Computational Material Chemistry

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Aim

- Understand the basic theory behind quantum chemistry calculation
- Learn running quantum chemistry program
- Understand what the output is saying
- Get a feeling of what method to use for what problem

Grading

- Oral Presentation (15-20 minutes) by student in class: 25%

Report on the calculation that they performed and compare with experiment if available

- Homework (Once): 25%
- Test on the last day: 50%

Schedule

1. Born Oppenheimer Approximation, LCAO H_2^+ calculation
2. $H_{2,}$ homonuclear and heteronuclear diatomic molecule, Restricted Hartree Fock.
3. Unrestricted Hartree Fock, Roothan Equation, Basis Set Gaussian Calculation Input/structure optimization.
4. Potential Energy Surface, Barrier Transition State.

Schedule

5. Electron correlation (DFT, MP2, QCISD, CCSD, CASSCF, MRCI, G2 G3)
6. Vibrational Spectroscopy, Electronic Spectroscopy
7. Force field parametrization, intermolecular potential
8. Molecular dynamics simulation of liquid

Born-Oppenheimer Approximation

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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})

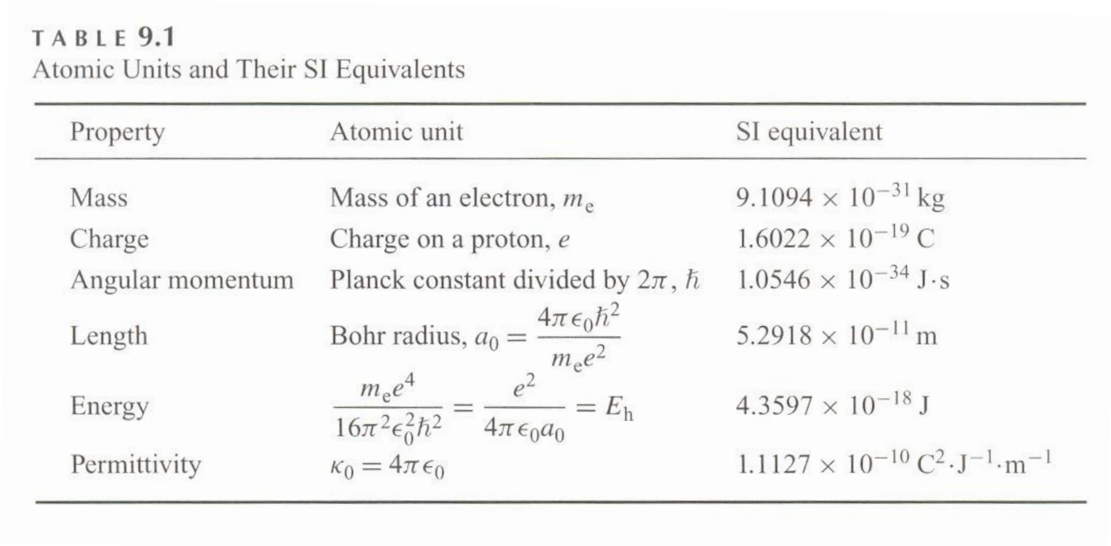
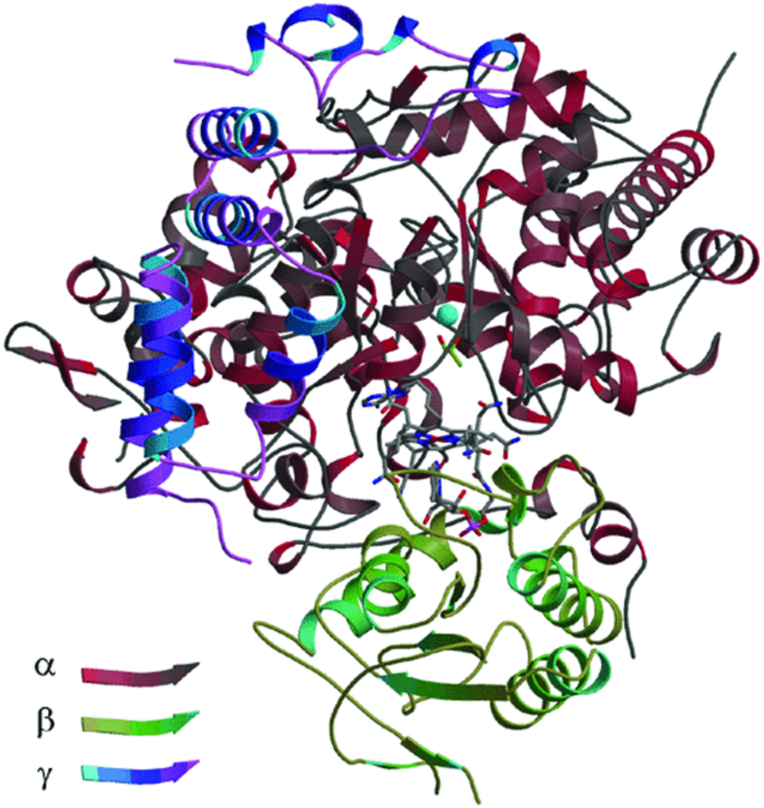


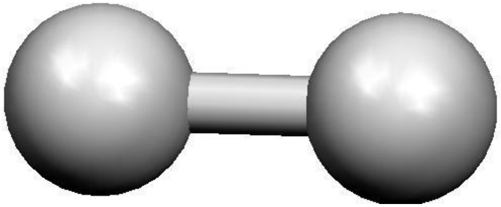
TABLE 9.1
Atomic Units and Their SI Equivalents

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} $C^2 \cdot J^{-1} \cdot m^{-1}$

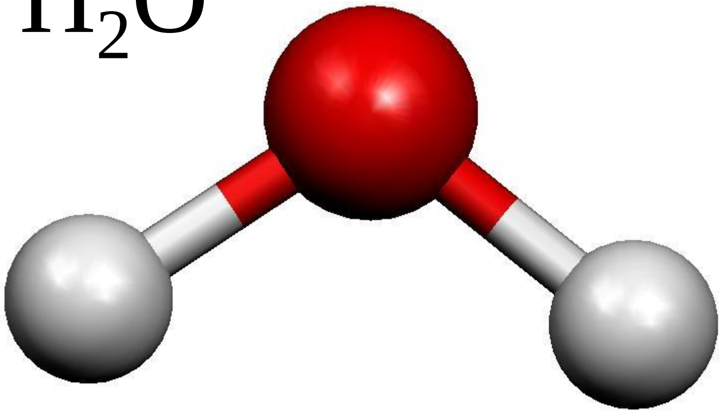
Proteins, Molecules



H_2



H_2O



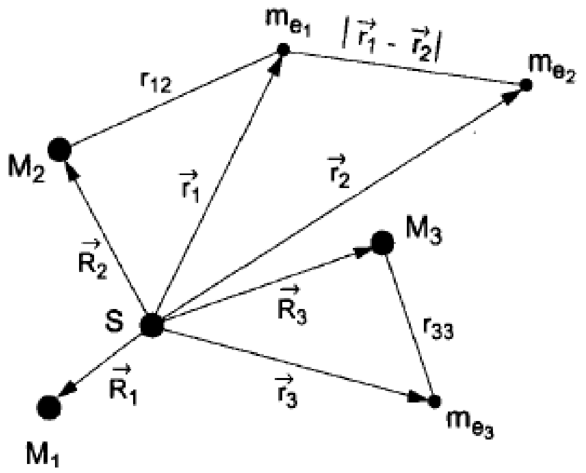
You always write where the nucleus is but you never write the electrons or the electrons are written as a line!!!
YOU ARE ALREADY ASSUMING BORN-OPPENHEIMER APPROXIMATION

Full Problem

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

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

$$V(\mathbf{r},\mathbf{R}) = \frac{e^2}{4\pi\varepsilon_0}\left[\sum_{I=1}^{N}\sum_{J\neq I}^{N}\frac{Z_I Z_J}{\left|\mathbf{R}_I - \mathbf{R}_J\right|} - \sum_{I=1}^{N}\sum_{i=1}^{n}\frac{Z_I}{\left|\mathbf{R}_I - \mathbf{r}_i\right|} + \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}\right]$$



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

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

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

Born-Oppenheimer Approximation in words

Mass of electron versus mass of nucleus

1 <<< 1830 (at least)

electron moves much faster than nucleus, so electron can instantly adjust to change in nuclear coordinate, so nucleus moves in an average field made up by the electrons

At a given value for the nuclear geometry **R,** there exist a well defined electronic state distribution

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

This electronic state depends on position of nucleus, but not on the momentum

BO Approximation in equation 1

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

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

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

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

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

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} = \delta_{mn}$$

$$\Psi(\mathbf{r},\mathbf{R}) = \chi_n^{NU}(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

BO Approximation 2

Born-Oppenheimer Approximation

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

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

Nuclear wavefunction is given by solving the rest!

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

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

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.

Potential Energy Curve

- Molecular Mechanics Force Field
- Ab initio electronic state calculation
- Semi empirical calculation

Most accurate will be to used ab initio methods and solve the electron Schrodinger equation, but that requires too much time so people have used equations such as harmonic oscillators and cosine functions to model the potential energy curve and used it for molecular dynamics simulations.

