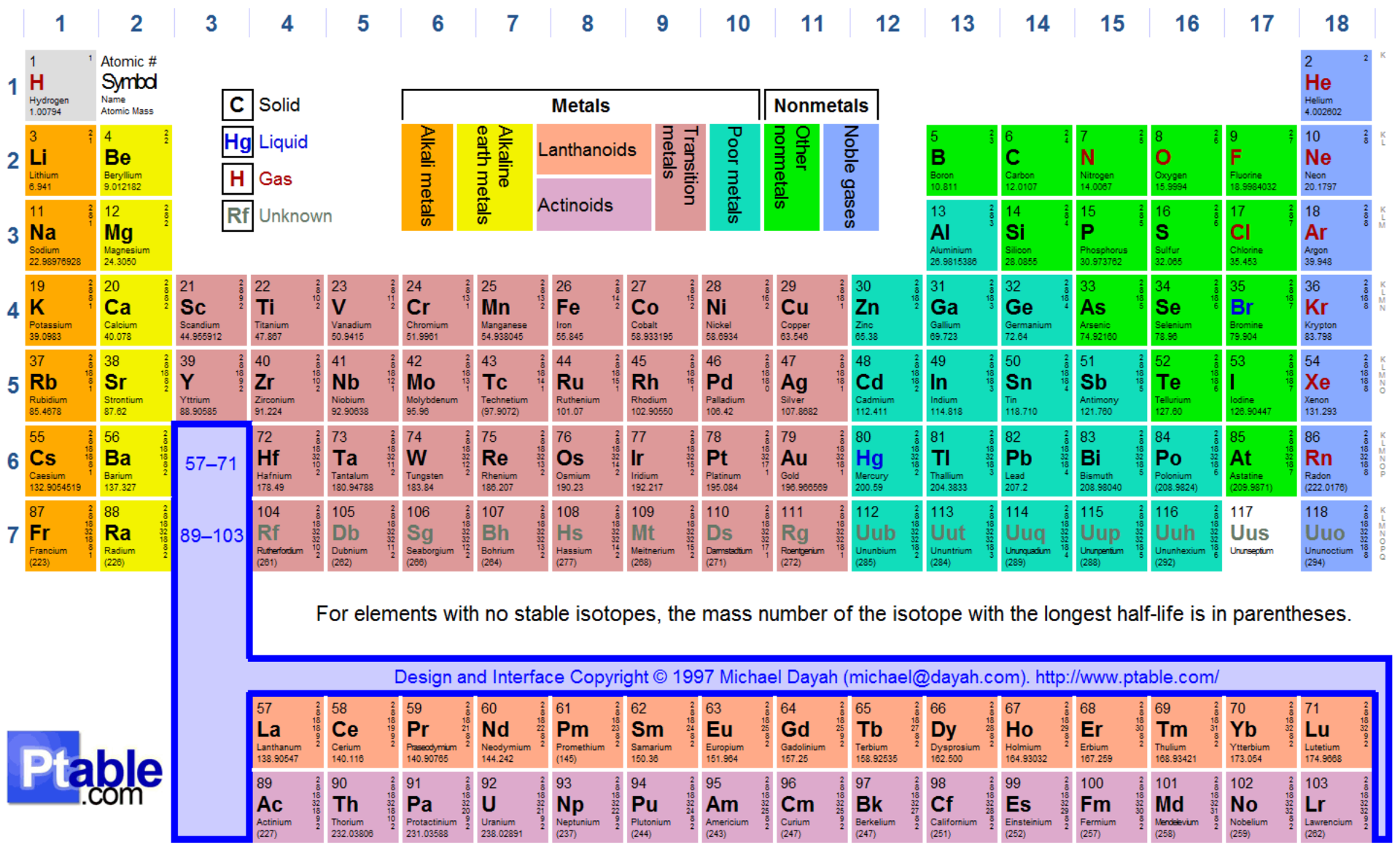
Homework IP/EA of Atoms

Periodic Table of Elements



