Born-Oppenheimer Approximation

Kaito Takahashi

Atomic Units

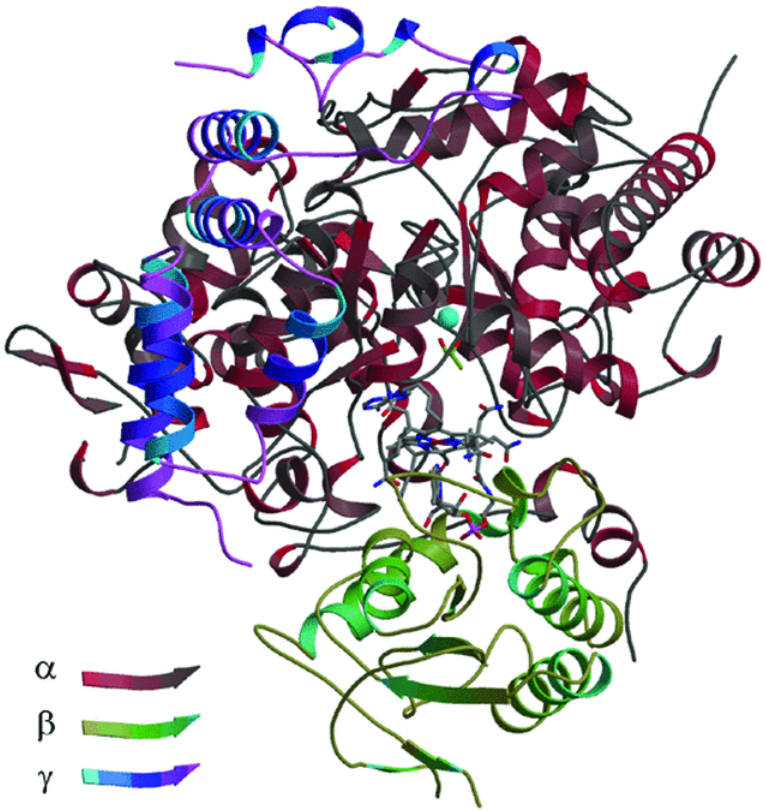
For quantum systems such as electrons and molecules it is easier to use units that fit them=ATOMIC UNIT

Use mass of electron (not kg)
Use charge of electron (not coulomb)
Use hbar for angular momentum (not kg m^2 s^{-1})
Use $4\pi\varepsilon_0$ for permittivity (not C^2 s^2 kg^{-1} m^{-3})

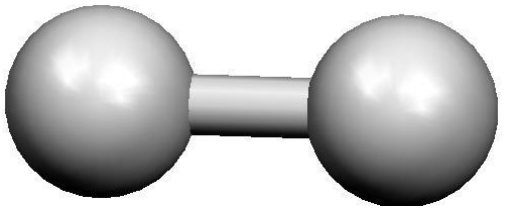
TABLE 9.1
Atomic Units and Their SI Equivalents

Property	Atomic unit	SI equivalent
Mass	Mass of an electron, m_e	9.1094×10^{-31} kg
Charge	Charge on a proton, e	1.6022×10^{-19} C
Angular momentum	Planck constant divided by 2π, $\hbar$	1.0546×10^{-34} J·s
Length	Bohr radius, $a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
Energy	$\dfrac{m_e e^4}{16\pi^2\epsilon_0^2\hbar^2} = \dfrac{e^2}{4\pi\epsilon_0 a_0} = E_h$	4.3597×10^{-18} J
Permittivity	$\kappa_0 = 4\pi\epsilon_0$	1.1127×10^{-10} $C^2 \cdot J^{-1} \cdot m^{-1}$

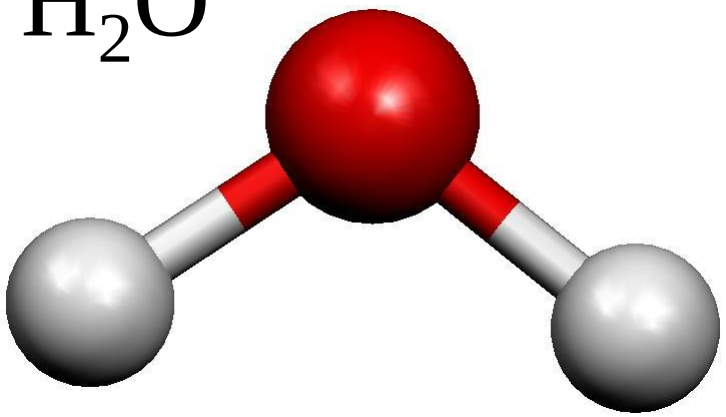
Proteins, Molecules



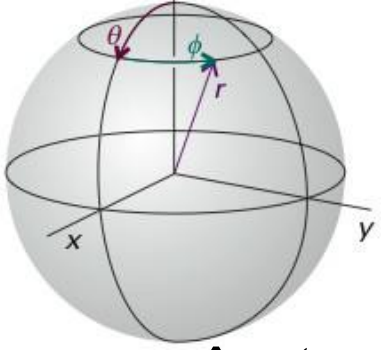
H_2



H_2O



You always write where the nucleus is but you never write the electrons or the electrons are written as a line!!!
YOU ARE ALREADY ASSUMING BORN-OPPENHEIMER APPROXIMATION



Solve the hydrogen atom

$$\hat{H}\psi(r,\theta,\phi)=\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{e^2}{4\pi\varepsilon_0 r}\right.$$

$$\left.-\frac{\hbar^2}{2\mu}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{\hbar^2}{2\mu}\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi)$$

$$=E\psi(r,\theta,\phi)$$

$$E_n=-\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2}=-\frac{\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}=-\frac{e^2}{8\pi\varepsilon_0 a_0 n^2}$$

$$Y_l^{m_l}(\theta,\phi)=\frac{1}{(2\pi)^{1/2}}\exp(im\phi)\left[\frac{2l+1}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}\right]^{1/2}P_l^{|m_l|}(\cos\theta)$$

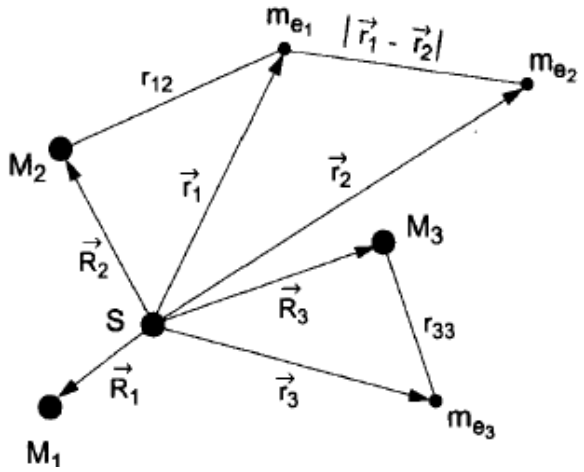
$$R_{nl}(r)=\left\{\frac{(n-l-1)!}{2n[(n+1)!]^3}\right\}^{1/2}\left(\frac{2}{na_0}\right)^{3/2}\left(\frac{2r}{na_0}\right)^l\exp\left(-\frac{r}{na_0}\right)L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

Full Problem

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + V(\mathbf{r},\mathbf{R})$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \qquad \nabla_I^2 = \frac{\partial^2}{\partial X_I^2} + \frac{\partial^2}{\partial Y_I^2} + \frac{\partial^2}{\partial Z_I^2}$$

$$V(\mathbf{r},\mathbf{R}) = \frac{e^2}{4\pi\varepsilon_0}\Big[\qquad \Big]$$



$$\mathbf{R}_I = \vec{R}_I = X_I\vec{e}_x + Y_I\vec{e}_y + Z_I\vec{e}_z$$

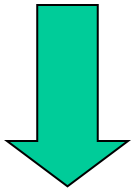
$$\mathbf{r}_i = \vec{r}_i = x_i\vec{e}_x + y_i\vec{e}_y + z_i\vec{e}_z$$

$$\hat{H}\Psi(\mathbf{r},\mathbf{R}) = E_{el,NU}\Psi(\mathbf{r},\mathbf{R})$$

Born-Oppenheimer Approximation in words

Mass of electron versus mass of nucleus

1 <<< 1830 (at least)



$$\phi_n^{el}(\mathbf{r};\mathbf{R})$$

BO Approximation in equation 1

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + V(\mathbf{r},\mathbf{R})$$

$$= \hat{T}_{el} + \hat{T}_{NU} + \hat{V} = \hat{T}_{el} + \hat{V} + \hat{T}_{NU} = \hat{H}^0 + \hat{T}_{NU}$$