LCAO Approximation for Diatomic Molecules

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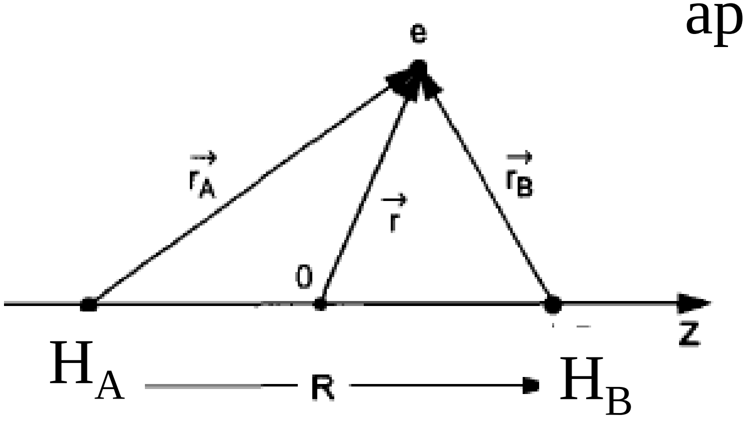
H_2^+ Most Simple Diatom

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

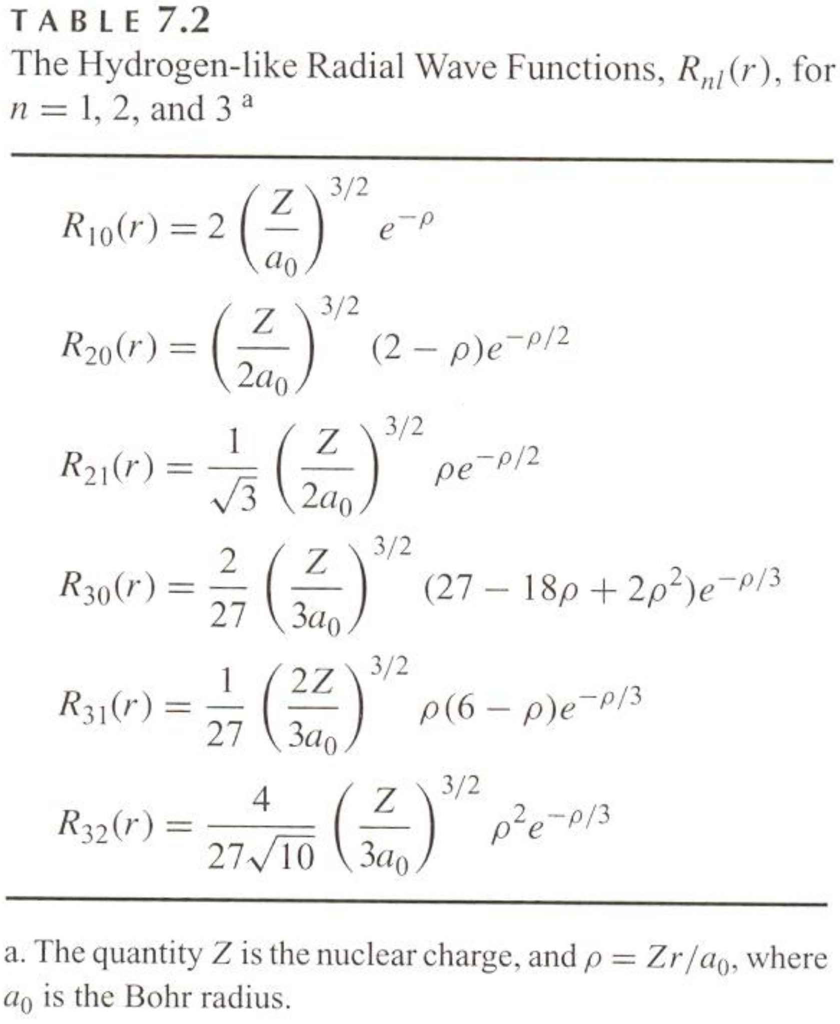


TABLE 7.2

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.

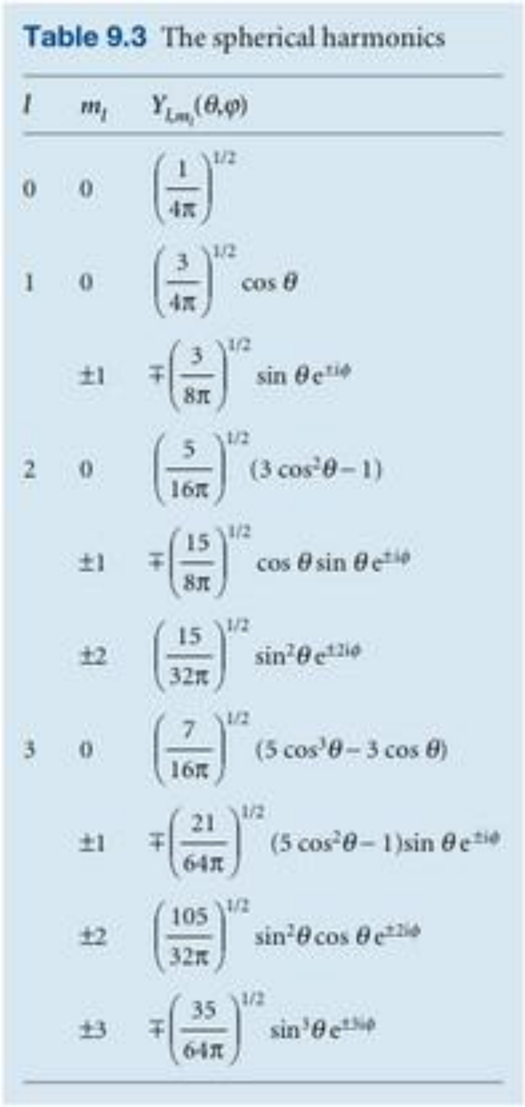
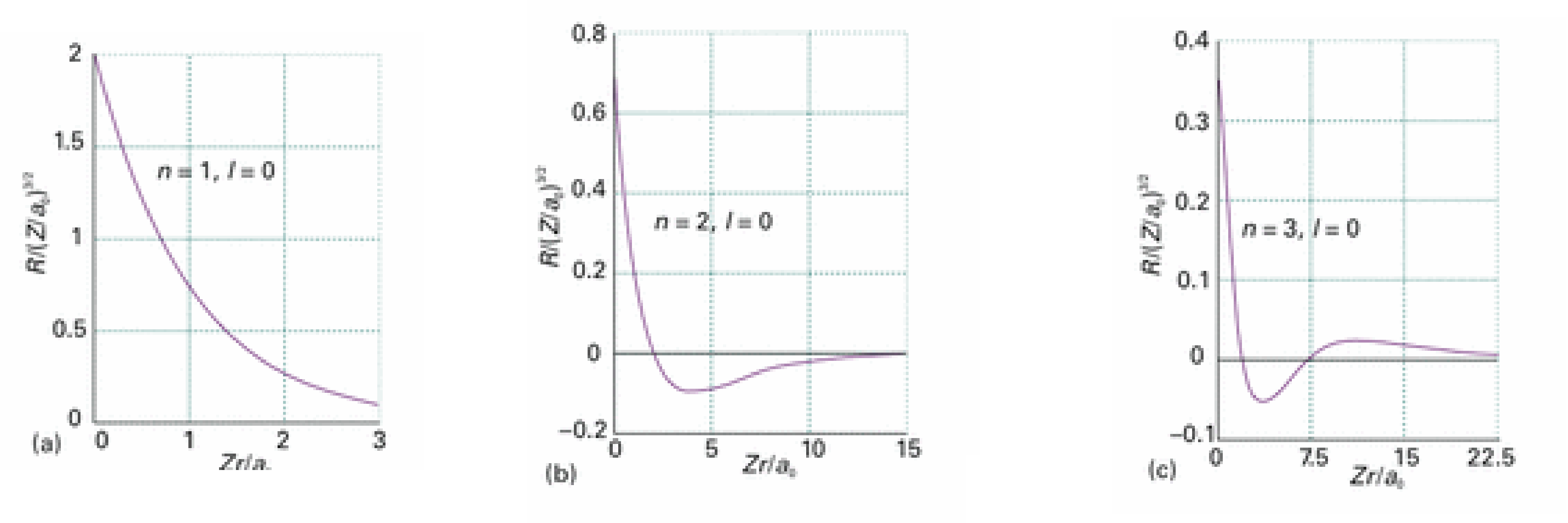


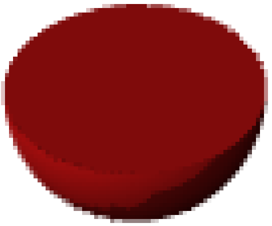
Table 9.3 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\varphi)$
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	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

