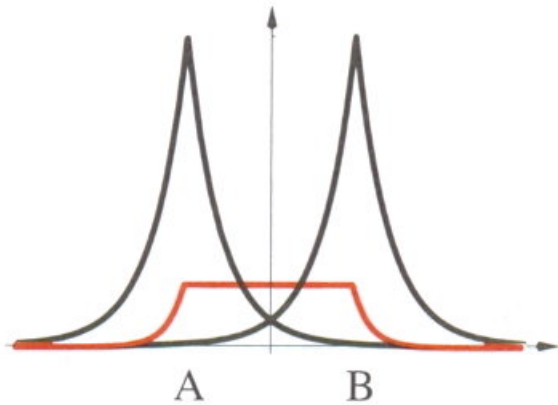


FIGURE 10.9

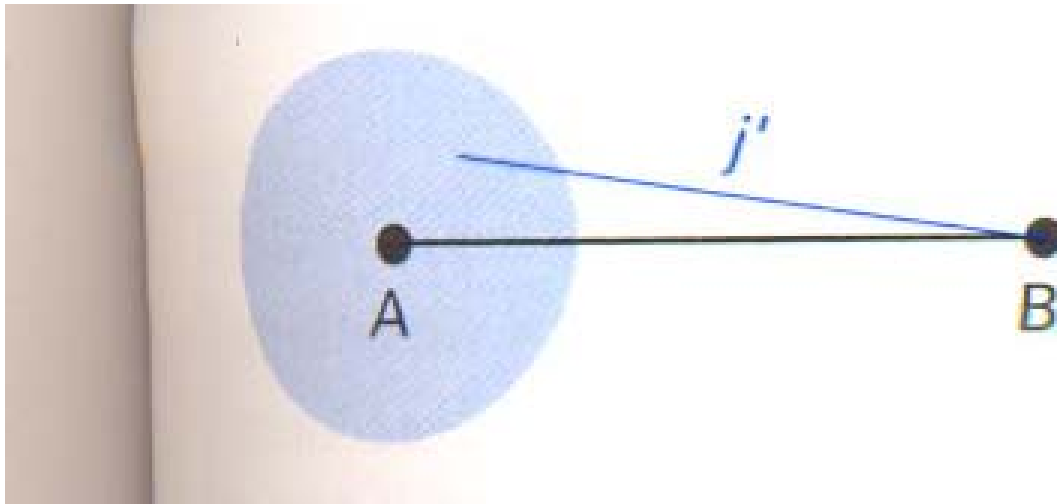
The overlap of the 1s orbitals centered on hydrogen nuclei located at A and B, a distance R apart. The orange curve is the product of the two orbitals.

$$S(R) = e^{-R} \left(1 + R + \frac{R^2}{3} \right)$$

Atomic Integral

$$\begin{aligned} H(R)_{AA} &= \langle A | \hat{H} | A \rangle = \left\langle A \left[-\frac{1}{2} \nabla^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_A|} - \frac{1}{|\mathbf{r}_B|} \right] \right] A \right\rangle \\ &= E_{1S} + \left\langle A \left| -\frac{1}{|\mathbf{r}_B|} \right| A \right\rangle + -\frac{1}{|\mathbf{R}|} \langle A | A \rangle \end{aligned}$$

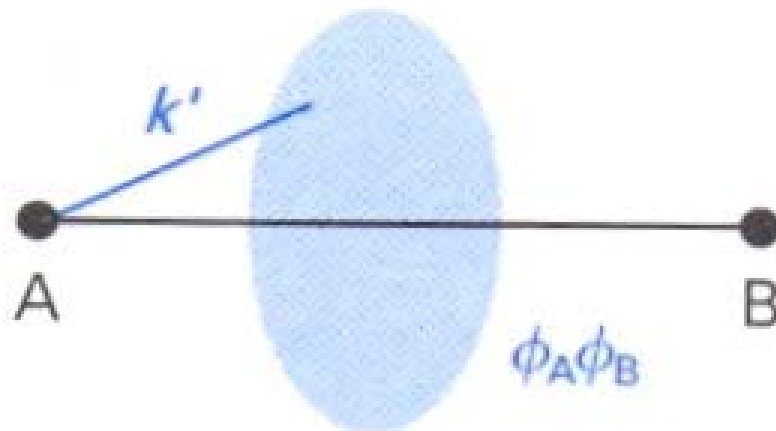
Electron is assigned one of the hydrogen orbitals: Coulomb Integral (Atomic Integral)



Exchange Integral

$$H(R)_{AB} = \langle A | \hat{H} | B \rangle = \left\langle A \left[-\frac{1}{2} \nabla^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_A|} - \frac{1}{|\mathbf{r}_B|} \right] \right] B \right\rangle$$
$$= \left\langle A \left| -\frac{1}{2} \nabla^2 \right| B \right\rangle + \left\langle A \left| -\frac{1}{|\mathbf{r}_A|} \right| B \right\rangle + \left\langle A \left| -\frac{1}{|\mathbf{r}_B|} \right| B \right\rangle - \frac{1}{|\mathbf{R}|} \langle A | B \rangle$$

Electron is assigned to both nuclei, or can exchange from one nuclei to the other :exchange integral (overlap charge integral)



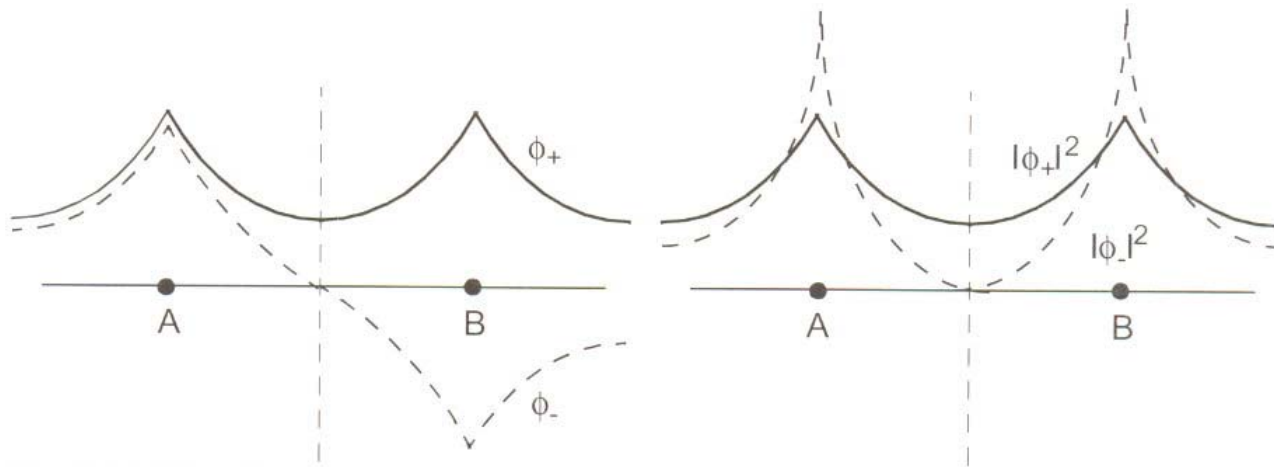
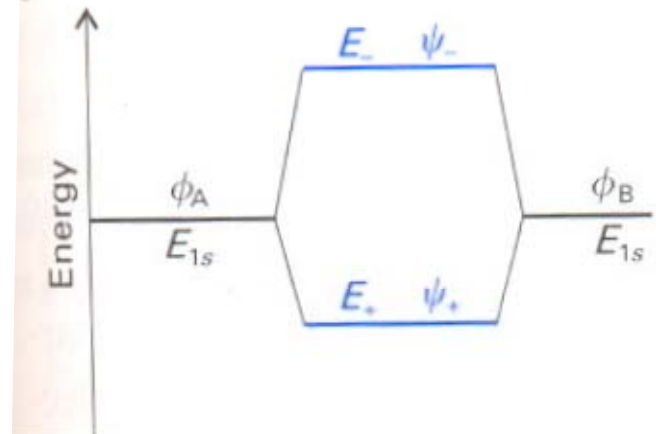
Solve Secular Equation