$$\hat{H}^0(\mathbf{r};\mathbf{R}) = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + V(\mathbf{r},\mathbf{R}) \qquad \hat{T}_{NU} = -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2$$

$$\hat{H}\Psi(\mathbf{r},\mathbf{R}) = E_{el,NU}\Psi(\mathbf{r},\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_{m}^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})$$

$$\chi_m(\mathbf{R}) =$$

BO Approximation 2

$$\left(\hat{H} - E_{el,NU}\right)\Psi(\mathbf{r},\mathbf{R}) = 0$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H} - E_{el,NU}\right)\sum_m^{\infty} \chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r} = 0$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H}^0 + \hat{T}_{NU} - E_{el,NU}\right)\sum_m^{\infty} \chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r} = 0$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H}^0 + \hat{T}_{NU} - E_{el,NU}\right)\sum_m^{\infty} \chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r} = 0$$

$$\sum_m^{\infty} \chi_m(\mathbf{R})\Big[\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\Big]$$

$$+\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 0$$

BO Approximation 3

$$\sum_m^{\infty} \chi_m(\mathbf{R}) \left[\int \phi_n^{el*}(\mathbf{r};\mathbf{R}) \left(\hat{H}^0 - E_{el,NU} \right) \phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r} \right]$$

$$= \sum_m^{\infty} \chi_m(\mathbf{R}) \left[\left(E_m(\mathbf{R}) - E_{el,NU} \right) \langle n \| m \rangle_r \right] = \left(E_n(\mathbf{R}) - E_{el,NU} \right) \chi_n(\mathbf{R})$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R}) \left(\hat{T}_{NU} \right) \sum_m^{\infty} \chi_m(\mathbf{R}) \phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r}$$

$$= \int \phi_n^{el*}(\mathbf{r};\mathbf{R}) \left(-\frac{1}{2} \sum_{I=1}^{N} \frac{1}{M_I} \nabla_I^2 \right) \sum_m^{\infty} \chi_m(\mathbf{R}) \phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r}$$

$$|n\rangle = \psi_n(x) \qquad \langle m| = \psi_m{}^*(x)$$

Using Bra-Ket Notation

$$\langle n|\hat{x}|m\rangle = \int_{-\infty}^{\infty} \psi_n{}^*(x)\, x\, \psi_m(x) dx$$

$$\langle n|\hat{1}|m\rangle = \langle n|m\rangle = \langle n\|m\rangle = \int_{-\infty}^{\infty} \psi_n{}^*(x) \psi_m(x) dx$$

BO Approximation 4

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}$$

$$= \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\sum_m^{\infty}\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_m(\mathbf{R})\right)\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}$$

$$+$$

$$+$$

$$= \sum_m^{\infty} -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_m(\mathbf{R})\langle n\|m\rangle_r = -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_n(\mathbf{R})$$

$$+\sum_m^{\infty}\left\langle n\left|-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right|m\right\rangle\chi_m(\mathbf{R})+\sum_m^{\infty}\left\langle n\left|-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\right|m\right\rangle\nabla_I\chi_m(\mathbf{R})$$

BO Approximation 5

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(E_n(\mathbf{R})+\hat{T}_{NU}-E_{el,NU}\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}=0$$

$$=\left(E_n(\mathbf{R})-E_{el,NU}\right)\chi_n(\mathbf{R})-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_n(\mathbf{R})+\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})=0$$

$$\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})$$

$$\equiv$$

$$\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2+E_n(\mathbf{R})\right)\chi_n(\mathbf{R})+\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})=E_{el,NU}\chi_n(\mathbf{R})$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})=E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

BO Approximation 6

Born-Oppenheimer Approximation ignore C_{nm}

$$\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + E_n(\mathbf{R}) \right)\chi_n(\mathbf{R}) = E_{el,NU}\,\chi_n(\mathbf{R})$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

Nuclear wavefunction is given by the expansion coefficient!

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

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

The nucleus is moving in an potential that is the result of averaging the contribution coming from the electron at a given nuclear geometry! In essence you have separated the motion of the electron and nucleus.

Separation of Variables by Time Scale

$$\hat{H}^{0}(\mathbf{r};\mathbf{R})\phi_{n}^{el}(\mathbf{r};\mathbf{R}) = E_{n}(\mathbf{R})\phi_{n}^{el}(\mathbf{r};\mathbf{R})$$

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

$$\Psi(\mathbf{r},\mathbf{R}) = \phi_{n}^{el}(\mathbf{r};\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R})$$

Now you can say nuclear wave function on the n-th electronic state

You can write the energy of the electron as a function of the nuclear coordinate and consider it as a potential that the nucleus feels.

Adiabatic Approximation

Include diagonal coupling term C_{nn}

$$C_{nn} = \left\langle n \left| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 \right| n \right\rangle + \left\langle n \left| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I \right| n \right\rangle \nabla_I$$

$$\langle n \| n \rangle = 1 \rightarrow \nabla_I \langle n \| n \rangle = \nabla_I \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= 2\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} = 0$$

$$\nabla_I^2 \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= 2\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\nabla_I^2 \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} + 2\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\right)^2 d\mathbf{r} = 0$$

$$C_{nn} =$$

LCAO Approximation for Diatomic Molecules

Kaito Takahashi

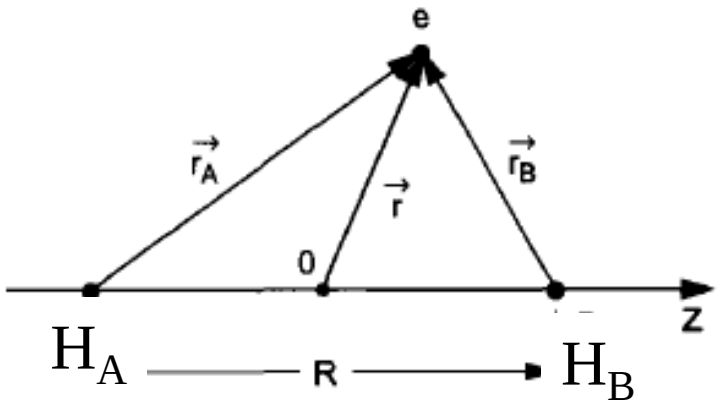
H_2^+ Most Simple Diatom

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



Atomic Orbital Review

TABLE 7.2
The Hydrogen-like Radial Wave Functions, $R_{nl}(r)$, for $n = 1$, 2, and 3 [a]

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

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

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

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

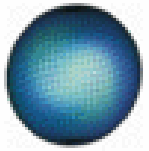
$$R_{31}(r) = \frac{1}{27}\left(\frac{2Z}{3a_0}\right)^{3/2} \rho(6-\rho)e^{-\rho/3}$$

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

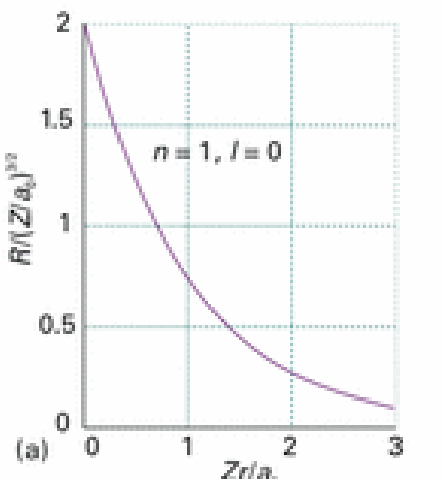
a. The quantity Z is the nuclear charge, and $\rho = Zr/a_0$, where a_0 is the Bohr radius.