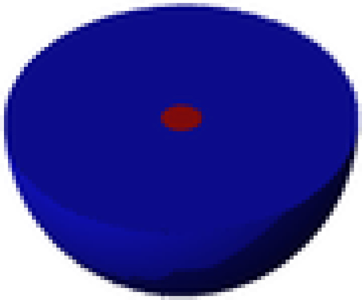
s Wavefunction

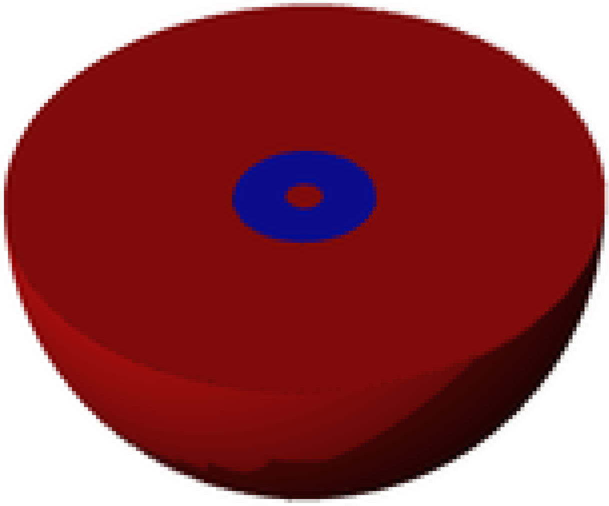


1s

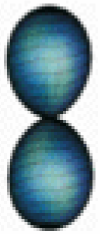


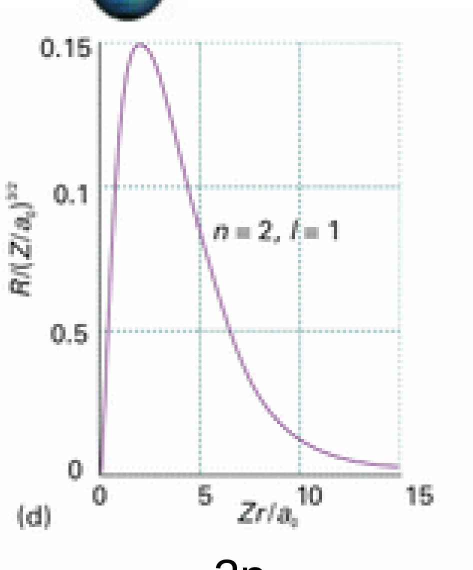
2s



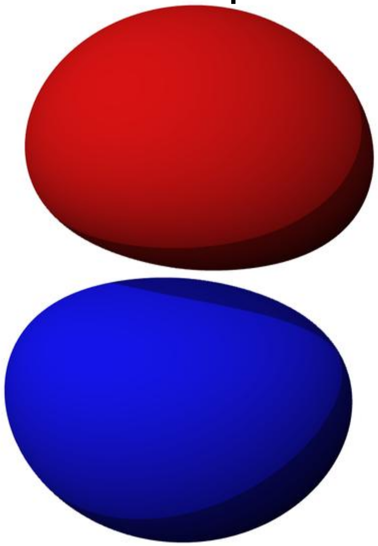


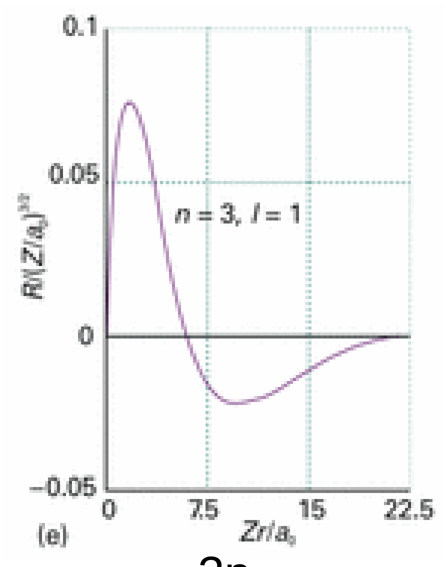
p Wavefunction



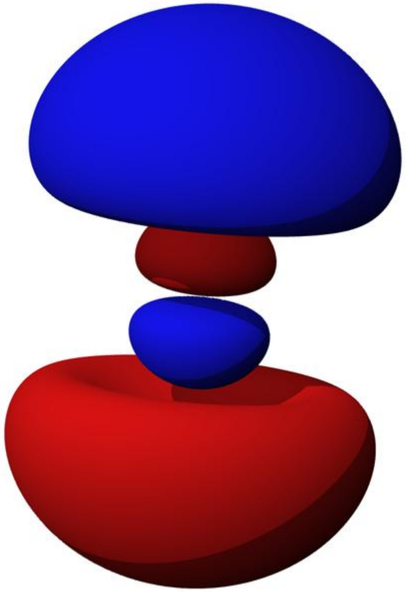


2p

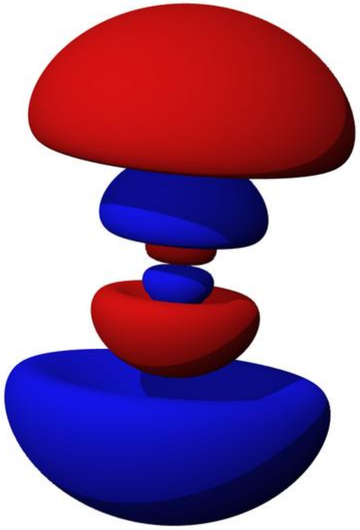




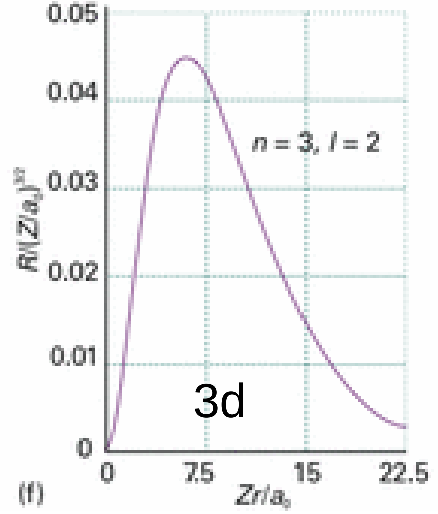
3p



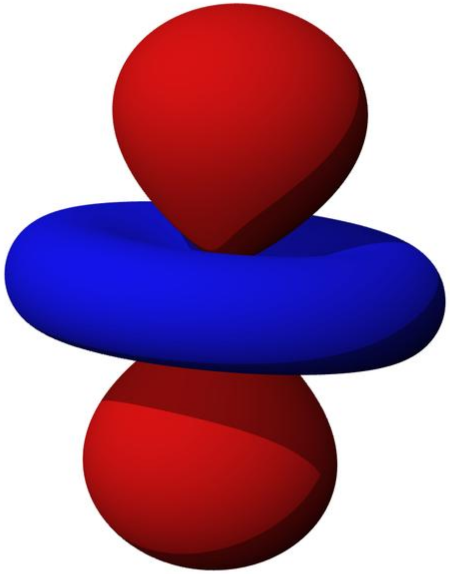
4p



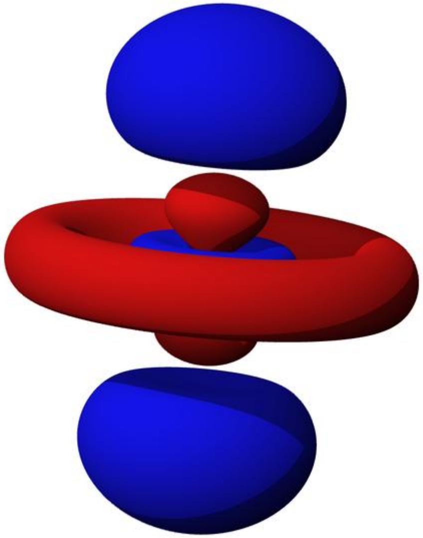
d Wavefunction



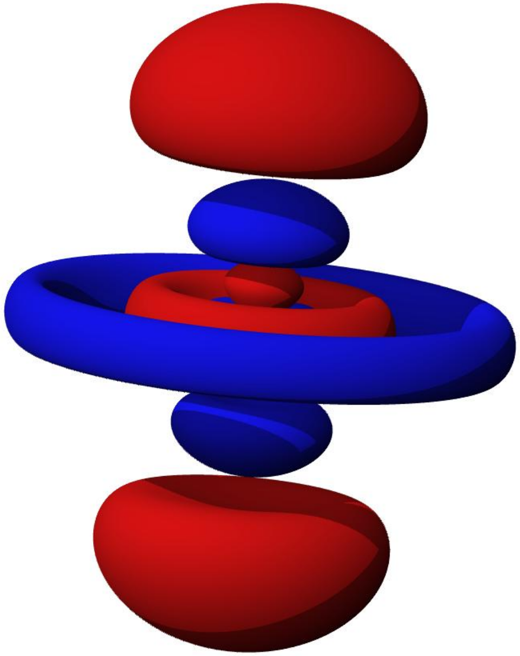
3d



4d



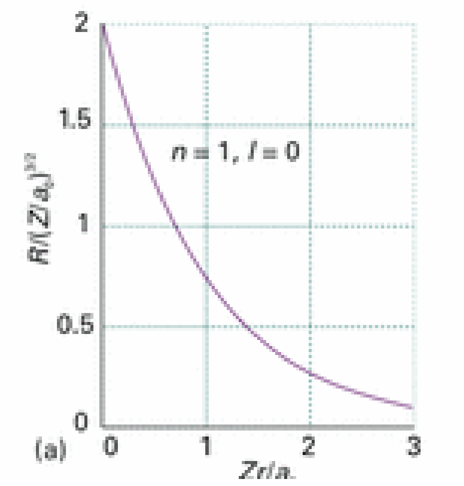
5d

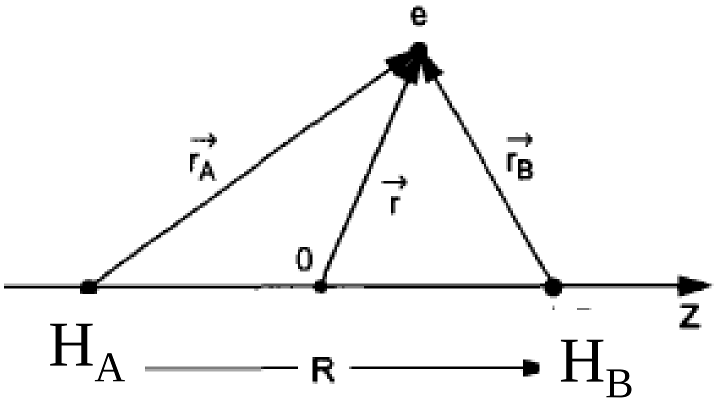


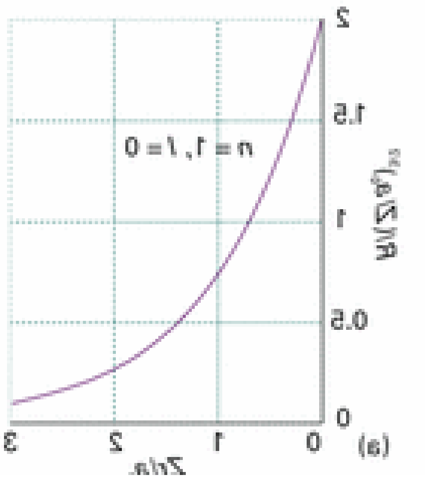
LCAO

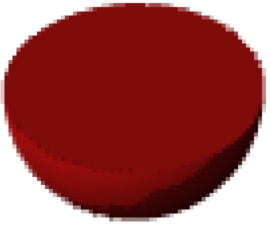
To make the molecular orbital (the electronic wavefunction for the molecule) let just add up each atomic orbital (electronic wave function for the atoms making the molecule)