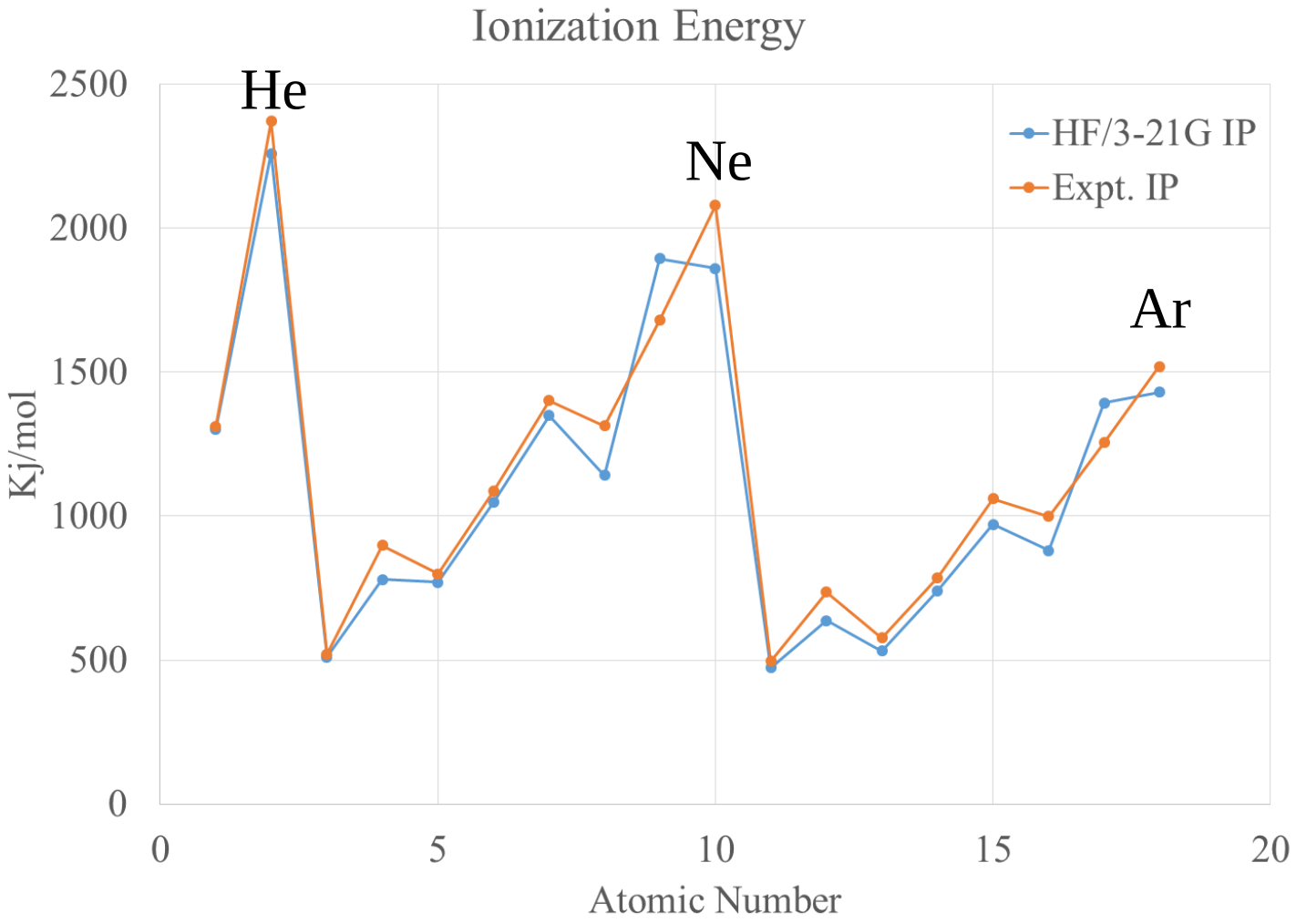
For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