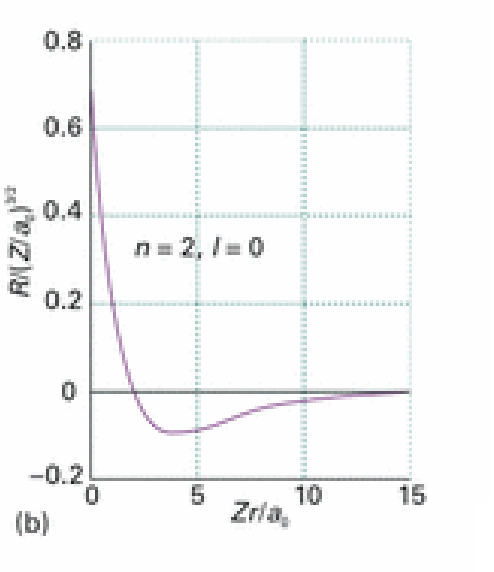
Table 9.3 The spherical harmonics

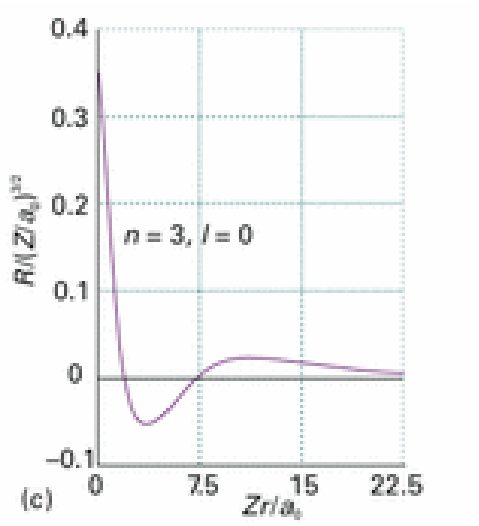
l	m_l	$Y_{Lm_l}(\theta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta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