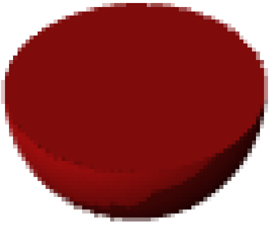
$$\Psi_n^{el}(\mathbf{r}) = C_A\psi_{1S,A}(\mathbf{r}) + C_B\psi_{1S,B}(\mathbf{r})$$











Variational Theory 1

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

$$\psi_{trial} = \sum_{i=1}^{n} c_i \phi_i$$

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

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

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

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

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*

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

Take derivative with c_j

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

Due to stationary condition of the solution

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

Variational Theory

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

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

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

H_2^{+}

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

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

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

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

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

$$S = \left\langle A\middle|B\right\rangle = \left\langle B\middle|A\right\rangle$$

$$\left\langle A\middle|A\right\rangle = \left\langle B\middle|B\right\rangle = 1$$

Overlap Integral

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

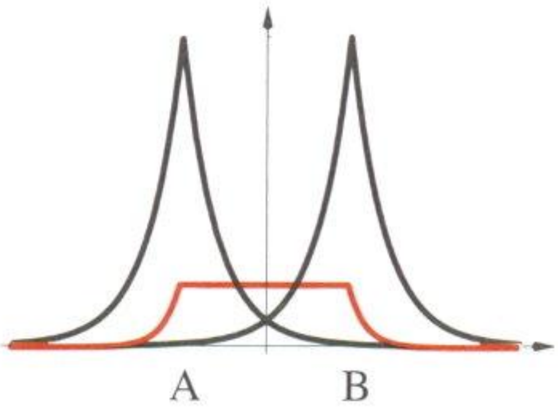


FIGURE 10.9
The overlap of the 1*s* orbitals centered on hydrogen nuclei located at A and B, a distance *R* apart. The orange curve is the product of the two orbitals.

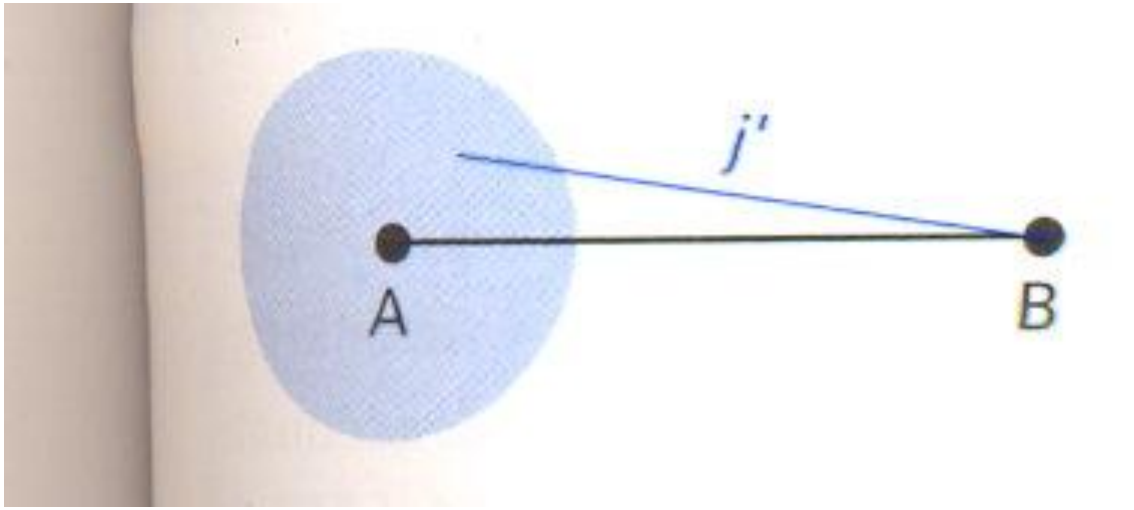
$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

Atomic Integral

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

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

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

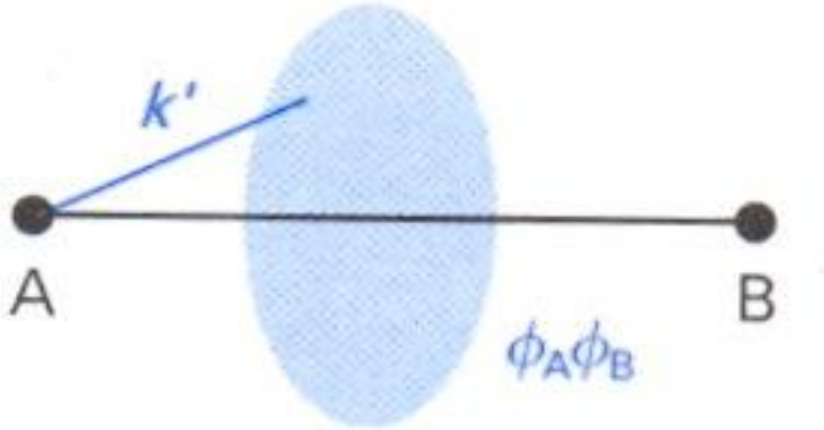


Exchange Integral

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

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

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



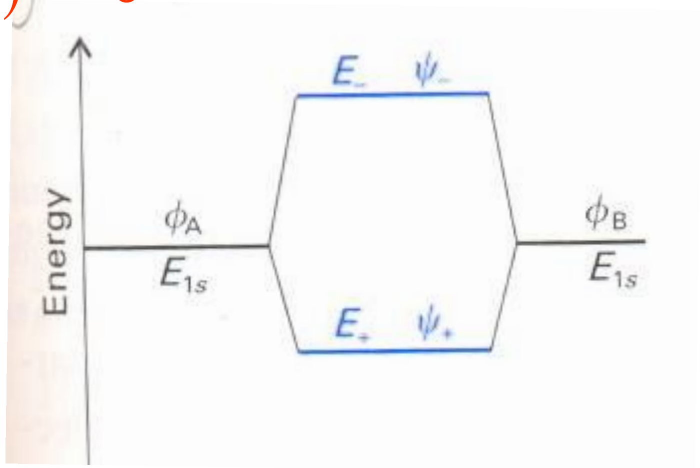
Solve Secular Equation

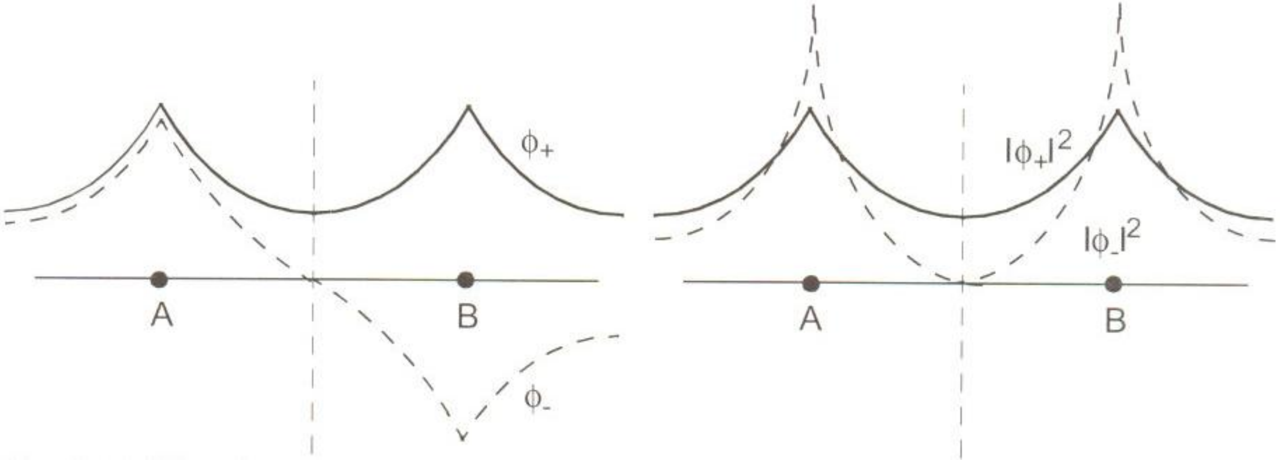
$$\begin{vmatrix} H(R)_{AA} - E(R) & H(R)_{AB} - E(R)S \\ H(R)_{BA} - E(R)S & H(R)_{BB} - E(R) \end{vmatrix} = 0$$