$$\begin{vmatrix} H(R)_{AA} - E(R) & H(R)_{AB} - E(R)S \\ H(R)_{BA} - E(R)S & H(R)_{BB} - E(R) \end{vmatrix} = 0$$

$$(H(R)_{AA} - E(R))^2 - (H(R)_{BA} - E(R)S(R))^2 = 0$$

$$E_{\pm}(R) = \frac{H(R)_{AA} \pm H(R)_{AB}}{1 \pm S(R)}$$

$$\Psi_{\pm} = |\pm\rangle = \frac{|A\rangle \pm |B\rangle}{\sqrt{2 \pm 2S}}$$



Bonding and Antibonding Orbital

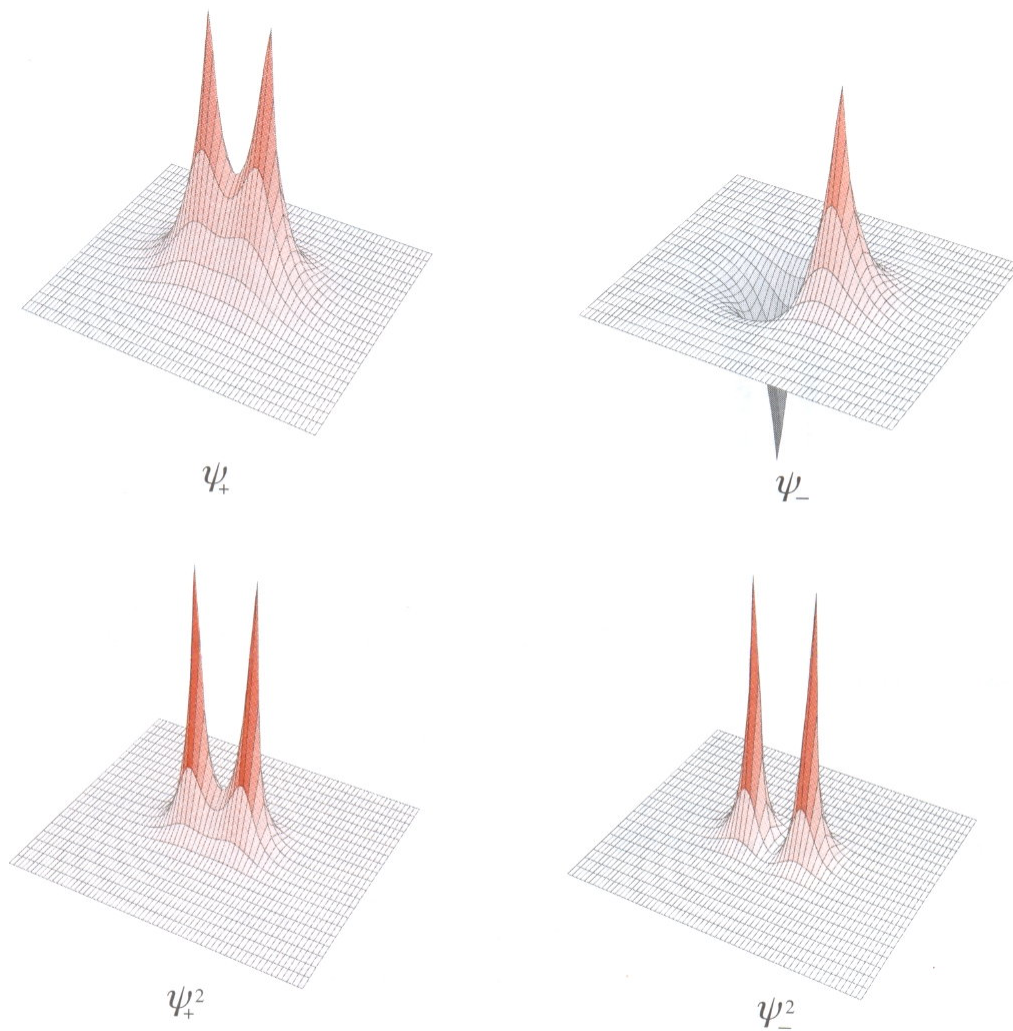


FIGURE 10.14
Surface plots of the molecular orbitals ψ_+ (a bonding orbital) and ψ_- (an antibonding orbital) and their squares.