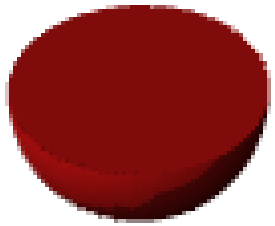
s Wavefunction



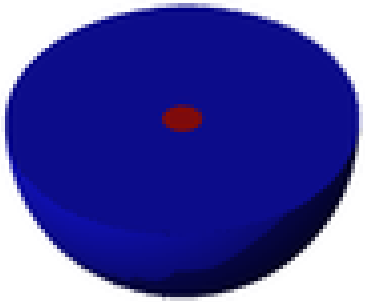


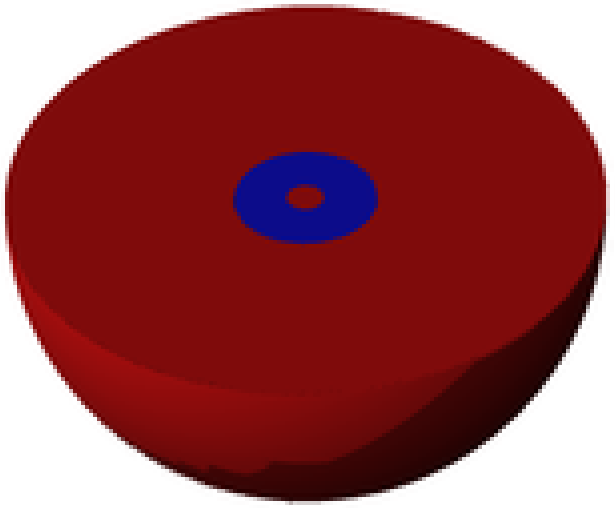


1s

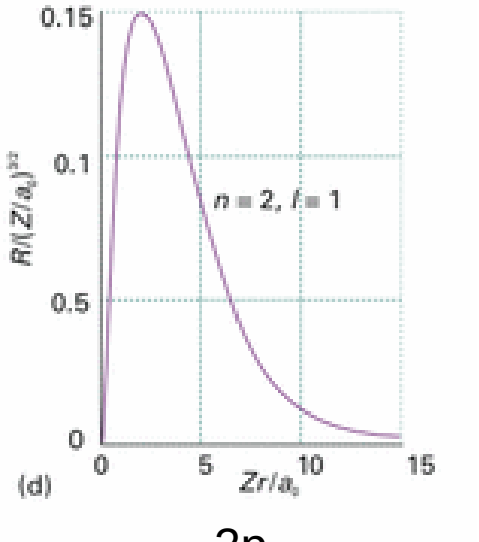


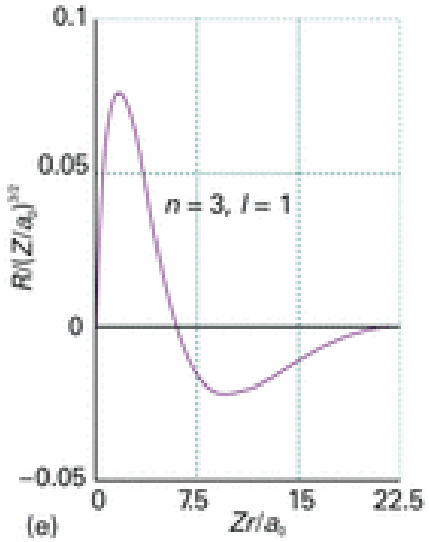
2s



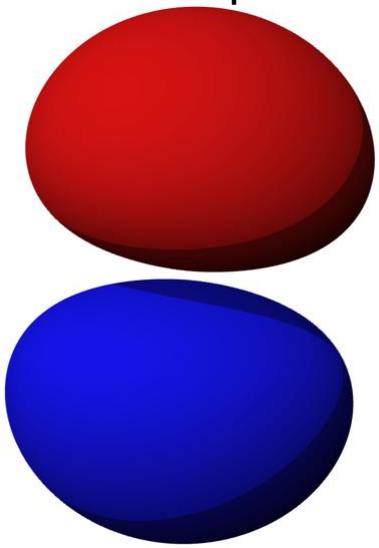


p Wavefunction

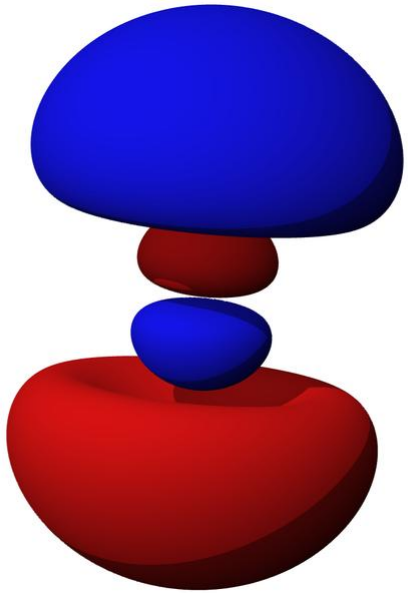




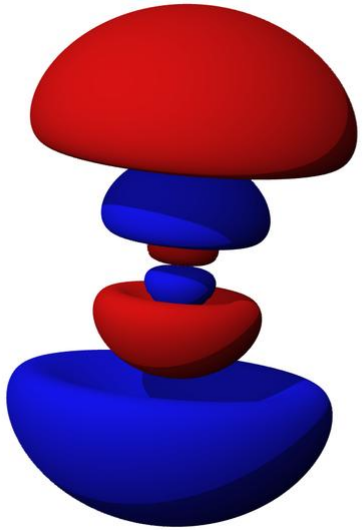
2p



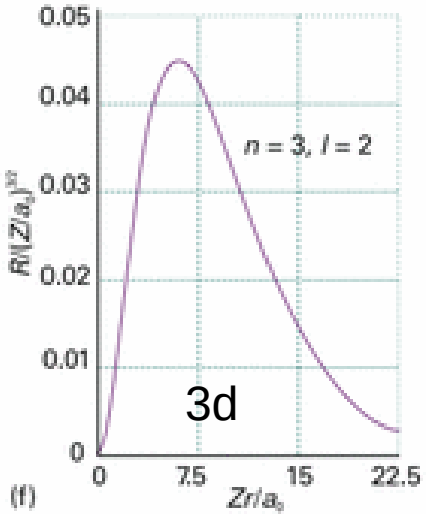
3p



4p

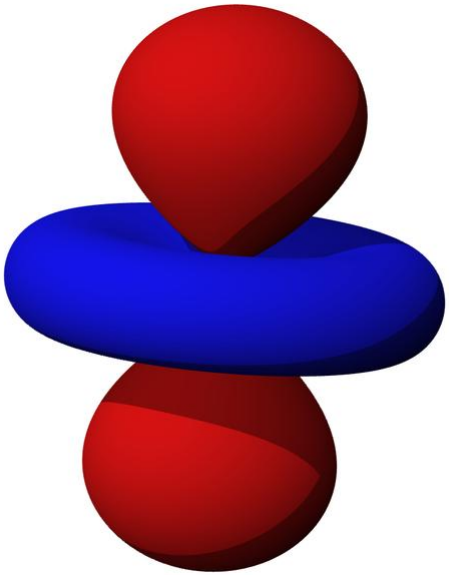


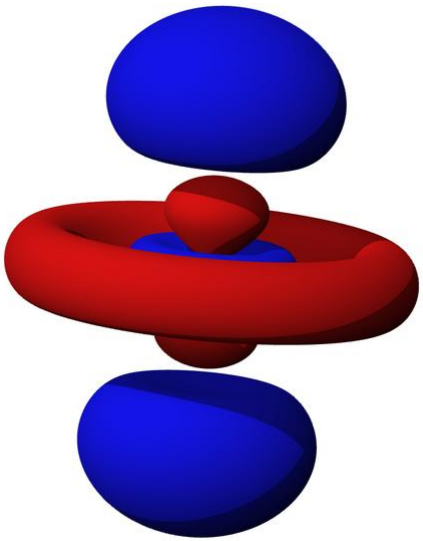
d Wavefunction

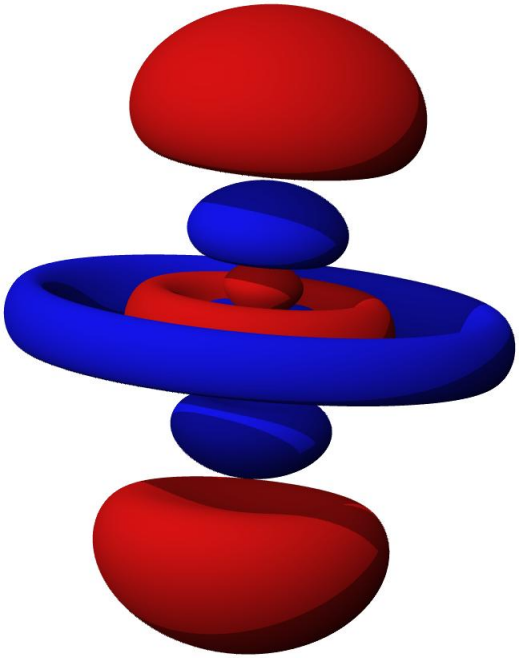


4d

5d

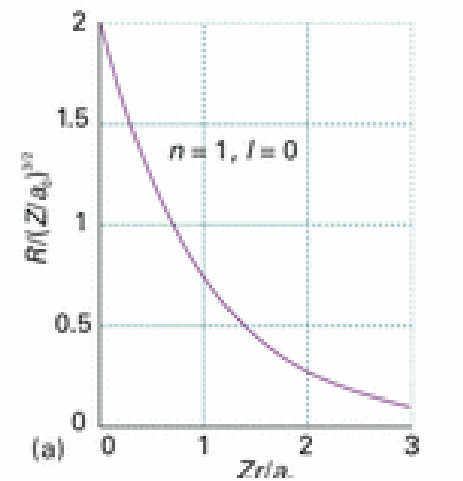


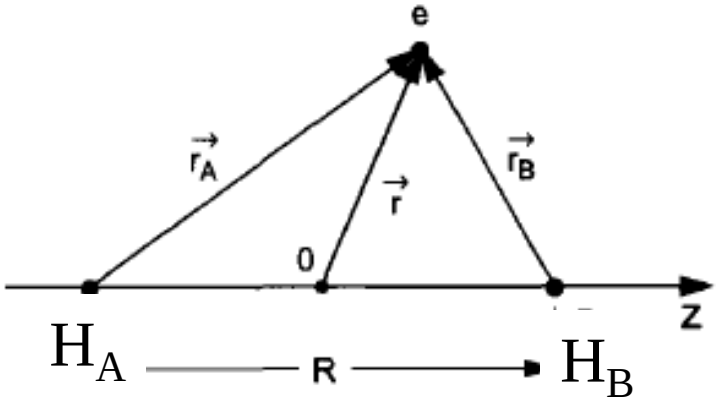


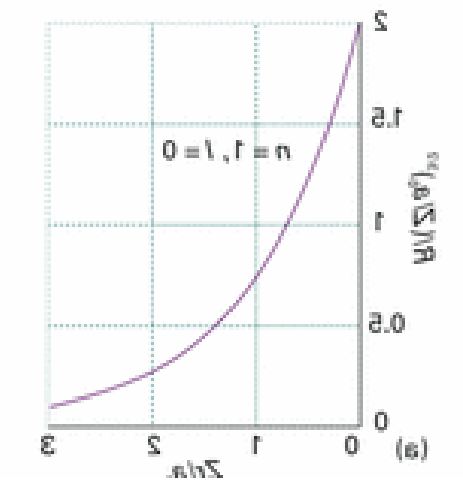


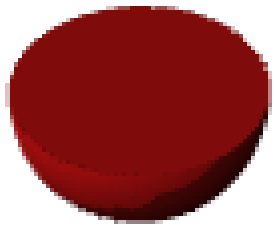
LCAO

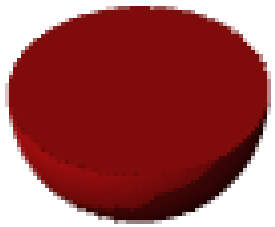
To make the molecular orbital (the electronic wavefunction for the molecule) let just add up each atomic orbital (electronic wave function for the atoms making the molecule)











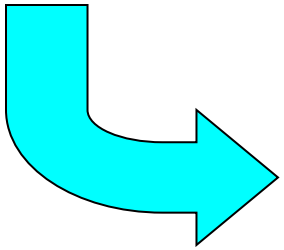
Variational Theory 1

$$E_{exact} = \qquad < E_{trial} =$$

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

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

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



Variational Theory 2

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

Take derivative with c_i^*

Take derivative with c_j

Due to stationary condition of the solution

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

Variational Theory

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

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

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

H_2^+

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

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

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

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

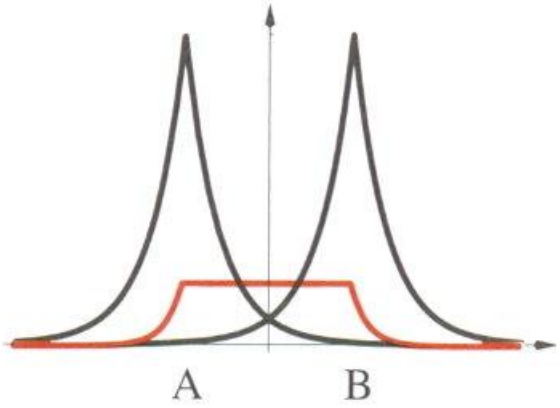
$$H(R)_{AB} = \langle A|\hat{H}|B\rangle = \langle B|\hat{H}|A\rangle = H(R)_{BA}$$

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

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

Overlap Integral

$$S(R) = \langle A | B \rangle = \langle B | A \rangle$$

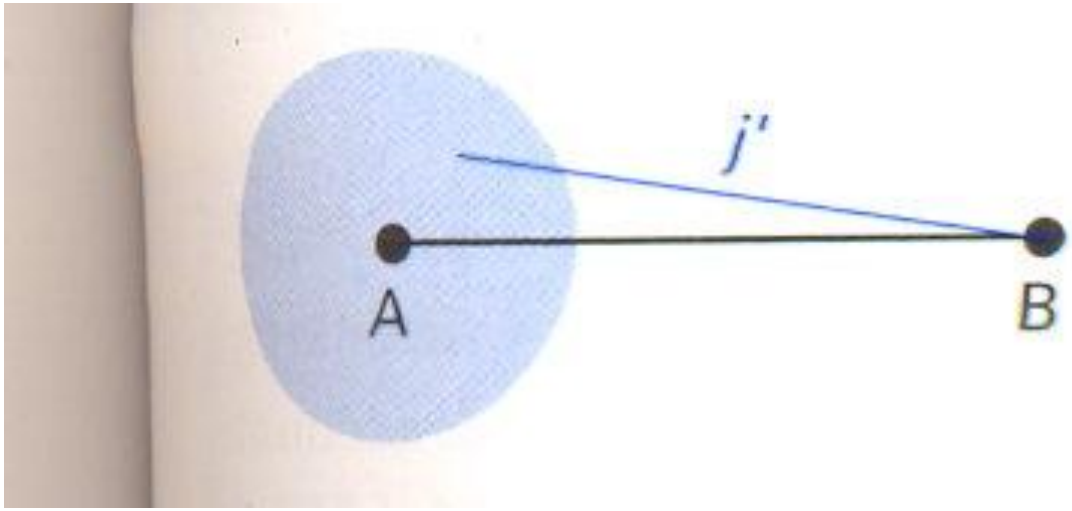


$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

Atomic Integral

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

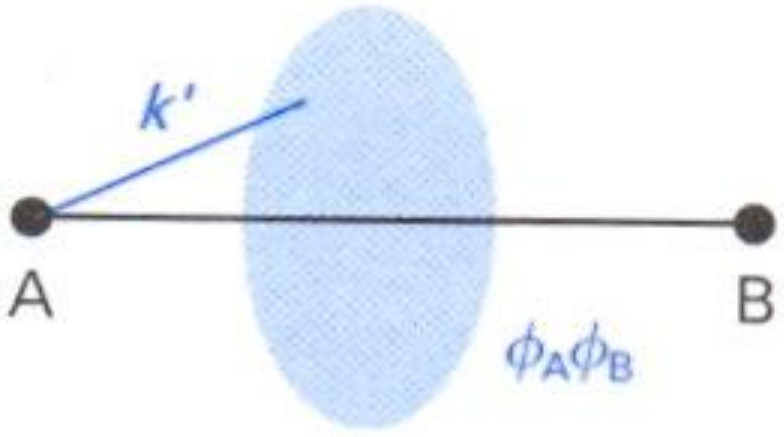
$$= E_{1S} + \left\langle A \middle| -\frac{1}{|\mathbf{r}_B|} \middle| A \right\rangle + \frac{1}{|\mathbf{R}|} \langle A \mid A \rangle$$