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

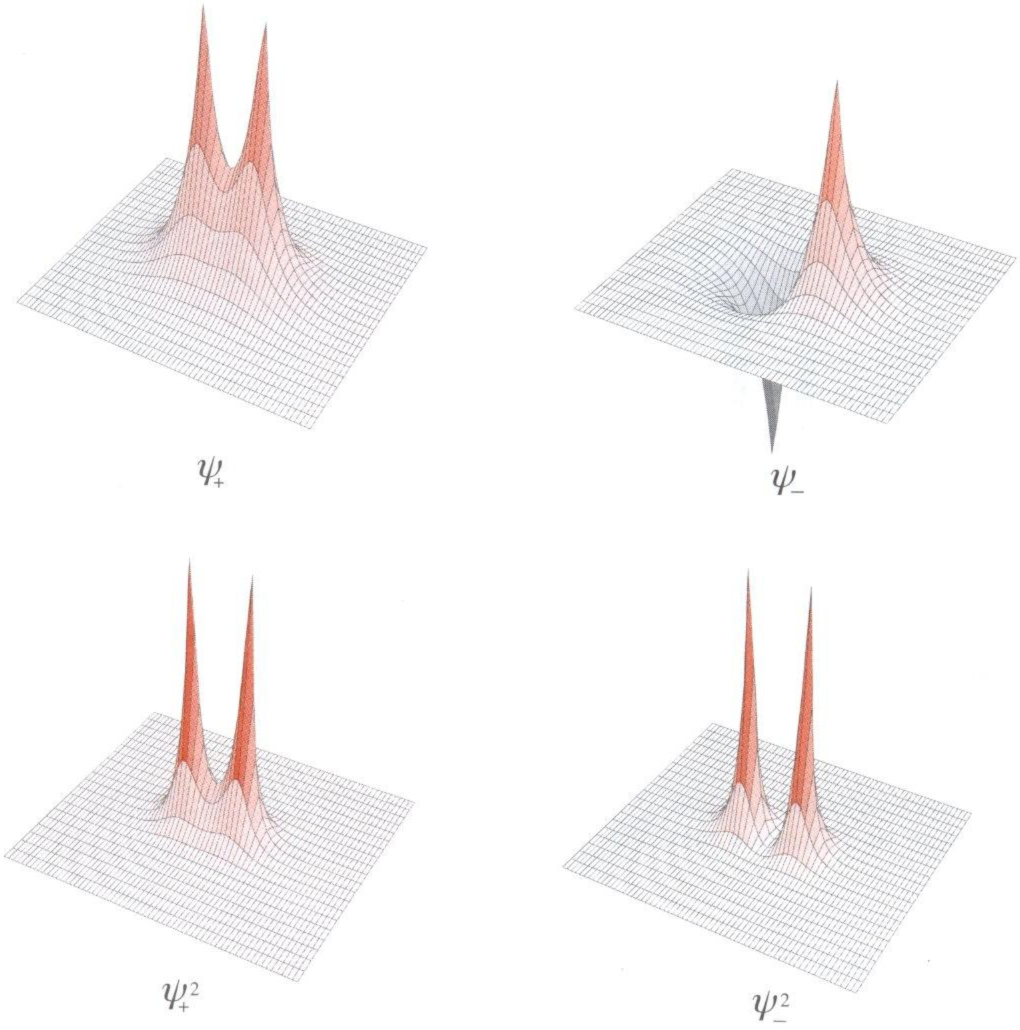
$$E_{\pm}(R) = \frac{H(R)_{AA} \pm H(R)_{AB}}{1 \pm S(R)}$$

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





Bonding and Antibonding Orbital


ψ_+ ψ_-

ψ_+^2 ψ_-^2

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

Electron Density Difference

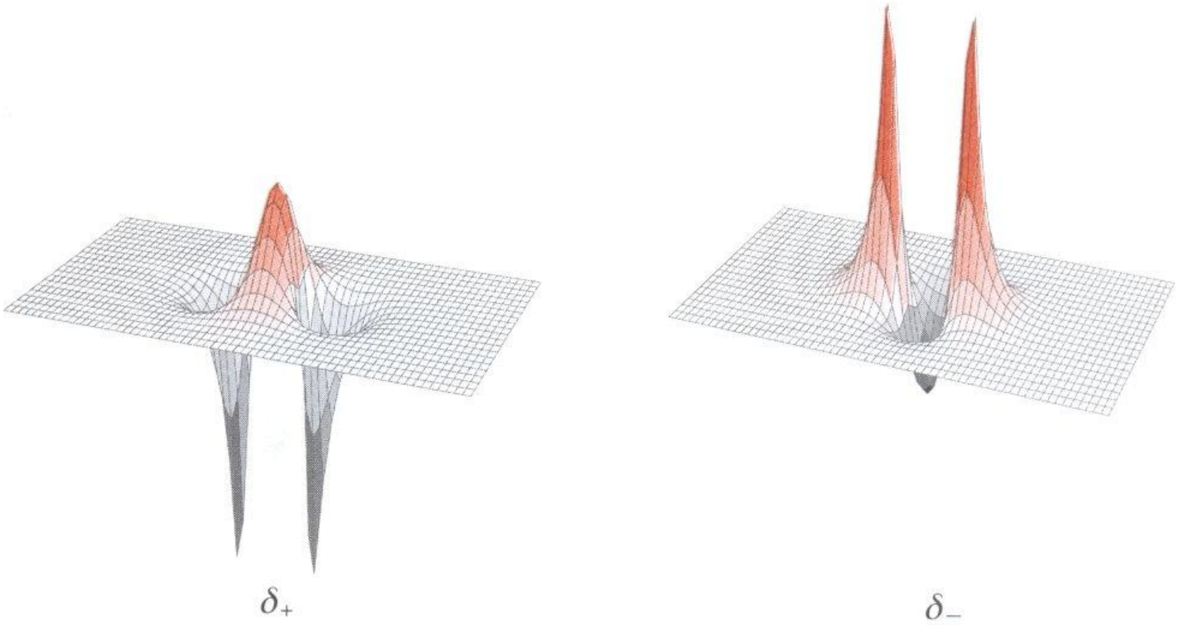
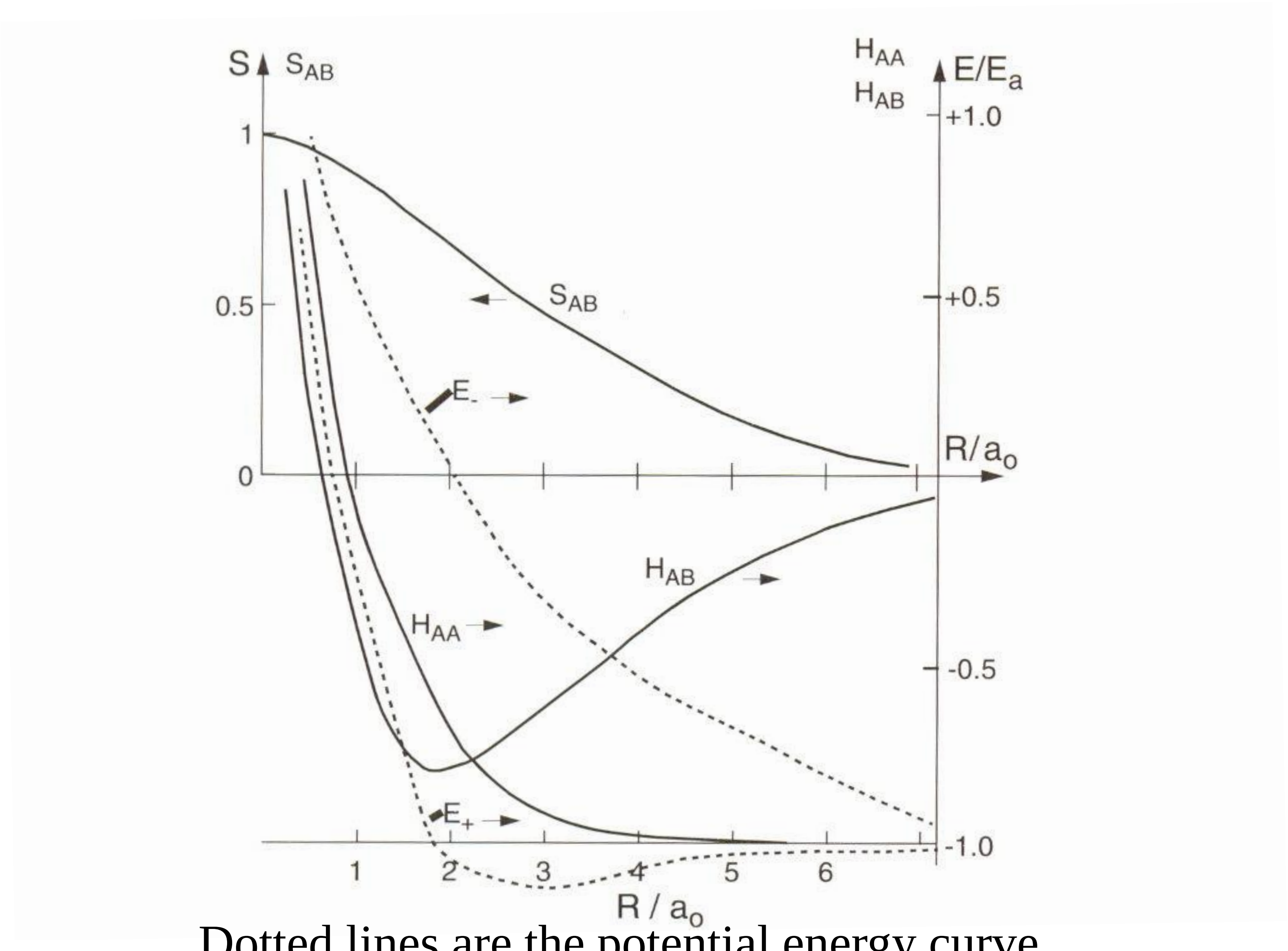