Electron Density Difference

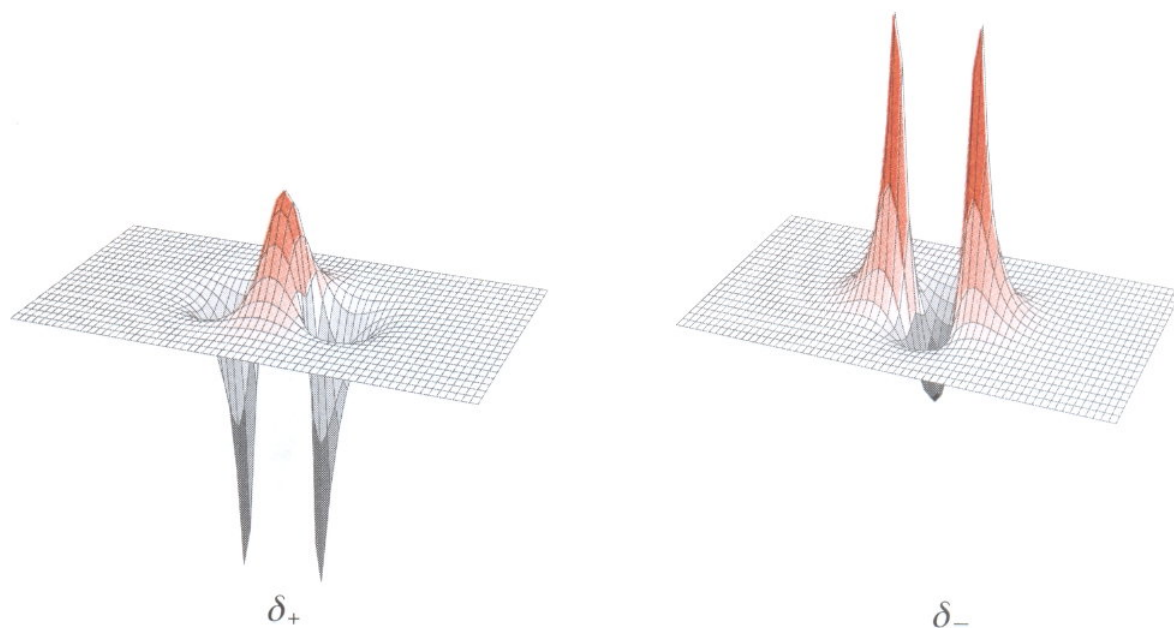
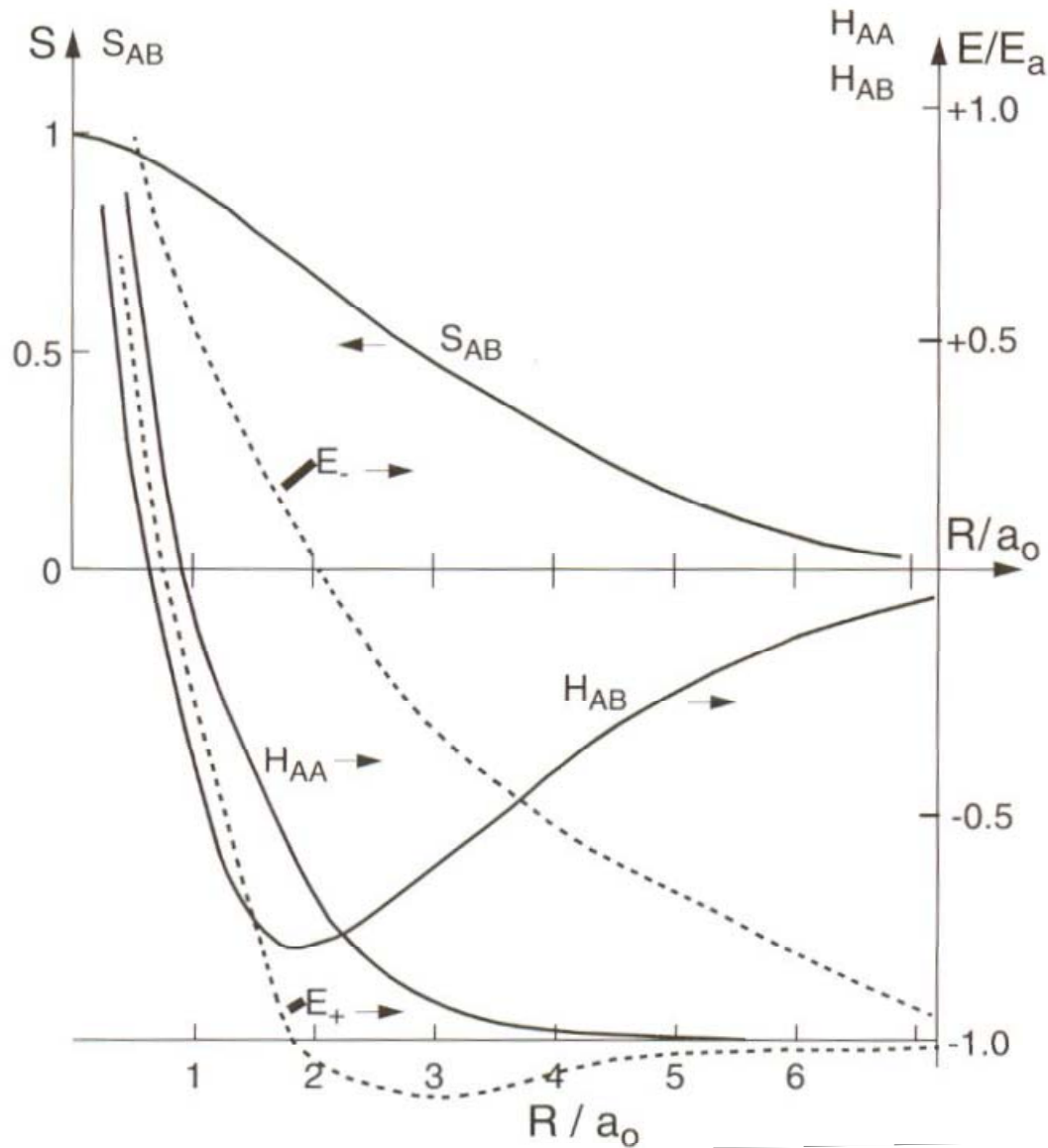


FIGURE 10.15

Surface plots of δ_+ and δ_- , the difference between the electron density in which the electron is delocalized over the two nuclei and the electron density in which the electron is localized on one of the nuclei.

R Dependence of Matrix Elements



Bonding Orbital Compare With Exact

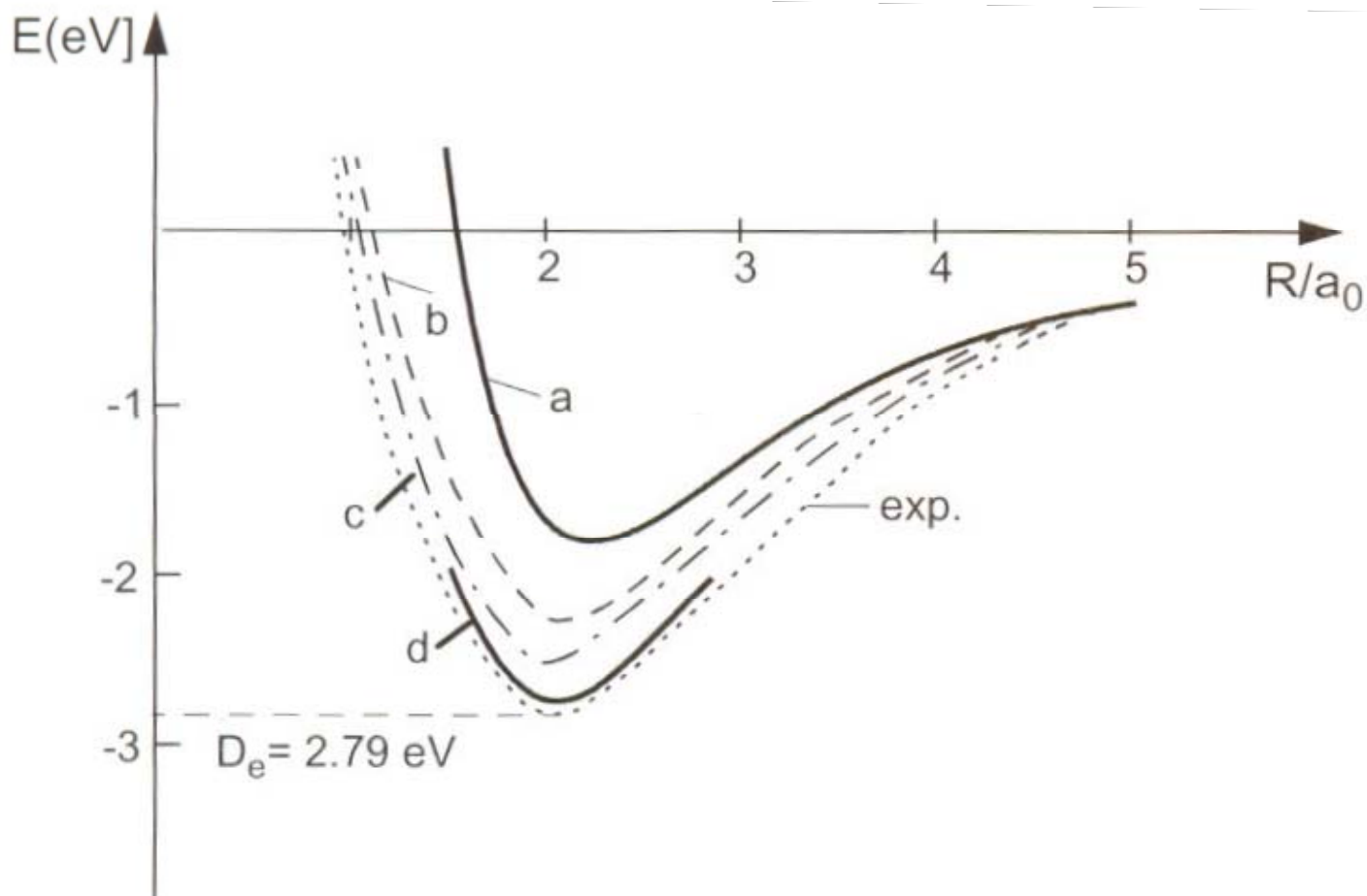


Fig. 2.30 Potential curve of the H_2^+ ground state as computed with a) simple LCAO, b) optimized parameter η , c) polarization term, and d) exact treatment.