Exchange Integral

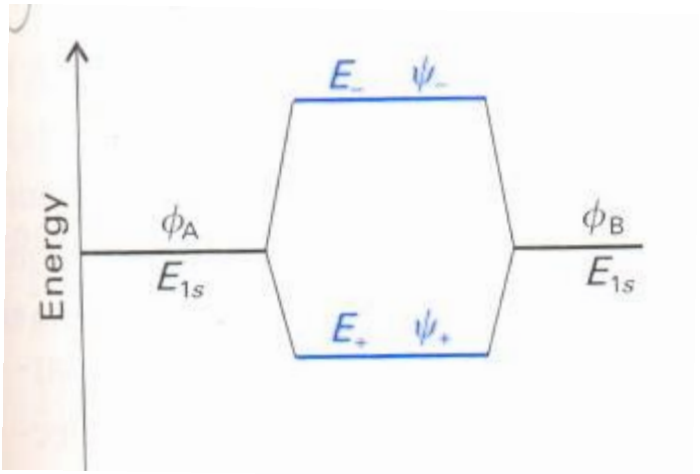
$$H(R)_{AB} = \langle A|\hat{H}|B\rangle = \left\langle A\left|\left[-\frac{1}{2}\nabla^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_A|} - \frac{1}{|\mathbf{r}_B|}\right]\right]\right|B\right\rangle$$

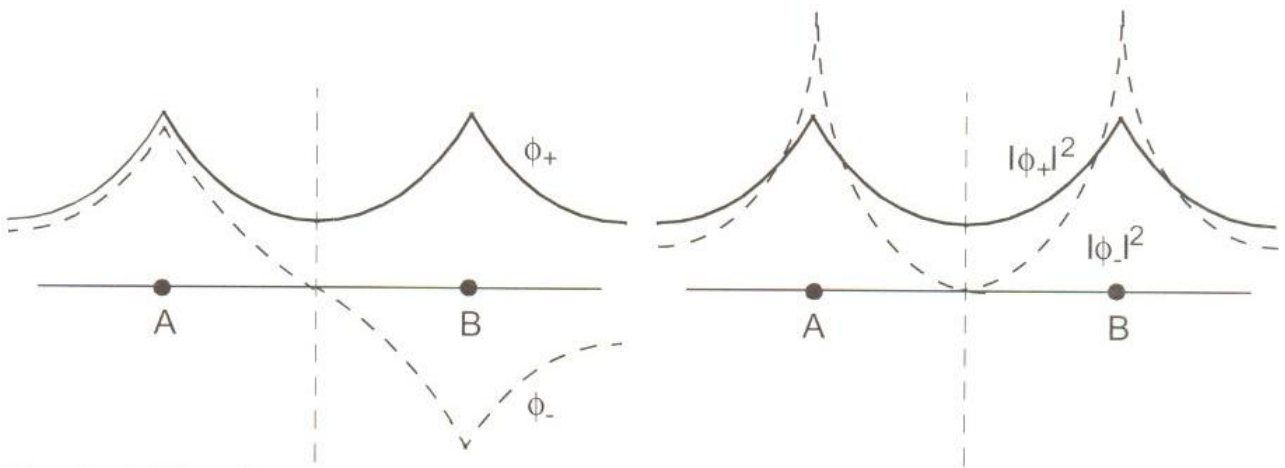
$$= \left\langle A\left|-\frac{1}{2}\nabla^2\right|B\right\rangle + \left\langle A\left|-\frac{1}{|\mathbf{r}_A|}\right|B\right\rangle + \left\langle A\left|-\frac{1}{|\mathbf{r}_B|}\right|B\right\rangle + \frac{1}{|\mathbf{R}|}\langle A\,|\,B\rangle$$



Solve Secular Equation

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





Bonding and Antibonding Orbital

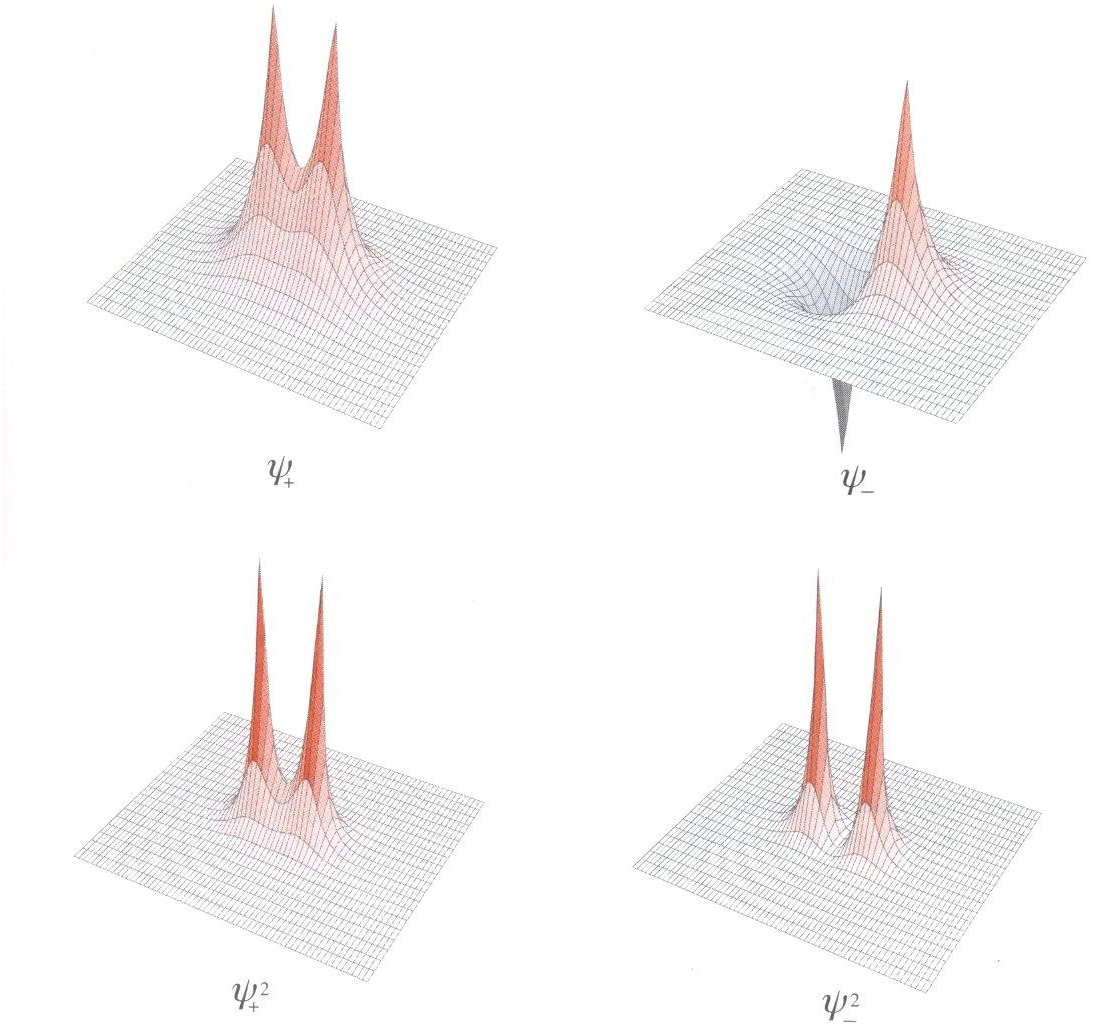


FIGURE 10.14
Surface plots of the molecular orbitals ψ_+ (a bonding orbital) and ψ_- (an antibonding orbital) and their squares.