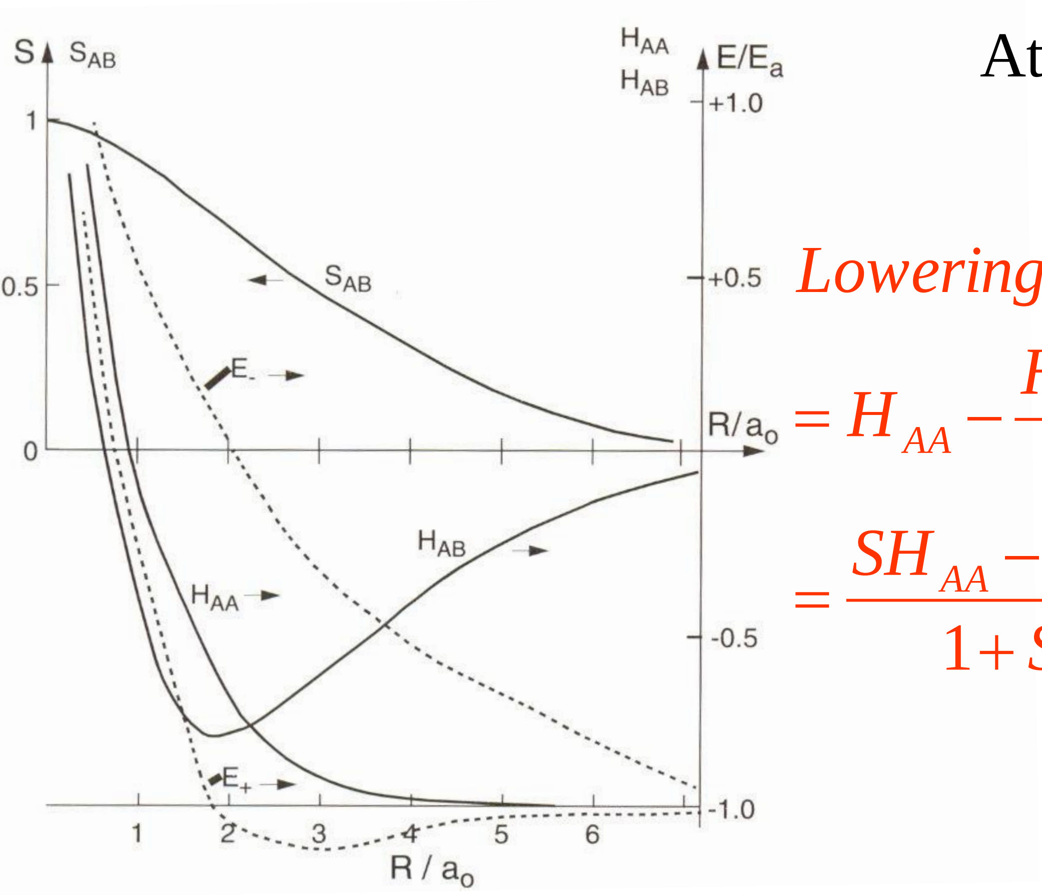
FIGURE 10.15
Surface plots of δ_+ and δ_-, the difference between the electron density in which the electron is delocalized over the two nuclei and the electron density in which the electron is localized on one of the nuclei.

R Dependence of Matrix Elements



Dotted lines are the potential energy curve

Energy Lowering and Rising



At equilibrium of E_+

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

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

$$\text{Rising} = E_- - H_{AA} = \frac{H_{AA} - H_{AB}}{1-S} - H_{AA} = \frac{SH_{AA} - H_{AB}}{1-S}$$

$$\Delta E = \frac{SH_{AA} - H_{AB}}{1-S} - \frac{SH_{AA} - H_{AB}}{1+S} = \left(SH_{AA} - H_{AB}\right)\left(\frac{1}{1-S} - \frac{1}{1+S}\right)$$

$$= \left(SH_{AA} - H_{AB}\right)\frac{2S}{1-S^2}$$

If S=0 then ΔE=0, S>0 then ΔE>0 rising is more than lowering!

Bonding Orbital Compare With Exact

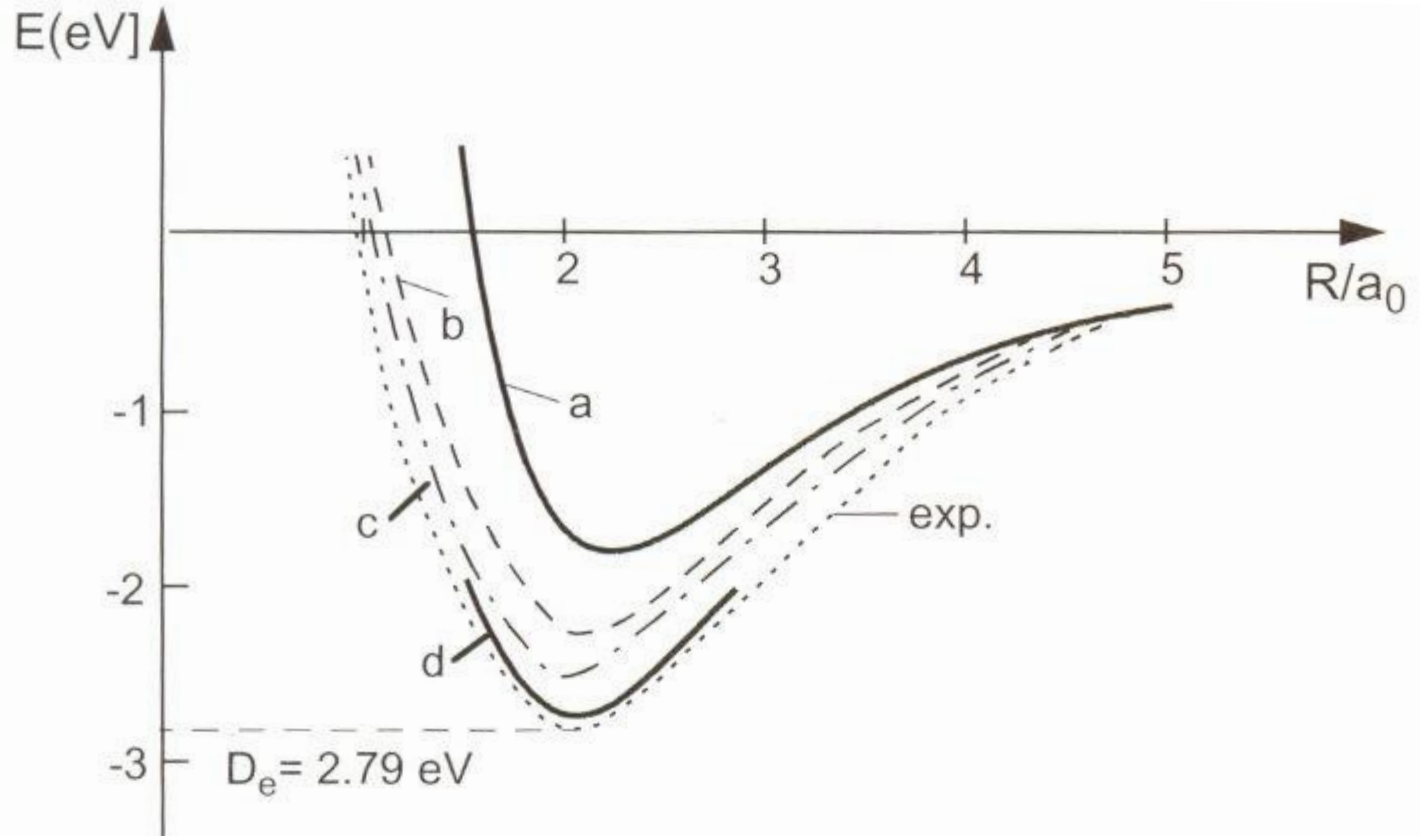
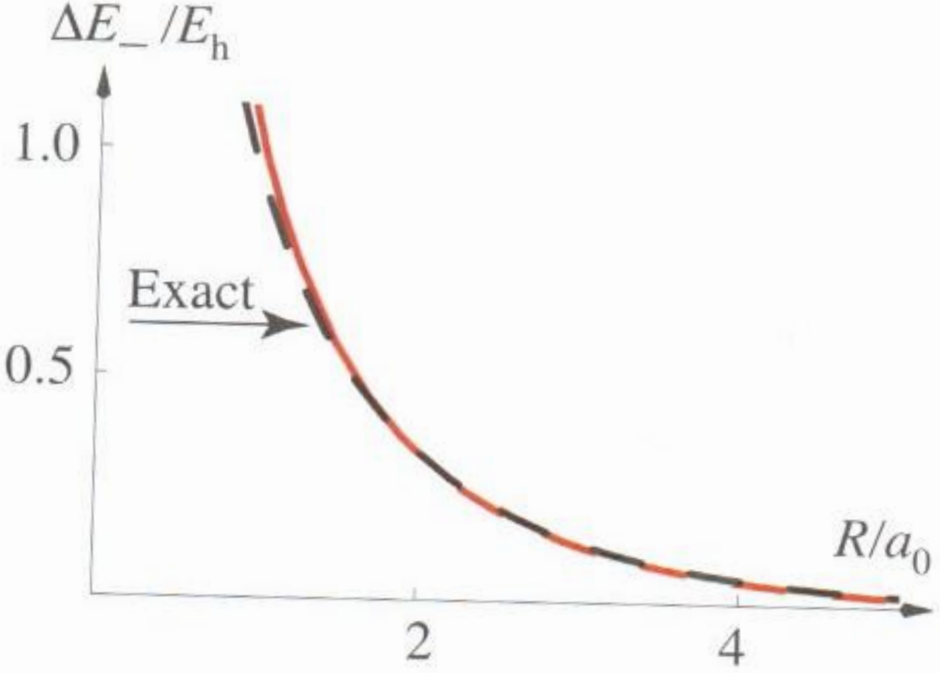


Fig. 2.30 Potential curve of the H_2^+ ground state as computed with a) simple LCAO, b) optimized parameter η, c) polarization term, and d) exact treatment.