Antibonding Orbital

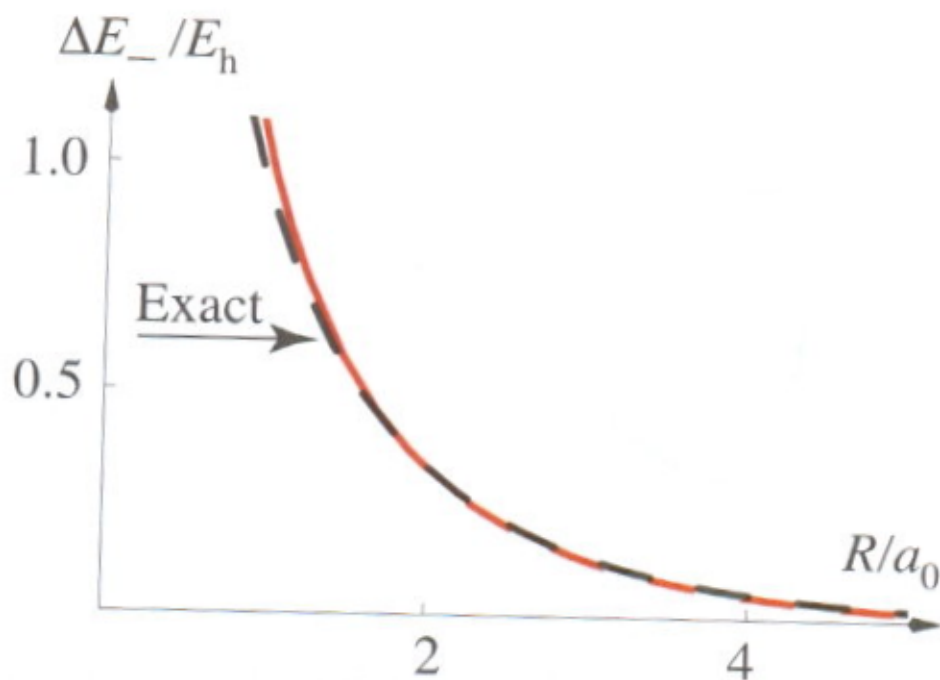


FIGURE 10.13

comparison of the energy $\Delta E_-(R)$ of the first excited state of H_2^+ calculated from equation 10.23 with the exact energy.

Addition of Orbitals

$$\Psi_n^{el}(\mathbf{r}) = \sum_i^n C_i \psi_i(\mathbf{r})$$

Adding in the contribution from 2S

$$\begin{aligned}\Psi_n^{el}(\mathbf{r}; R) &= C_1 |A1s\rangle + C_2 |B1s\rangle + C_3 |A2s\rangle + C_4 |B2s\rangle \\ &= 0.7071(|A1s\rangle + |B1s\rangle) + 0.00145(|A2s\rangle + |B2s\rangle)\end{aligned}$$

Adding in the contribution from 2p_z

$$\begin{aligned}\Psi_n^{el}(\mathbf{r}; R) &= C_1 |A1s\rangle + C_2 |B1s\rangle + C_3 |A2p_z\rangle + C_4 |B2p_z\rangle \\ &= C_A(|A1s\rangle + 0.1380|A1p_z\rangle) + C_B(|B1s\rangle + 0.1380|B1p_z\rangle)\end{aligned}$$

Additional Orbitals

TABLE 10.2

Results of Various Calculations of the Ground-State Electronic Energy of H_2^+ ^a

ϕ	E_{\min}/E_h	R_{eq}/a_0
$1s(\zeta = 1.000)$	-0.564 83	2.49
$1s(\zeta = 1.238)$	-0.586 51	2.00
$1s(\zeta = 1.000) + a2p_z(\zeta = 1.000)$	-0.565 91	2.00
$1s(\zeta = 1.247) + b2p_z(\zeta = 1.247)$	-0.599 07	2.00
$1s(\zeta = 1.2458) + c2p_z(\zeta = 1.4224)$	-0.600 36	2.00
$1s(\zeta = 1.244) + c_1 2p_z(\zeta = 1.152) + c_2 3d_{z^2}(\zeta = 1.333)$ ^b	-0.6020	2.00
Exact ^c	-0.602 64	2.00

^a The molecular orbitals are of the form $\psi_b = c_A \phi_A + c_B \phi_B$, where ϕ is given in the table.

^b Mulliken, R. S., Ermler, W. C. *Diatomic Molecules*. Academic Press: New York, 1977.

^c Bates, D. R., Ledsham, K., Stewart, A. L. Wave Functions of the Hydrogen Molecular Ion. *Philos. Trans. Roy. Soc. London, Ser. A.* **246**, 215 (1953).

H₂

$$\begin{aligned} \hat{H}\Psi_n^{el}(\mathbf{r}_1, \mathbf{r}_2; R) \\ = \left[-\frac{1}{2}\nabla_1^2 + -\frac{1}{2}\nabla_2^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_{1A}|} - \frac{1}{|\mathbf{r}_{1B}|} - \frac{1}{|\mathbf{r}_{2A}|} - \frac{1}{|\mathbf{r}_{2B}|} + \frac{1}{|\mathbf{r}_{12}|} \right] \right] \Psi_n^{el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) \\ = E_n(\mathbf{R})\Psi_n^{el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) \end{aligned}$$

Above equation is two H₂⁺ electrons with electron electron repulsion

$$\begin{aligned} = \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{|\mathbf{r}_{1A}|} - \frac{1}{|\mathbf{r}_{1B}|} - \frac{1}{2}\nabla_2^2 - \frac{1}{|\mathbf{r}_{2A}|} - \frac{1}{|\mathbf{r}_{2B}|} + \left[\frac{1}{|\mathbf{R}|} + \frac{1}{|\mathbf{r}_{12}|} \right] \right] \Psi_n^{el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) \\ = \left[h_1 + h_2 + \frac{1}{|\mathbf{R}|} + \frac{1}{|\mathbf{r}_{12}|} \right] \Psi_n^{el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) \end{aligned}$$

Spin Orbital and Spacial Orbitals

When you consider more than one electron you have to consider not only the **spacial coordinate \mathbf{r}** but also the spin **angular momentum s** and the Fermi principle:

Define \mathbf{x} as the summed coordinate for \mathbf{r} and s

$$\psi_i(\mathbf{x}) = \psi_i(\mathbf{r}, s) = \phi_i(\mathbf{r}) \begin{matrix} \alpha(s) \\ \beta(s) \end{matrix}$$

Hartree Product $\Psi^{HP}(\mathbf{x}_1, \mathbf{x}_2) = \psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)$

However the above does not satisfy the Fermi Principle!!
Exchange of electron leads to asymmetric wave function