Electron Density Difference

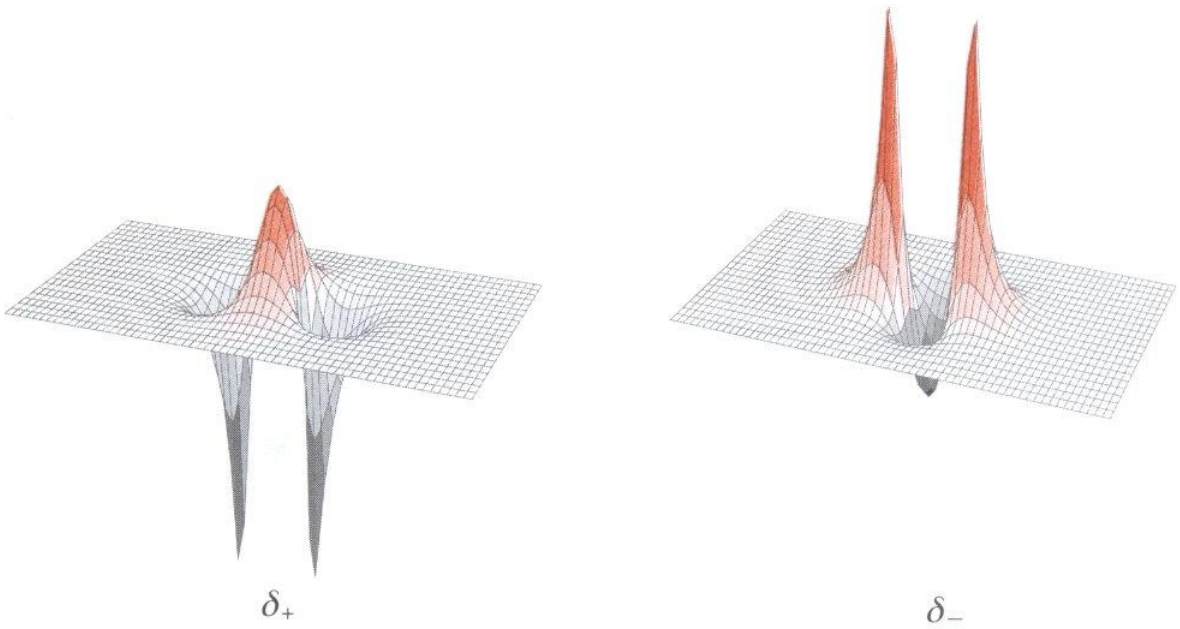
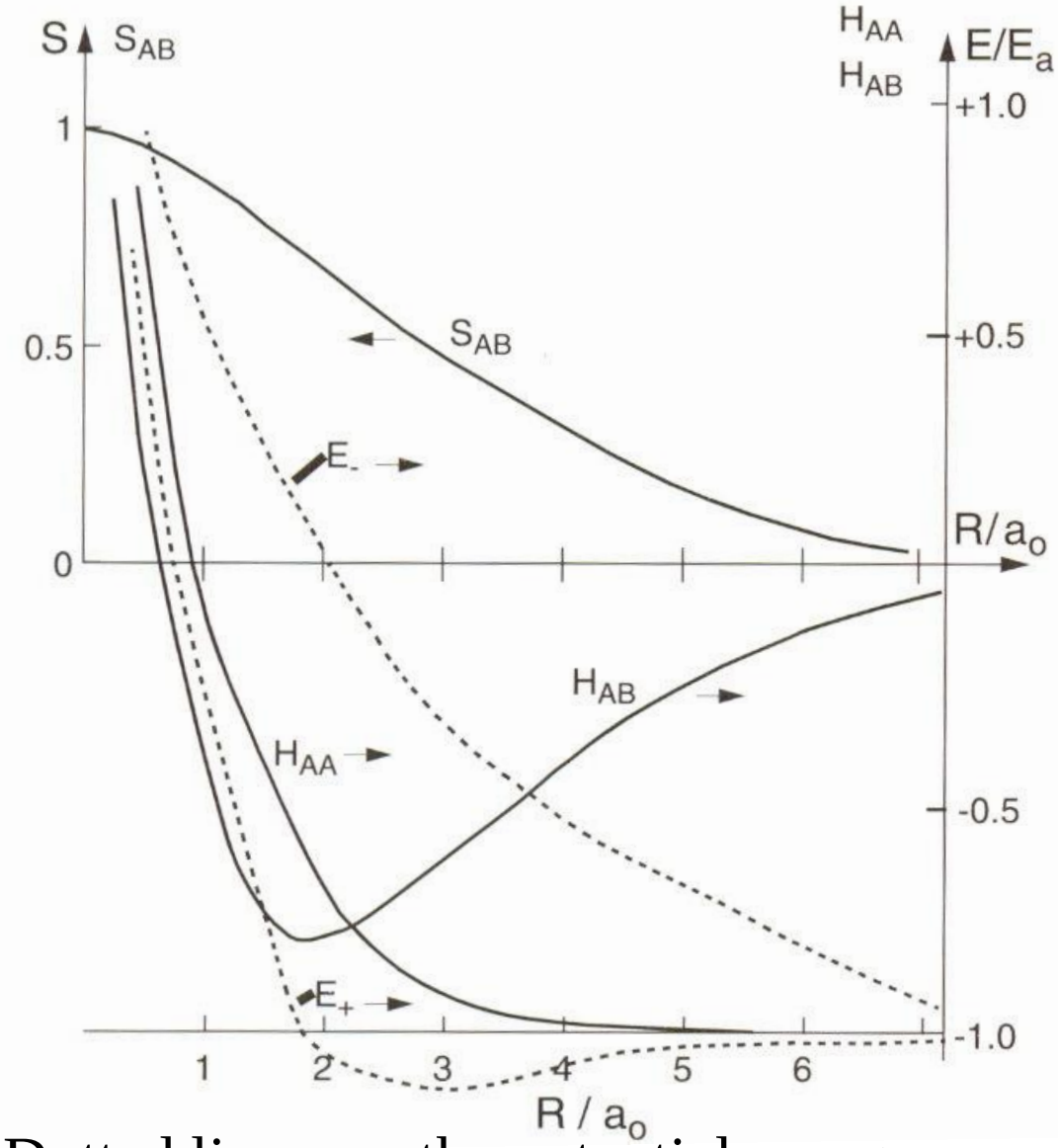


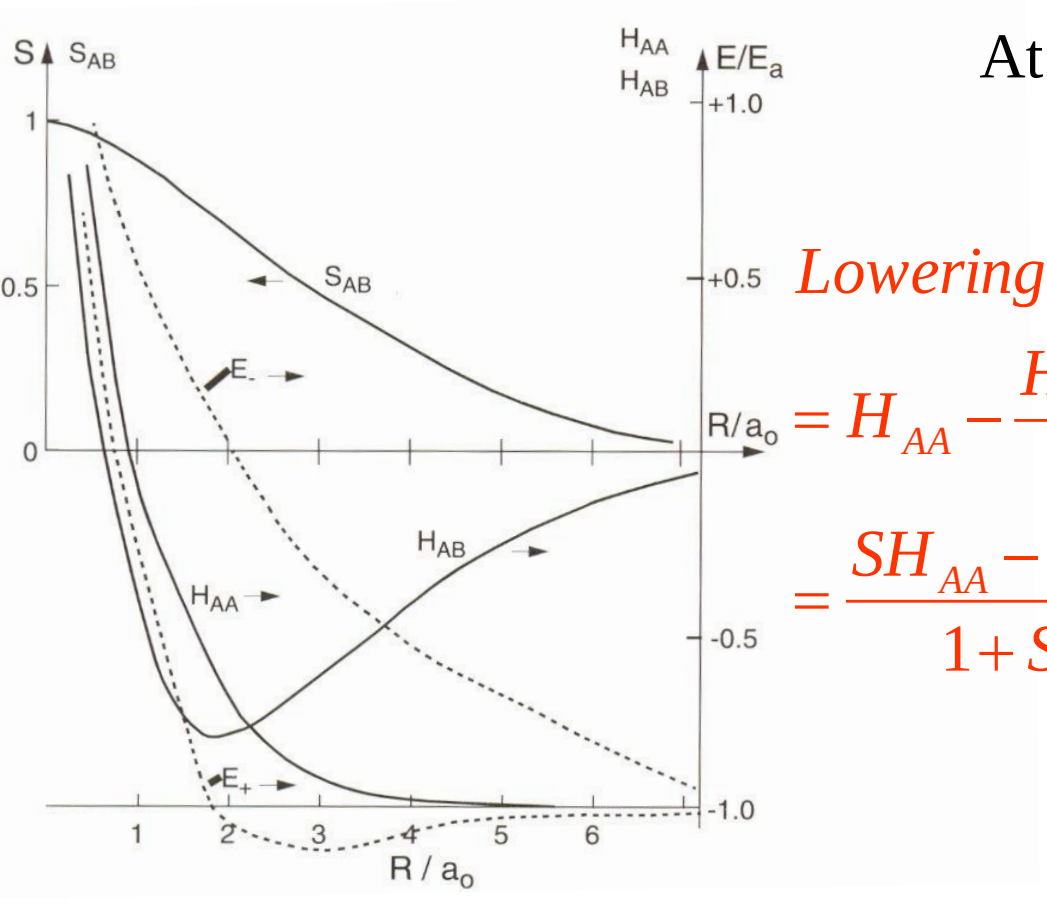
FIGURE 10.15
Surface plots of δ_+ and δ_-, the difference between the electron density in which the electron is delocalized over the two nuclei and the electron density in which the electron is localized on one of the nuclei.