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

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

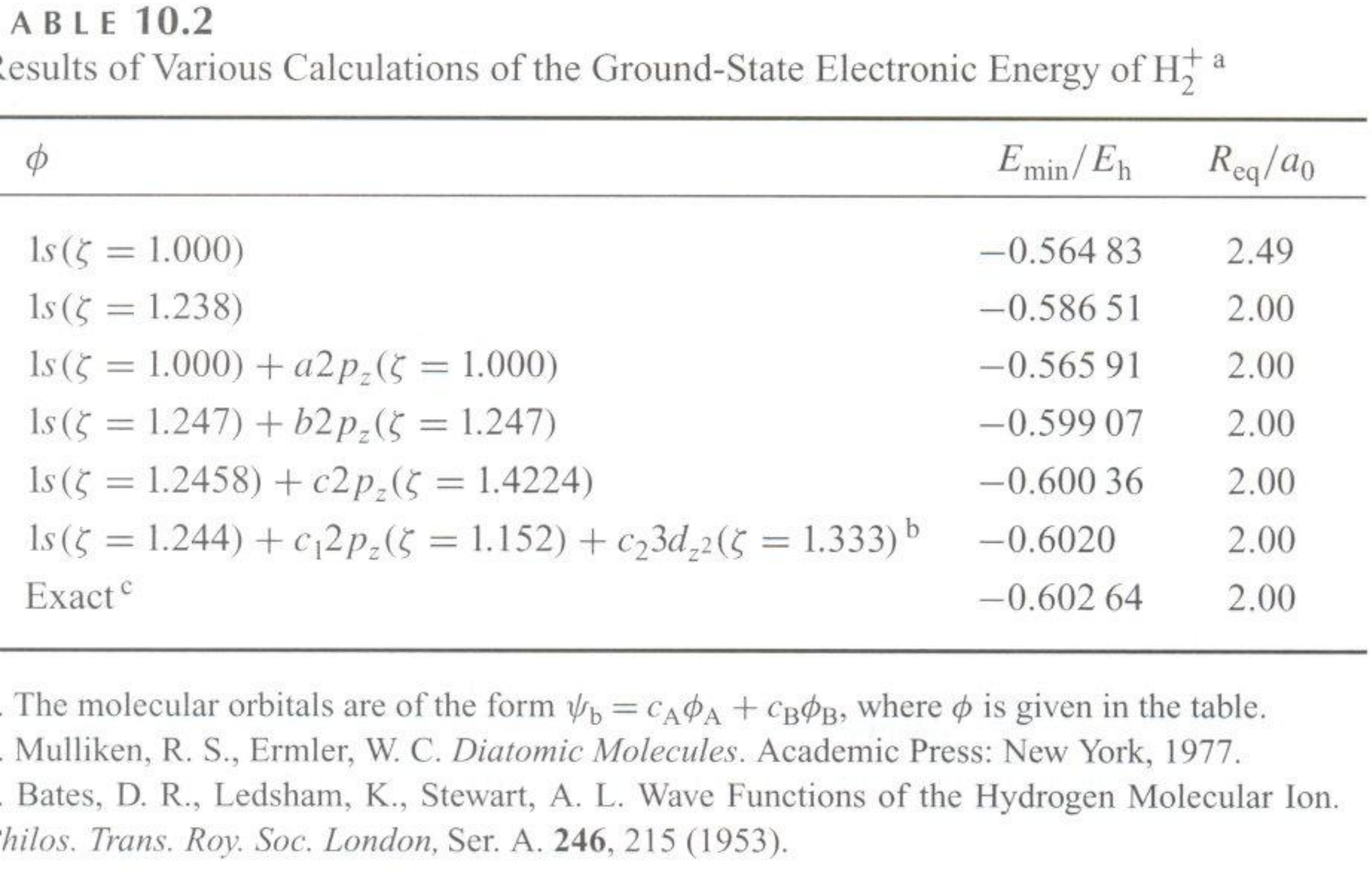
$$= 0.7071(|A1s\rangle + |B1s\rangle) + 0.00145(|A2s\rangle + |B2s\rangle)$$

Adding in the contribution from $2p_z$

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

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

Additional Orbitals



ABLE 10.2

esults of Various Calculations of the Ground-State Electronic Energy of H_2^+ [a]

ϕ	$E_{\mathrm{min}}/E_{\mathrm{h}}$	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 $\psi_{\mathrm{b}} = c_{\mathrm{A}}\phi_{\mathrm{A}} + c_{\mathrm{B}}\phi_{\mathrm{B}}$, 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

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

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

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

Above equation is two H_2^+ electrons with electron electron repulsion

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

$$=\left[h_1+h_2+\frac{1}{|\mathbf{R}|}+\frac{1}{|\mathbf{r}_{12}|}\right]\Psi_n^{el}\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)$$

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

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

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

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

Asymmetric wavefunction after exchange of electron coordinate

Generalization for n electron system: Slater Determinant

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

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

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

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

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

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

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

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

Potential Energy Curve

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

Incorrect Dissociation!

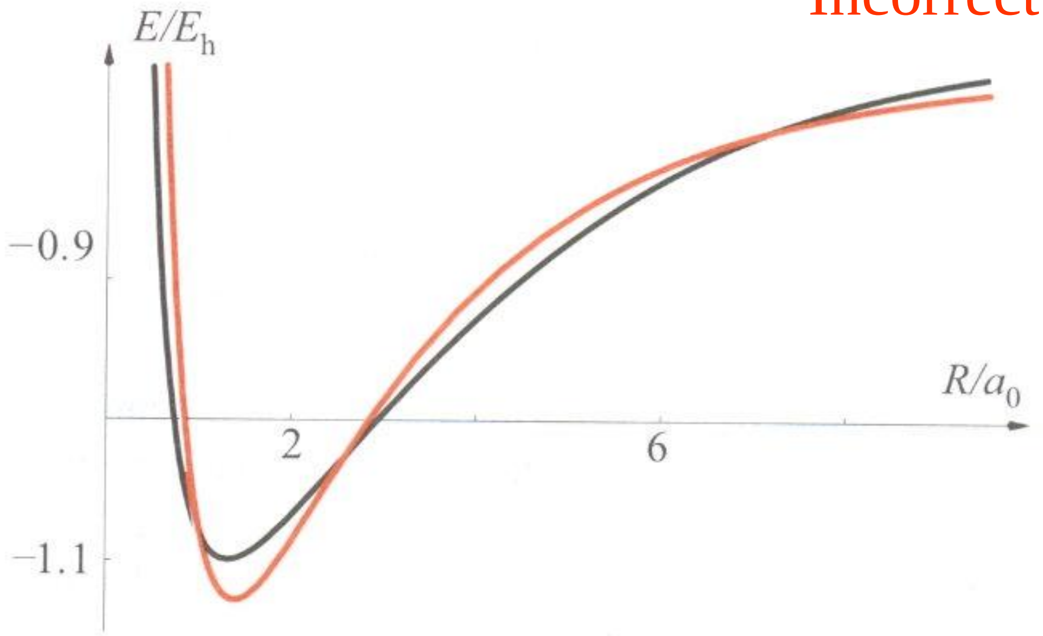


FIGURE 10.23
Both the optimized (orange) and the $\zeta = 1$ (black) molecular orbital energies calculated with Equation 10.41. In neither case does the energy go to the correct limit of $-1\ E_h$ as $R \to \infty$.