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2) \right)$$

Slater Determinant

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} (\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2))$$

$$\Psi(\mathbf{x}_2, \mathbf{x}_1) = \frac{1}{\sqrt{2}} (\psi_i(\mathbf{x}_2)\psi_j(\mathbf{x}_1) - \psi_j(\mathbf{x}_2)\psi_i(\mathbf{x}_1)) = -\Psi(\mathbf{x}_1, \mathbf{x}_2)$$

Asymmetric wavefunction after exchange of electron coordinate

Generalization for n electron system: Slater Determinant

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \dots & \psi_k(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \dots & \psi_k(\mathbf{x}_2) \\ \dots & \dots & \dots & \dots \\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \dots & \psi_k(\mathbf{x}_n) \end{vmatrix}$$

What Happens if we use direct product of H_2^+ solutions

$$|+\rangle = \frac{|A\rangle + |B\rangle}{\sqrt{2+2S}}$$

$$|\Psi_{\text{trial}}\rangle = \frac{1}{\sqrt{2!}} \begin{vmatrix} \alpha(1)|+\rangle_1 & \beta(1)|+\rangle_1 \\ \alpha(2)|+\rangle_2 & \beta(2)|+\rangle_2 \end{vmatrix}$$

$$= |+\rangle_1 |+\rangle_2 \left[\frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \right]$$

$$|+\rangle_1 |+\rangle_2 \approx (|A1s\rangle_1 + |B1s\rangle_1) \times (|A1s\rangle_2 + |B1s\rangle_2)$$

Hamiltonian does not include any spin terms so we could obtain the R dependence of the energy using only the spatial part of the electronic wavefunction

$${}_2\langle + | {}_1\langle + | \hat{H} | + \rangle_1 | + \rangle_2 (R)$$

Potential Energy Curve

$${}_2\langle + | {}_1\langle + | \hat{H} | + \rangle_1 | + \rangle_2 (R)$$

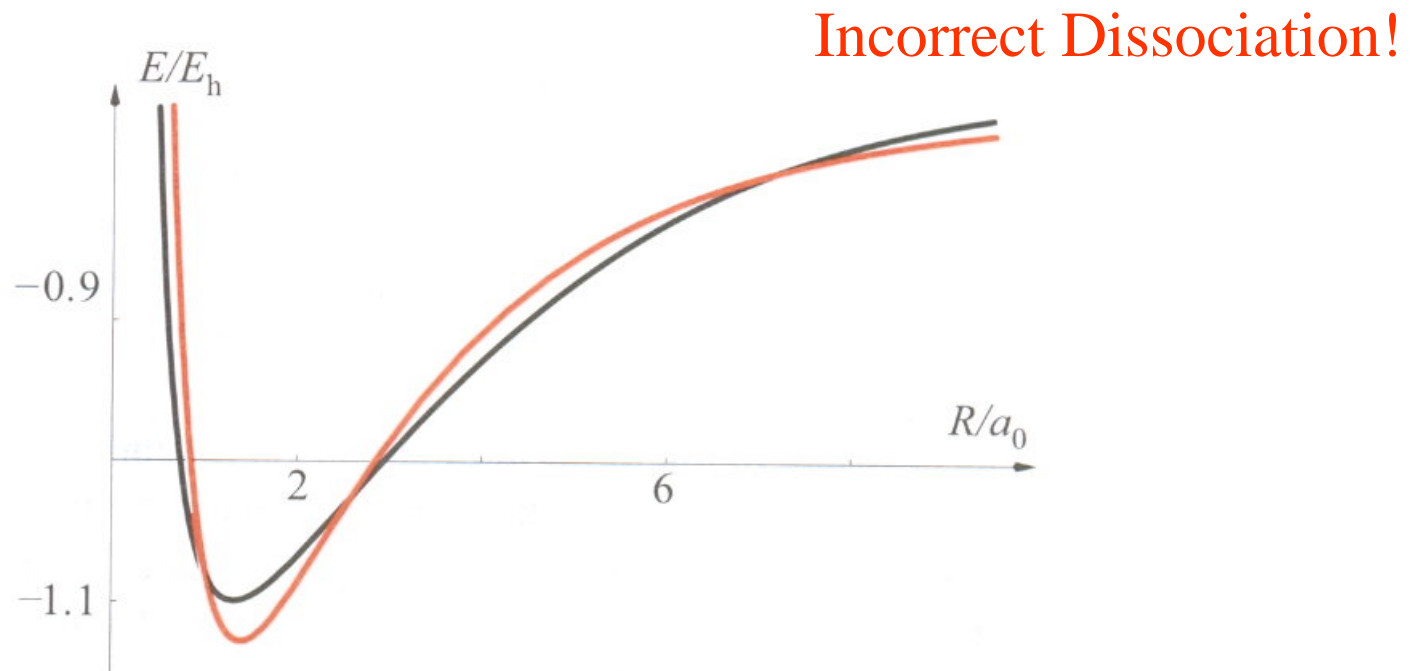


FIGURE 10.23

Both the optimized (orange) and the $\zeta = 1$ (black) molecular orbital energies calculated with Equation 10.41. In neither case does the energy go to the correct limit of $-1 E_h$ as $R \rightarrow \infty$.

What is the Problem of incorrect dissociation

$$\begin{aligned}
 |+\rangle_1 |+\rangle_2 &\approx (|A1s\rangle_1 + |B1s\rangle_1) \times (|A1s\rangle_2 + |B1s\rangle_2) \\
 &= |A1s\rangle_1 |A1s\rangle_2 + |B1s\rangle_1 |B1s\rangle_2 + |A1s\rangle_1 |B1s\rangle_2 + |B1s\rangle_1 |A1s\rangle_2
 \end{aligned}$$

First two terms have 2 electrons on one of the atoms: IONIC



Last two terms have one electrons on each one of the atoms:

Valance Bond



$$|+\rangle_1 |+\rangle_2 \approx |I\rangle + |VB\rangle$$

Solution: Configuration Interaction

Two 1S orbitals can make **TWO** molecular orbitals

Why not use the two and make combinations

$$|\Psi_1\rangle = C_1 \begin{vmatrix} \alpha(1)|+\rangle_1 & \beta(1)|+\rangle_1 \\ \alpha(2)|+\rangle_2 & \beta(2)|+\rangle_2 \end{vmatrix}$$

$$|\Psi_1\rangle \approx |++\rangle(\alpha\beta - \beta\alpha)$$

$$|\Psi_2\rangle = C_2 \begin{vmatrix} \alpha(1)|-\rangle_1 & \beta(1)|-\rangle_1 \\ \alpha(2)|-\rangle_2 & \beta(2)|-\rangle_2 \end{vmatrix}$$

$$|\Psi_2\rangle \approx |--\rangle(\alpha\beta - \beta\alpha)$$

$$|\Psi_3\rangle = C_3 \begin{vmatrix} \alpha(1)|+\rangle_1 & \alpha(1)|-\rangle_1 \\ \alpha(2)|+\rangle_2 & \alpha(2)|-\rangle_2 \end{vmatrix}$$

$$|\Psi_3\rangle \approx (|+-\rangle - |-+\rangle)\alpha\alpha$$

$$|\Psi_4\rangle = C_4 \begin{vmatrix} \alpha(1)|+\rangle_1 & \beta(1)|-\rangle_1 \\ \alpha(2)|+\rangle_2 & \beta(2)|-\rangle_2 \end{vmatrix}$$

$$|\Psi_4\rangle \approx |+-\rangle\alpha\beta - |-+\rangle\beta\alpha$$

$$|\Psi_5\rangle = C_5 \begin{vmatrix} \beta(1)|+\rangle_1 & \alpha(1)|-\rangle_1 \\ \beta(2)|+\rangle_2 & \alpha(2)|-\rangle_2 \end{vmatrix}$$