R Dependence of Matrix Elements



Dotted lines are the potential energy curve

Energy Lowering and Rising



At equilibrium of E_+

$$H_{AA}, H_{AB} < 0; S > 0$$

$$Lowering = H_{AA} - E_+ \quad \text{Rising} = E_- - H_{AA}$$

$$= H_{AA} - \frac{H_{AA} + H_{AB}}{1+S} \qquad = \frac{H_{AA} - H_{AB}}{1-S} - H_{AA}$$

$$= \frac{SH_{AA} - H_{AB}}{1+S} \qquad = \frac{SH_{AA} - H_{AB}}{1-S}$$

If S=0 then $\Delta E=0$, S>0 then $\Delta E>0$ rising is more than lowering!

Bonding Orbital Compare With Exact

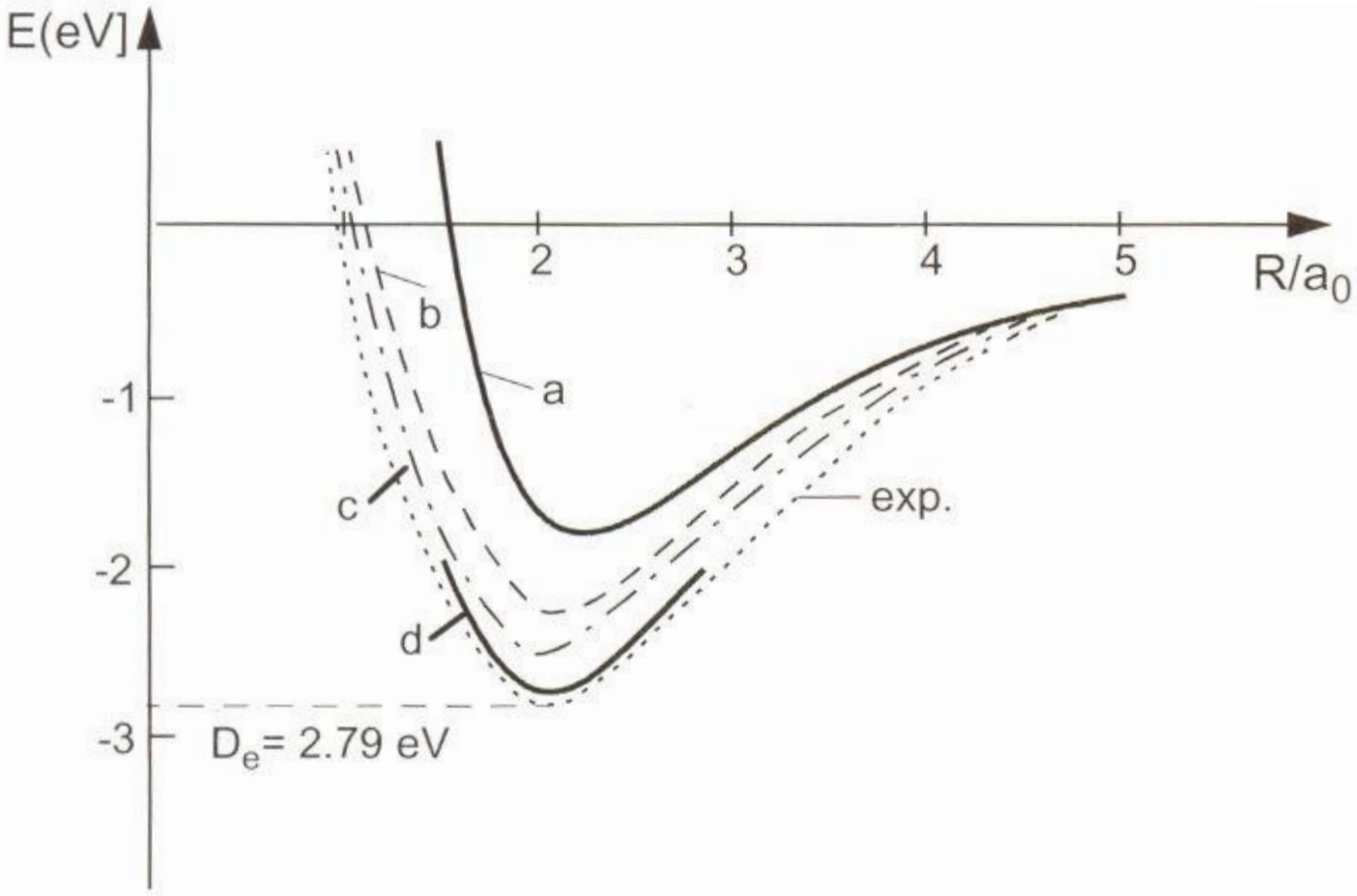
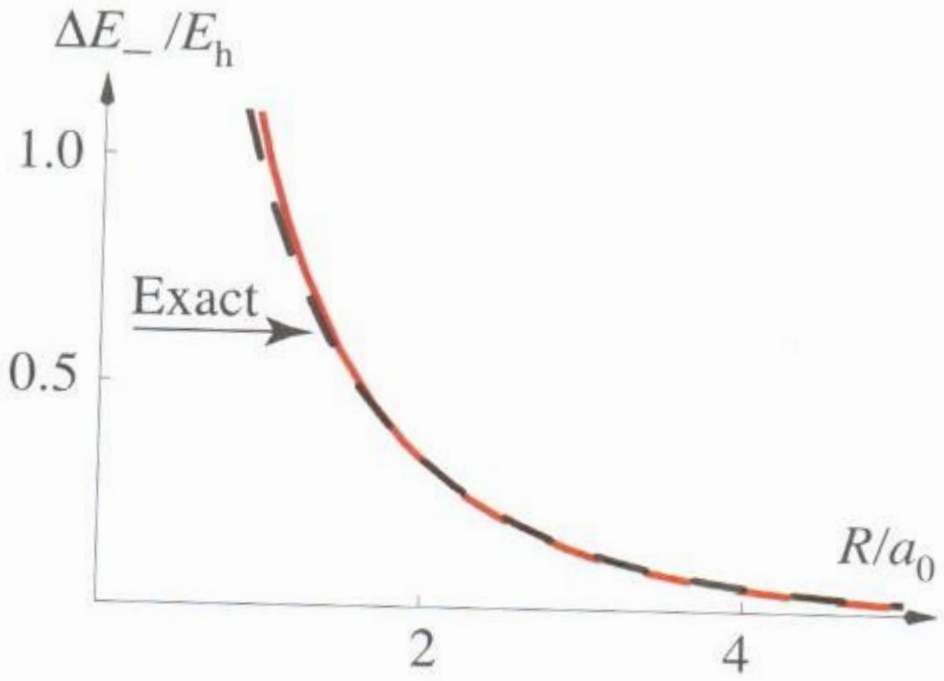


Fig. 2.30 Potential curve of the H_2^+ ground state as computed with a) simple LCAO, b) optimized parameter η, c) polarization term, and d) exact treatment.

Antibonding Oribital



IGURE 10.13

comparison of the energy $\Delta E_-(R)$ of the first excited state of H_2^+ calculated from quation 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

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

$$= 0.7071\left(|A1s\rangle + |B1s\rangle\right) + 0.00145\left(|A2s\rangle + |B2s\rangle\right)$$

Adding in the contribution from $2p_z$

$$\Psi_n^{el}(\mathbf{r};R) = C_1|A1s\rangle + C_2|B1s\rangle + C_3|A2p_z\rangle + C_4|B2p_z\rangle$$

$$= C_A\left(|A1s\rangle + 0.1380|A1p_z\rangle\right) + C_B\left(|B1s\rangle + 0.1380|B1p_z\rangle\right)$$

Additional Orbitals

ABLE 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

. The molecular orbitals are of the form $\psi_b = c_A\phi_A + c_B\phi_B$, where ϕ is given in the table.
. Mulliken, R. S., Ermler, W. C. *Diatomic Molecules*. Academic Press: New York, 1977.
. Bates, D. R., Ledsham, K., Stewart, A. L. Wave Functions of the Hydrogen Molecular Ion. *hilos. Trans. Roy. Soc. London,* Ser. A. **246**, 215 (1953).

Basis Set

- If you use more atomic orbitals to define the molecular orbital usually the energy gets closer to the exact solution

Using a bigger basis set to describe the system

- However bigger basis set you need more time to calculate.