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

$H_A:$ and H_B^+; H_A and $H_B:$

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

$H_A\cdot$ and $\cdot H_B$; $H_A\cdot$ and $\cdot H_B$

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

Solution: Configuration Interaction

Two 1S orbitals can make TWO molecular orbitals
Why not use the two and make combinations

$$|\Psi_1\rangle = C_1 \begin{vmatrix} \alpha(1)|+\rangle_1 & \beta(1)|+\rangle_1 \\ \alpha(2)|+\rangle_2 & \beta(2)|+\rangle_2 \end{vmatrix} \qquad |\Psi_2\rangle = C_2 \begin{vmatrix} \alpha(1)|-\rangle_1 & \beta(1)|-\rangle_1 \\ \alpha(2)|-\rangle_2 & \beta(2)|-\rangle_2 \end{vmatrix}$$

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

Configuration 1: two electron in bonding orbital

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

Configuration 2: two electron in antibonding orbital

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

Configuration Interaction

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

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

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

By correct selection of the value for C_1 and C_2 you get no Ionic wavefunciton contribuiton at long bond length

H2 Potential Curve Revisited

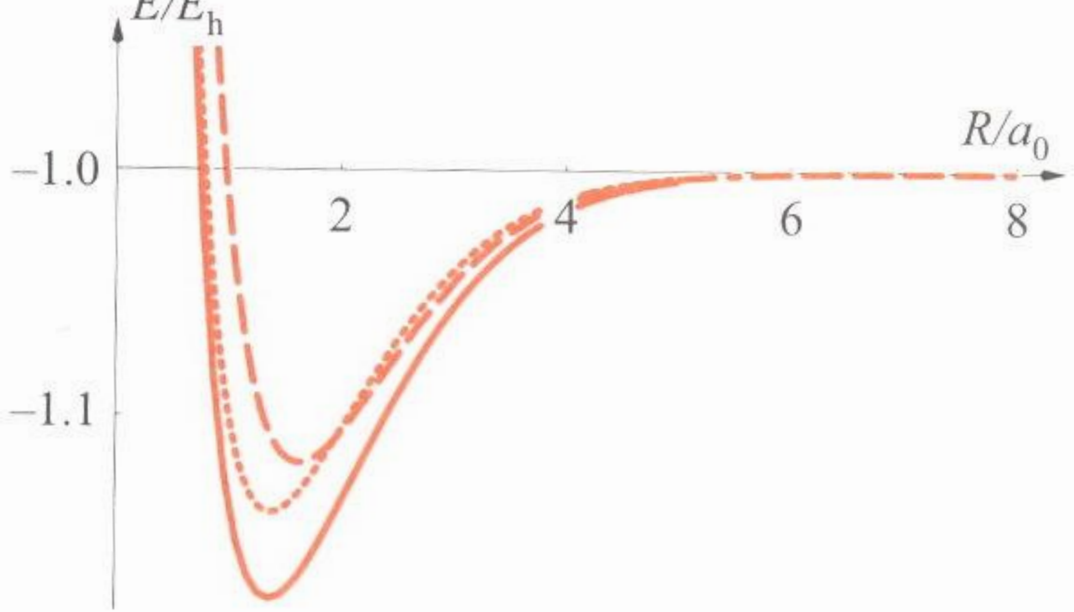


FIGURE 10.25
The configuration-interaction energy E_{CI} of the ground-state energy of H_2 for $\zeta = 1$ (dashed curve) and for an optimized value of ζ (dotted curve) plotted against R. The "exact" results of Kolos and Wolniewicz (solid curve) are shown for comparison.

R Dependence of Expanstion Coefficients

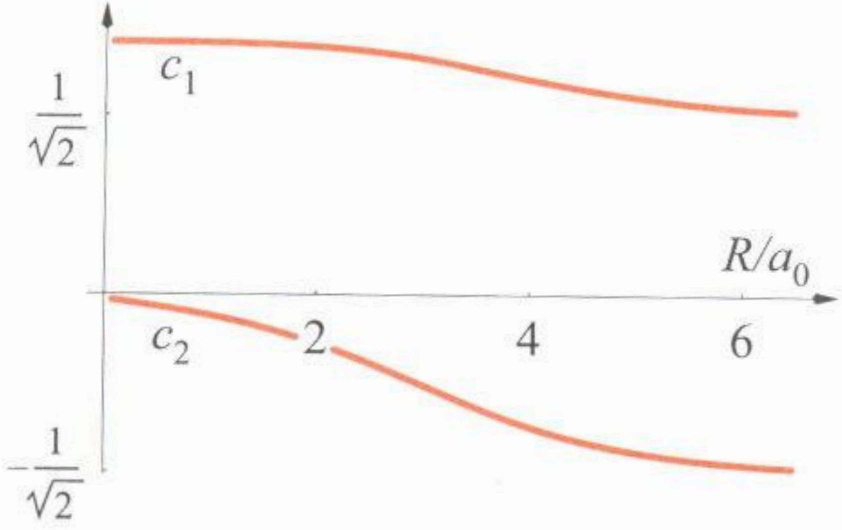


FIGURE 10.27
A plot of c_1 and c_2 for the optimized value of ζ in Equation 10.53 against R. Note that $c_1 \rightarrow 1/\sqrt{2}$ and $c_2 \rightarrow -1/\sqrt{2}$ as $R \rightarrow \infty$.

Use of more orbitals

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

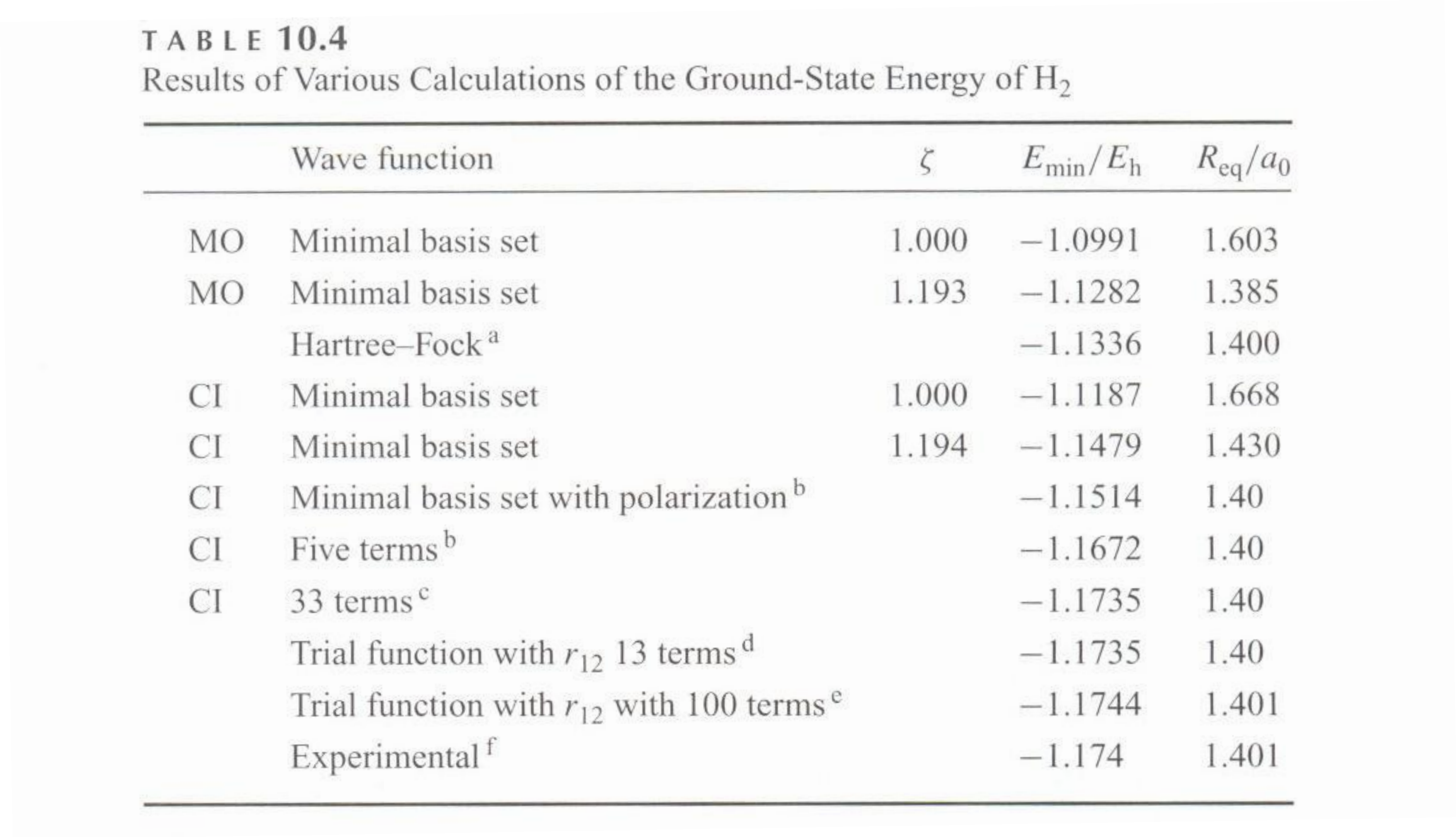


TABLE 10.4

Results of Various Calculations of the Ground-State Energy of H_2

	Wave function	ζ	$E_{\mathrm{min}}/E_{\mathrm{h}}$	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

Details

BO Approximation 2

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

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

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

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

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

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

BO Approximation 3

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

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

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

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

Using Bra-Ket Notation

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

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

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

BO Approximation 4

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

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

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

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

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

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

BO Approximation 5

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

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

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

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

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

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

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}

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

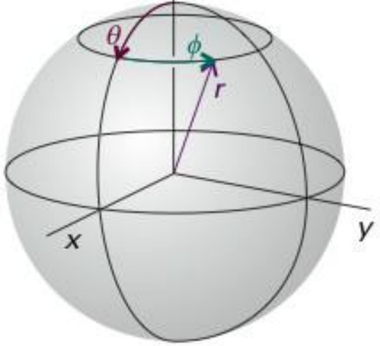
$$\langle n \| n \rangle = 1 \rightarrow \nabla_I \langle n \| n \rangle = \nabla_I \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

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

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

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

$$C_{nn} = \left\langle n \left| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 \right| n \right\rangle = \frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\right)^2 d\mathbf{r}$$



Solve the hydrogen atom

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

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

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

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

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

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

Solution: Configuration Interaction

Two 1S orbitals can make TWO molecular orbitals

Why not use the two and make combinations

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

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

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

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

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

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

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

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

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

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

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

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

Symmetry of Spacial Orbitals

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

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

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

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

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

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

Hamiltonian is invariant over exchange of electron
so only Ψ_2 mix with Ψ_1

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