$$|\Psi_5\rangle \approx |+-\rangle\beta\alpha - |-+\rangle\alpha\beta$$

$$|\Psi_6\rangle = C_6 \begin{vmatrix} \beta(1)|+\rangle_1 & \beta(1)|-\rangle_1 \\ \beta(2)|+\rangle_2 & \beta(2)|-\rangle_2 \end{vmatrix}$$

$$|\Psi_6\rangle \approx (|+-\rangle - |-+\rangle)\beta\beta$$

Symmetry of Spacial Orbitals

$$|\Psi_1\rangle \approx |++\rangle(\alpha\beta - \beta\alpha)$$

$$|\Psi_2\rangle \approx |--\rangle(\alpha\beta - \beta\alpha)$$

$$|\Psi_3\rangle \approx (|+-\rangle - |-+\rangle)\alpha\alpha$$

$$|\Psi_4\rangle \approx |+-\rangle\alpha\beta - |-+\rangle\beta\alpha$$

$$|\Psi_5\rangle \approx |+-\rangle\beta\alpha - |-+\rangle\alpha\beta$$

$$|\Psi_6\rangle \approx (|+-\rangle - |-+\rangle)\beta\beta$$

If you exchange the position/spin of electron 1 and electron 2

$|\Psi_1\rangle$ and $|\Psi_2\rangle$ stay the same sign

$|\Psi_3\rangle$ and $|\Psi_4\rangle$ and $|\Psi_5\rangle$ and $|\Psi_6\rangle$ invert the same sign

Hamiltonian is invariant over exchange of electron

so only Ψ_2 mix with Ψ_1

$$H = \left[-\frac{1}{2} \nabla_1^2 + -\frac{1}{2} \nabla_2^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_{1A}|} - \frac{1}{|\mathbf{r}_{1B}|} - \frac{1}{|\mathbf{r}_{2A}|} - \frac{1}{|\mathbf{r}_{2B}|} + \frac{1}{|\mathbf{r}_{12}|} \right] \right]$$

Configuration Interaction

$$|\Psi_{CI}\rangle = C_1|\Psi_1\rangle + C_2|\Psi_2\rangle = C_1|++\rangle + C_2|--\rangle$$

$$\begin{aligned} |++\rangle &\approx (|A1s\rangle_1 + |B1s\rangle_1) \times (|A1s\rangle_2 + |B1s\rangle_2) \\ &= |A1s\rangle_1|A1s\rangle_2 + |B1s\rangle_1|B1s\rangle_2 + |A1s\rangle_1|B1s\rangle_2 + |B1s\rangle_1|A1s\rangle_2 \\ |--\rangle &\approx (|A1s\rangle_1 - |B1s\rangle_1) \times (|A1s\rangle_2 - |B1s\rangle_2) \\ &= |A1s\rangle_1|A1s\rangle_2 + |B1s\rangle_1|B1s\rangle_2 - |A1s\rangle_1|B1s\rangle_2 - |B1s\rangle_1|A1s\rangle_2 \end{aligned}$$

$$|\Psi_{CI}\rangle = C_1|\Psi_1\rangle + C_2|\Psi_2\rangle = (C_1 + C_2)|Ion\rangle + (C_1 - C_2)|VB\rangle$$

By correct selection of the value for C_1 and C_2 you get no Ionic wavefunction contribution

H2 Potential Curve Revisited

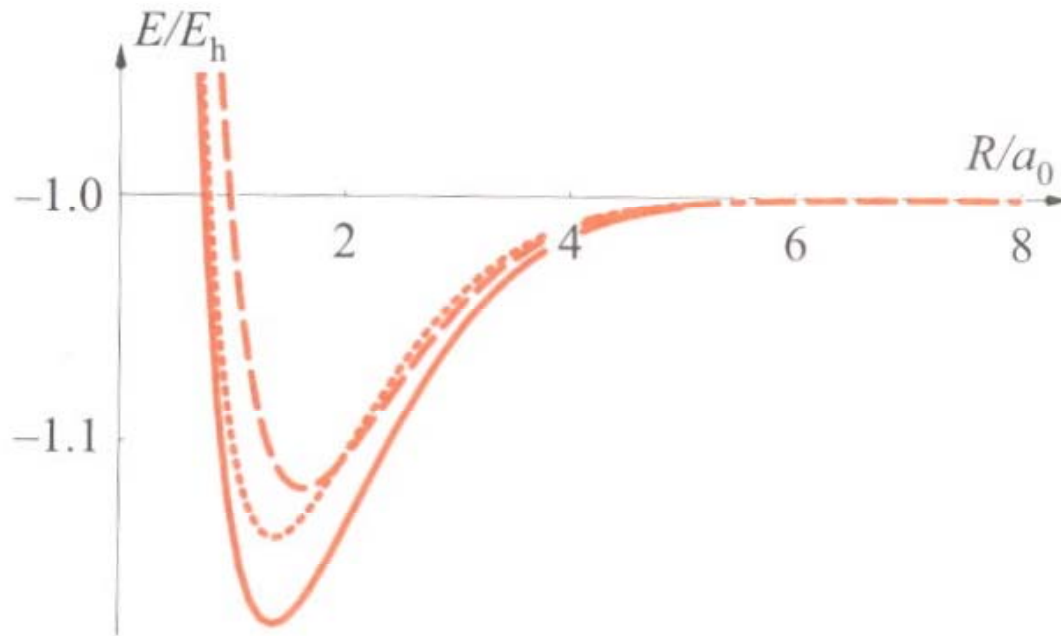


FIGURE 10.25

The configuration-interaction energy E_{CI} of the ground-state energy of H₂ for $\zeta = 1$ (dashed curve) and for an optimized value of ζ (dotted curve) plotted against R . The “exact” results of Kolos and Wolniewicz (solid curve) are shown for comparison.

R Dependence of Expansion Coefficients

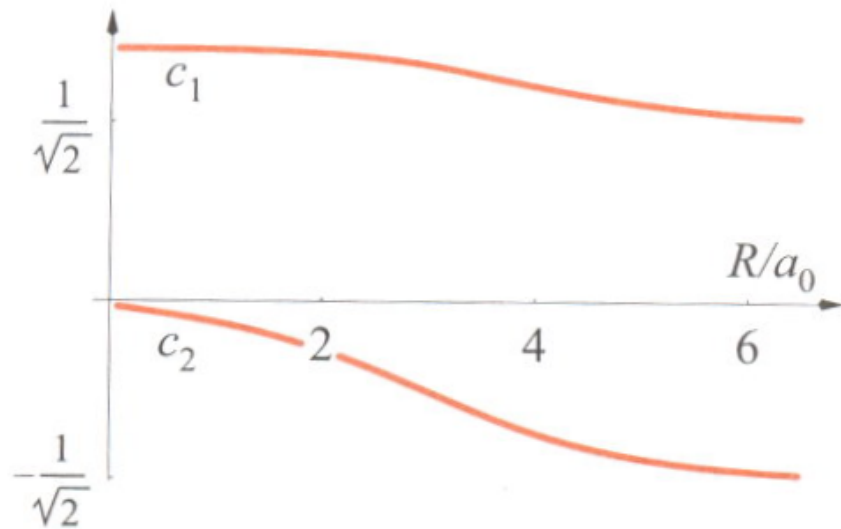


FIGURE 10.27

A plot of c_1 and c_2 for the optimized value of ζ in Equation 10.53 against R . Note that $c_1 \rightarrow 1/\sqrt{2}$ and $c_2 \rightarrow -1/\sqrt{2}$ as $R \rightarrow \infty$.