Ptable.com

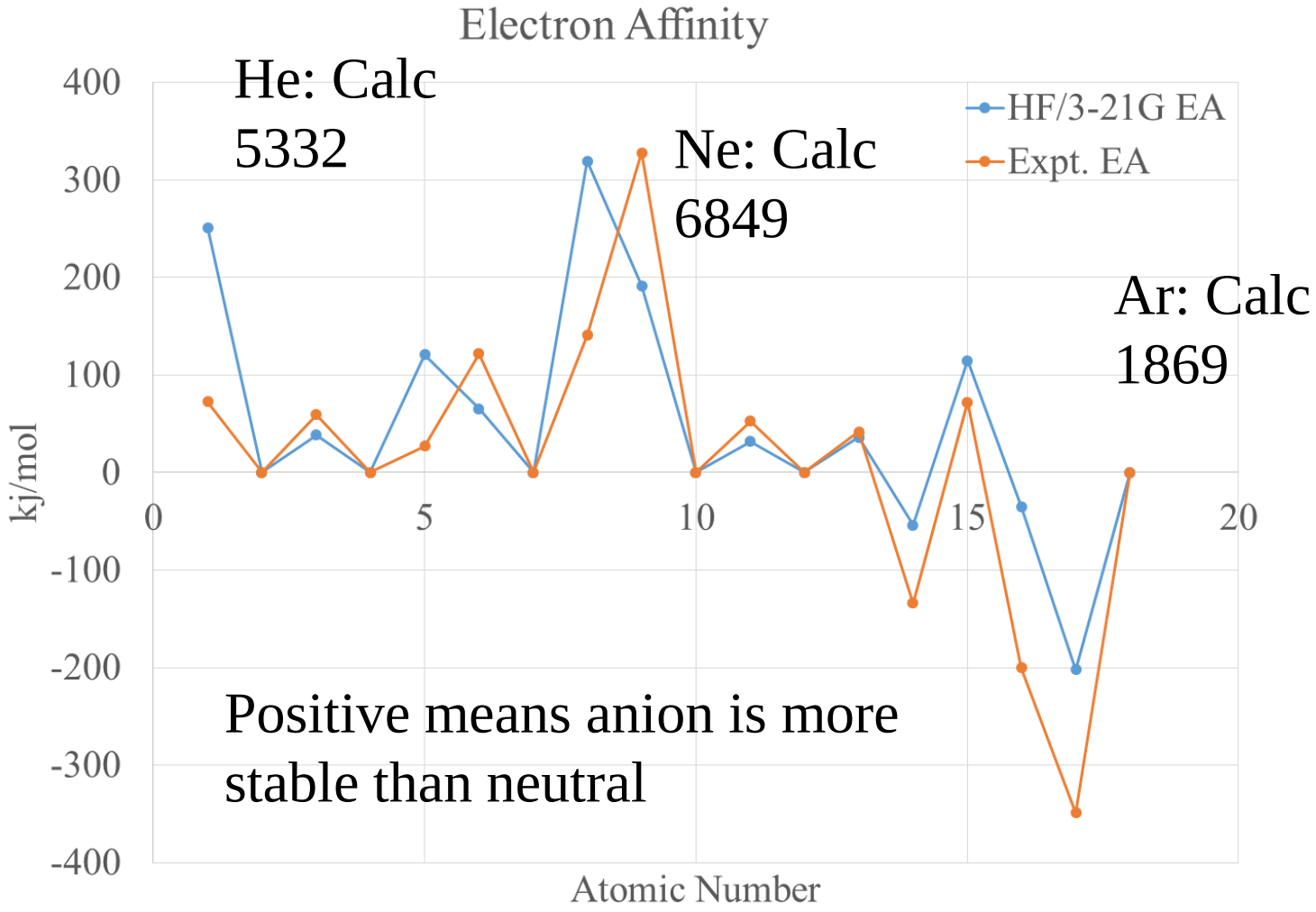
Results?