Diatomic Molecules

H_2

$$\hat{H}\Psi_n^{el}(\mathbf{r}_1,\mathbf{r}_2;R)$$

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

$$=E_n(\mathbf{R})\Psi_n^{el}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R})$$

Above equation is two H2+ electrons with electron electron repulsion

Spin Orbital and Spacial Orbitals

When you consider more than one electron you have to consider not only the spacial coordinate **r** but also the spin angular momentum s and the Fermi principle:
Define **x** as the summed coordinate for **r** and s

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

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

Slater Determinant

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

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

Asymmetric wavefunction after exchange of electron coordinate

Generalization for n electron system: Slater Determinant

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

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

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

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

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

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

Potential Energy Curve

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

Incorrect Dissociation!

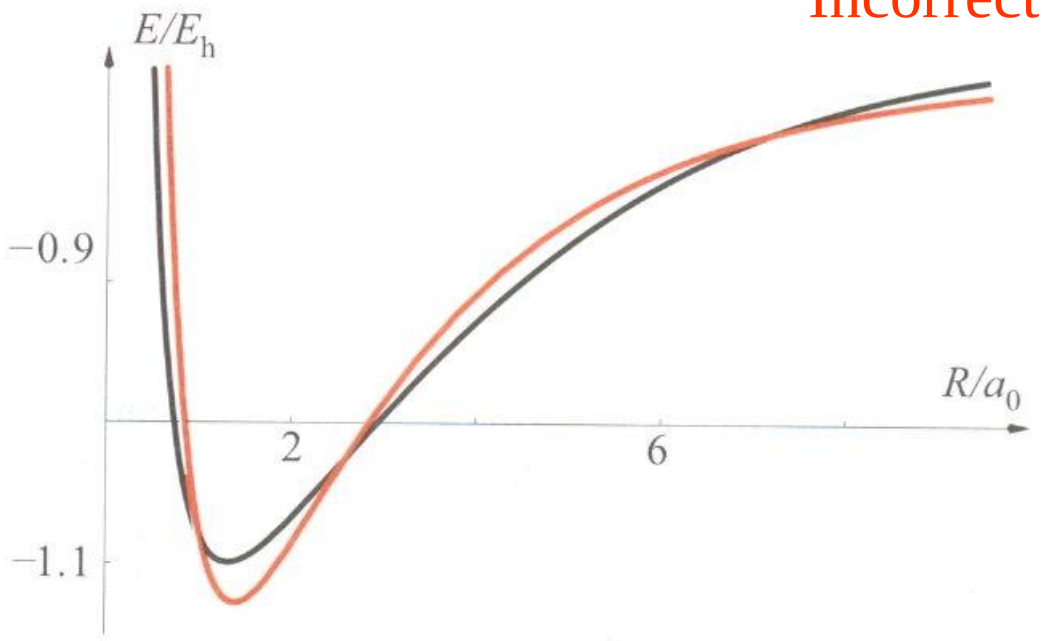


FIGURE 10.23
Both the optimized (orange) and the $\zeta = 1$ (black) molecular orbital energies calculated with Equation 10.41. In neither case does the energy go to the correct limit of $-1\,E_h$ as $R \to \infty$.

What is the Problem of incorrect dissociation

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

$$= |A1s\rangle_1|A1s\rangle_2 + |B1s\rangle_1|B1s\rangle_2 + |A1s\rangle_1|B1s\rangle_2 + |B1s\rangle_1|A1s\rangle_2$$

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

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

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

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

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

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

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

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

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

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

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

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

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

Symmetry of Spacial Orbitals

$$|\Psi_1\rangle \approx |++\rangle(\alpha\beta - \beta\alpha) \qquad |\Psi_2\rangle \approx |--\rangle(\alpha\beta - \beta\alpha)$$

$$|\Psi_3\rangle \approx (|+-\rangle - |-+\rangle)\alpha\alpha \qquad |\Psi_4\rangle \approx |+-\rangle\alpha\beta - |-+\rangle\beta\alpha$$

$$|\Psi_5\rangle \approx |+-\rangle\beta\alpha - |-+\rangle\alpha\beta \qquad |\Psi_6\rangle \approx (|+-\rangle - |-+\rangle)\beta\beta$$

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

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

Solution: Configuration Interaction

Two 1S orbitals can make TWO molecular orbitals

Why not use the two and make combinations

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

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

Configuration 1: two electron in bonding orbital

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

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

Configuration 2: two electron in antibonding orbital

Configuration Interaction

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

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

H2 Potential Curve Revisited

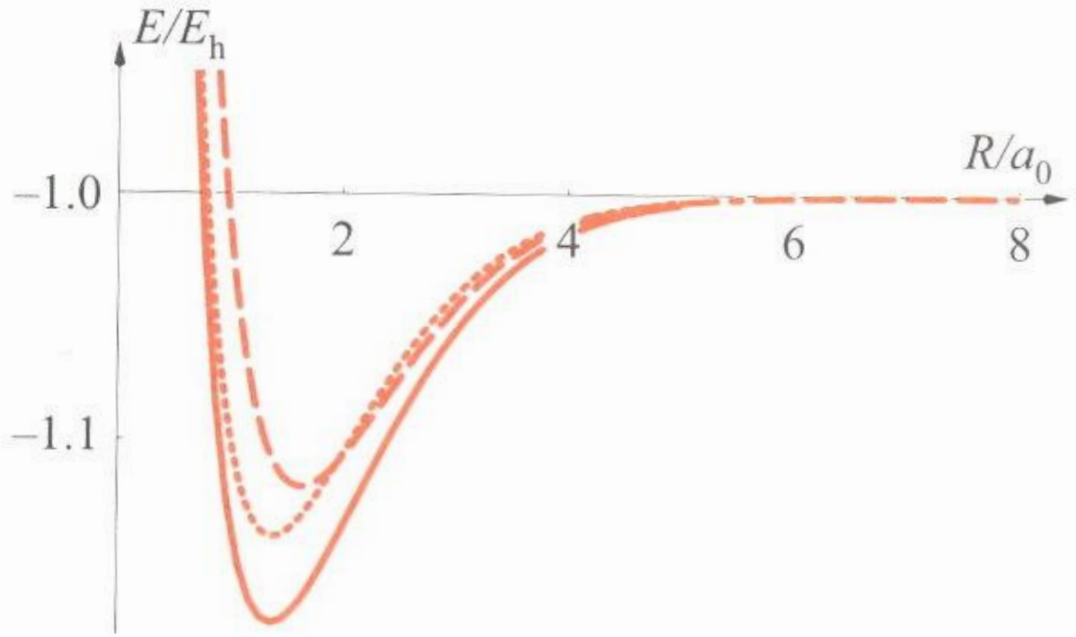


FIGURE 10.25
The configuration-interaction energy E_{CI} of the ground-state energy of H_2 for $\zeta = 1$ (dashed curve) and for an optimized value of ζ (dotted curve) plotted against R. The "exact" results of Kolos and Wolniewicz (solid curve) are shown for comparison.

R Dependence of Expanstion Coefficients

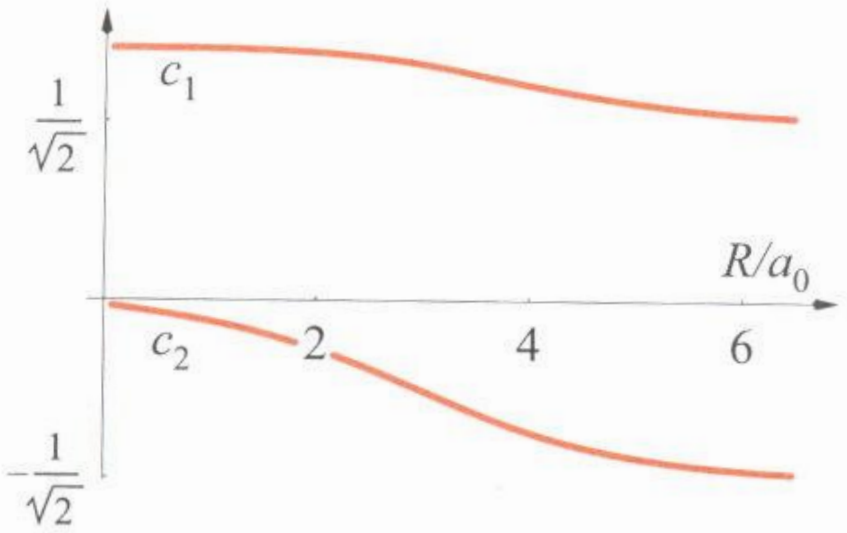


FIGURE 10.27
A plot of c_1 and c_2 for the optimized value of ζ in Equation 10.53 against R. Note that $c_1 \to 1/\sqrt{2}$ and $c_2 \to -1/\sqrt{2}$ as $R \to \infty$.

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 H_2

	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