Use of more orbitals

$$|\pm\rangle \approx C_A \left(|A1s\rangle + \alpha |A1p_z\rangle \right) \pm C_B \left(|B1s\rangle + \alpha |B1p_z\rangle \right)$$

TABLE 10.4

Results of Various Calculations of the Ground-State Energy of H₂

	Wave function	ζ	E_{\min}/E_h	R_{eq}/a_0
MO	Minimal basis set	1.000	-1.0991	1.603
MO	Minimal basis set	1.193	-1.1282	1.385
	Hartree-Fock ^a		-1.1336	1.400
CI	Minimal basis set	1.000	-1.1187	1.668
CI	Minimal basis set	1.194	-1.1479	1.430
CI	Minimal basis set with polarization ^b		-1.1514	1.40
CI	Five terms ^b		-1.1672	1.40
CI	33 terms ^c		-1.1735	1.40
	Trial function with r_{12} 13 terms ^d		-1.1735	1.40
	Trial function with r_{12} with 100 terms ^e		-1.1744	1.401
	Experimental ^f		-1.174	1.401

Energy Diagram

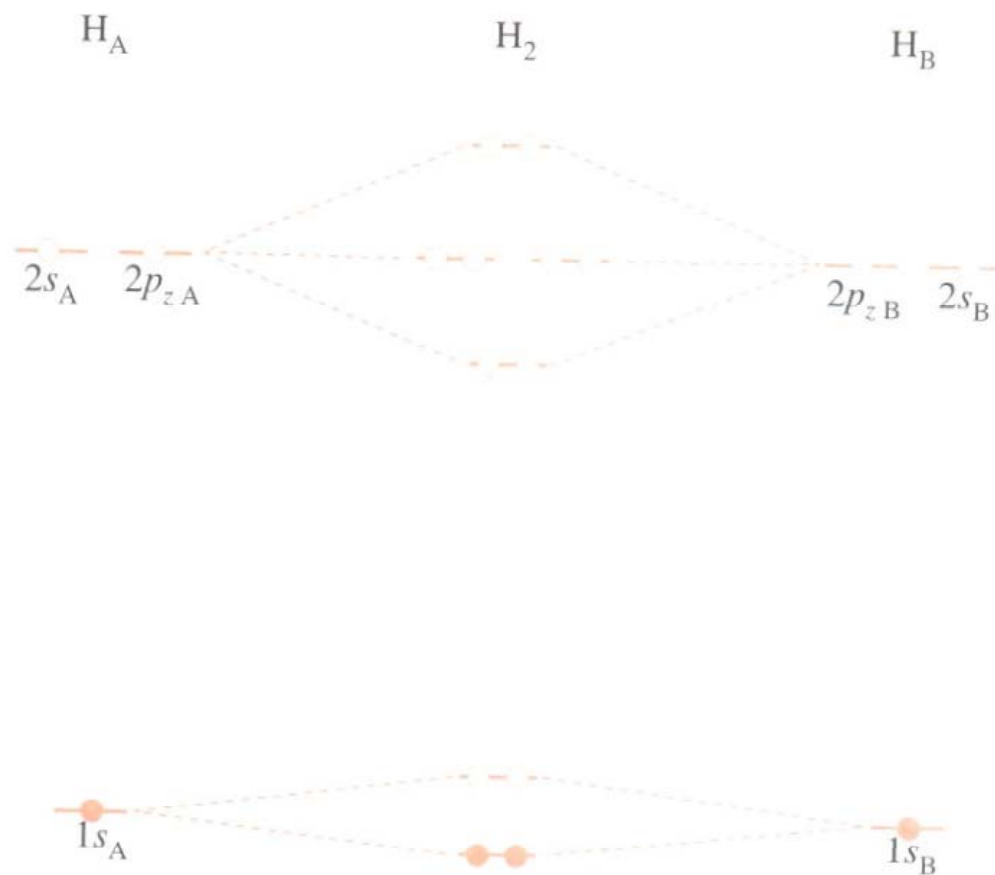
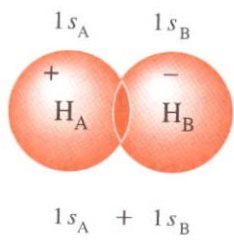


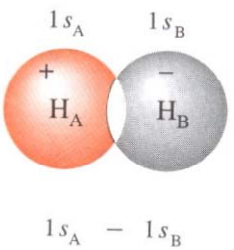
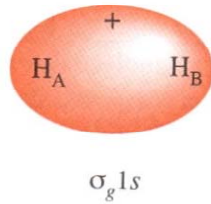
FIGURE 10.28

The six spatial molecular orbitals that are obtained when the LCAO-MO is a linear combination of six atomic orbitals, as in Equation 10.55. Only the molecular orbital of the lowest energy is occupied in the ground electronic state of H₂. The five unoccupied orbitals are called virtual orbitals.

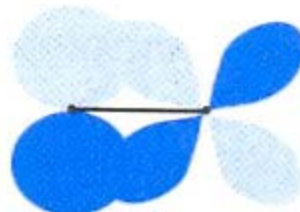
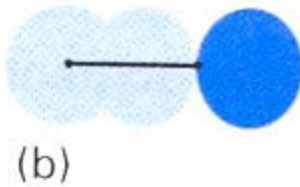
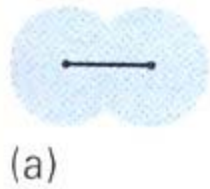
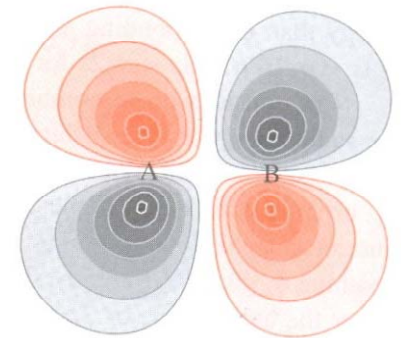
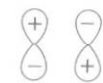
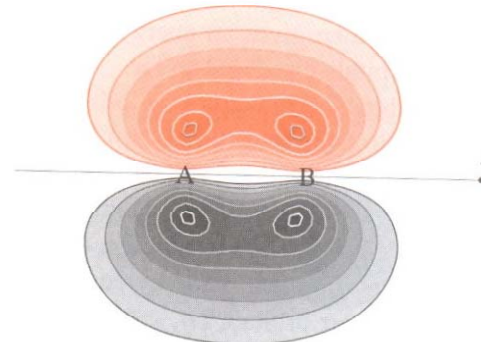
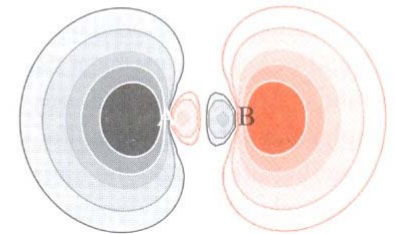
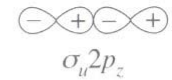
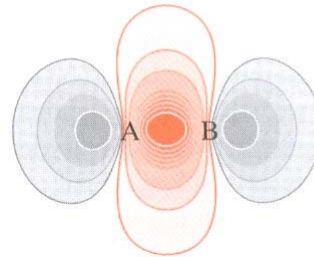
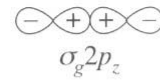
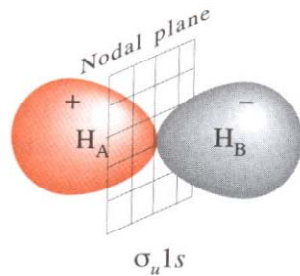
Molecular Orbitals



=



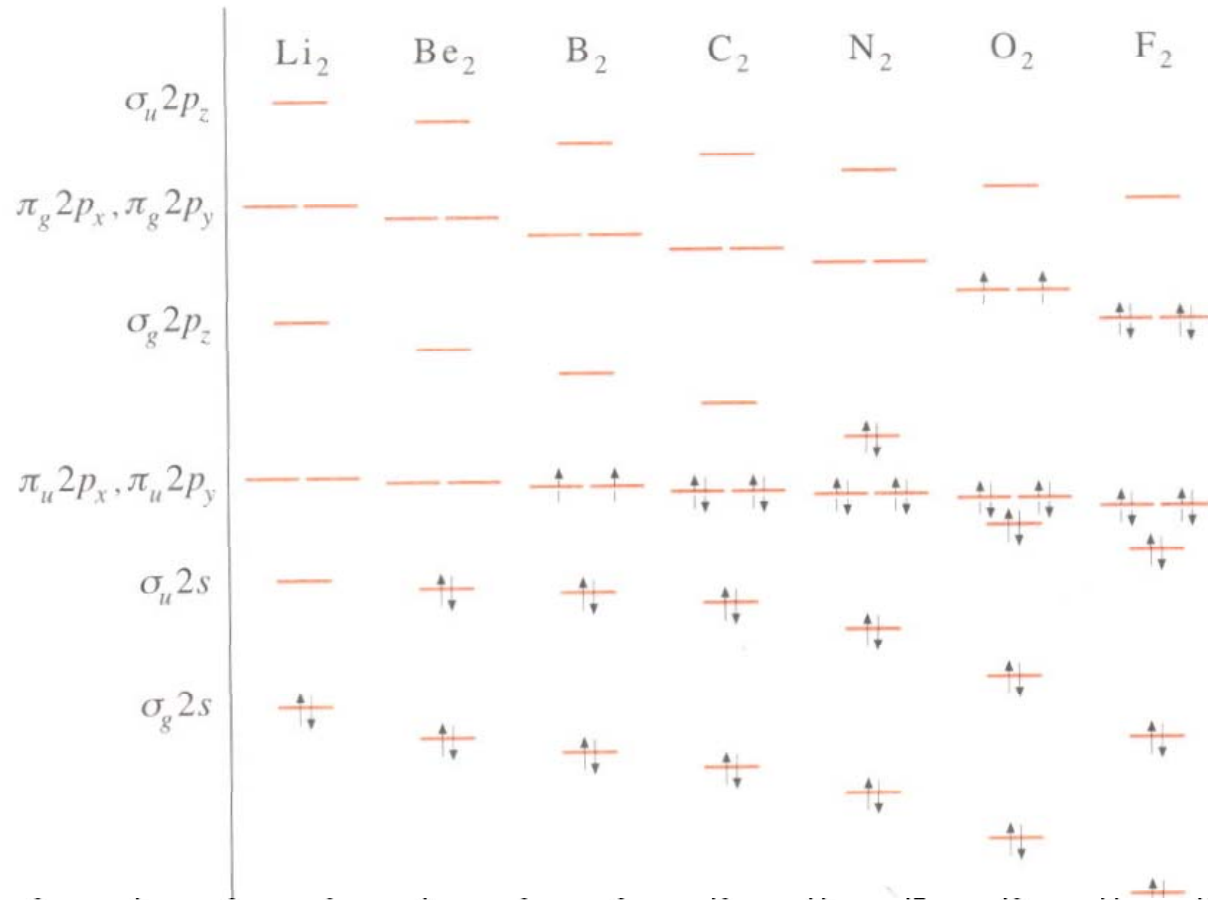
=



(c)

(d)

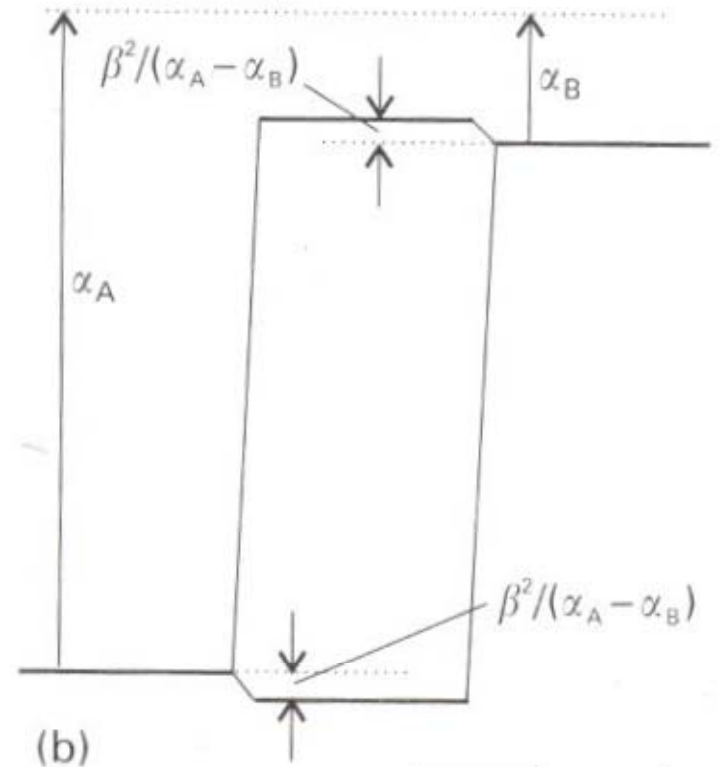
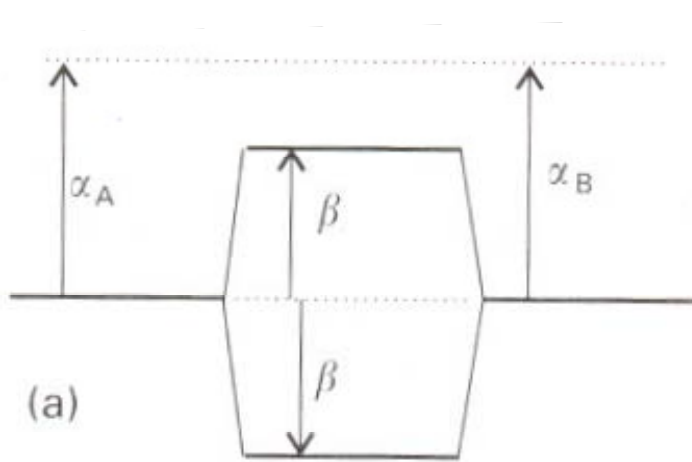
Homonuclear diatomic Molecules



hydrogen 1 H 1.0079	
lithium 3 Li 6.941 sodium 11	beryllium 4 Be 9.0122 magnesium 12

					helium 2 He 4.0026
boron 5 B 10.811 aluminium 13	carbon 6 C 12.011 silicon 14	nitrogen 7 N 14.007 phosphorus 15	oxygen 8 O 15.999 sulfur 16	fluorine 9 F 18.998 chlorine 17	neon 10 Ne 20.180 argon 18

Heteronuclear Diatomic Molecules



Bonding orbital localized on one nuclei