	IP	kJ/mol	EA	kJ/mol	2nd IP	kJ/mol	3rd IP	kJ/mol
	HF/3-21G	Exp	HF/3-21G	Exp	HF/3-21G	Exp	HF/3-21G	Exp
Ne	1860	2081	6849		4356	3952		
Na	473	496	-32	-53	4583	4562		
Fe	686	759	223	15	2002	1561		
Mo			127	72			4196	3891
I	909	1008	191	295				
Cs	335	376	-44	46	2204	2234		

Calculated Ionization Energies



Calculated Electron Affinites



In this plot the ones without experiment are made zero

H_2^+ molecule

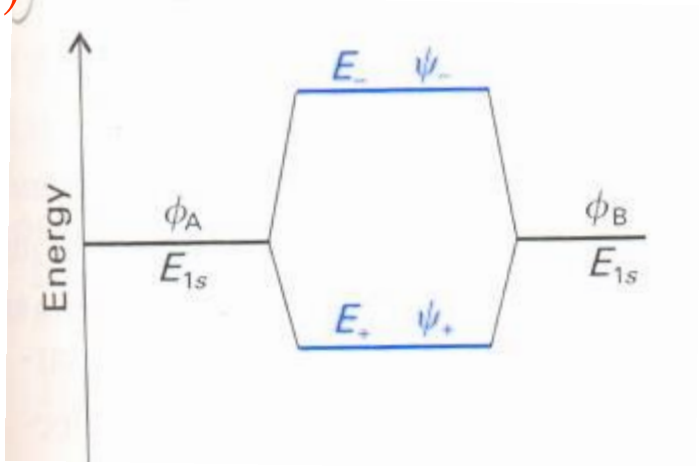
Solve Secular Equation

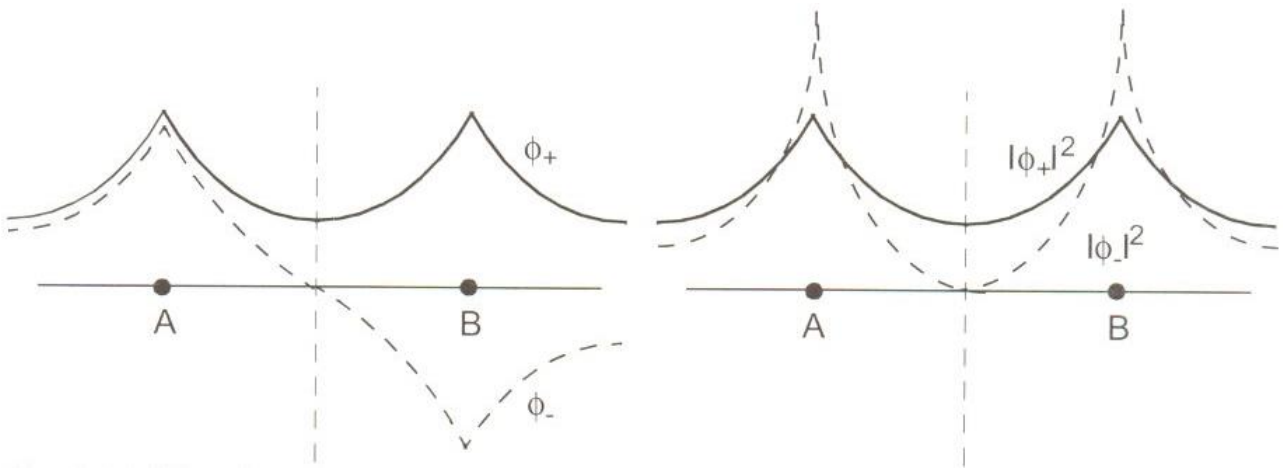
$$\begin{vmatrix} H(R)_{AA} - E(R) & H(R)_{AB} - E(R)S \\ H(R)_{BA} - E(R)S & H(R)_{BB} - E(R) \end{vmatrix} = 0$$

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

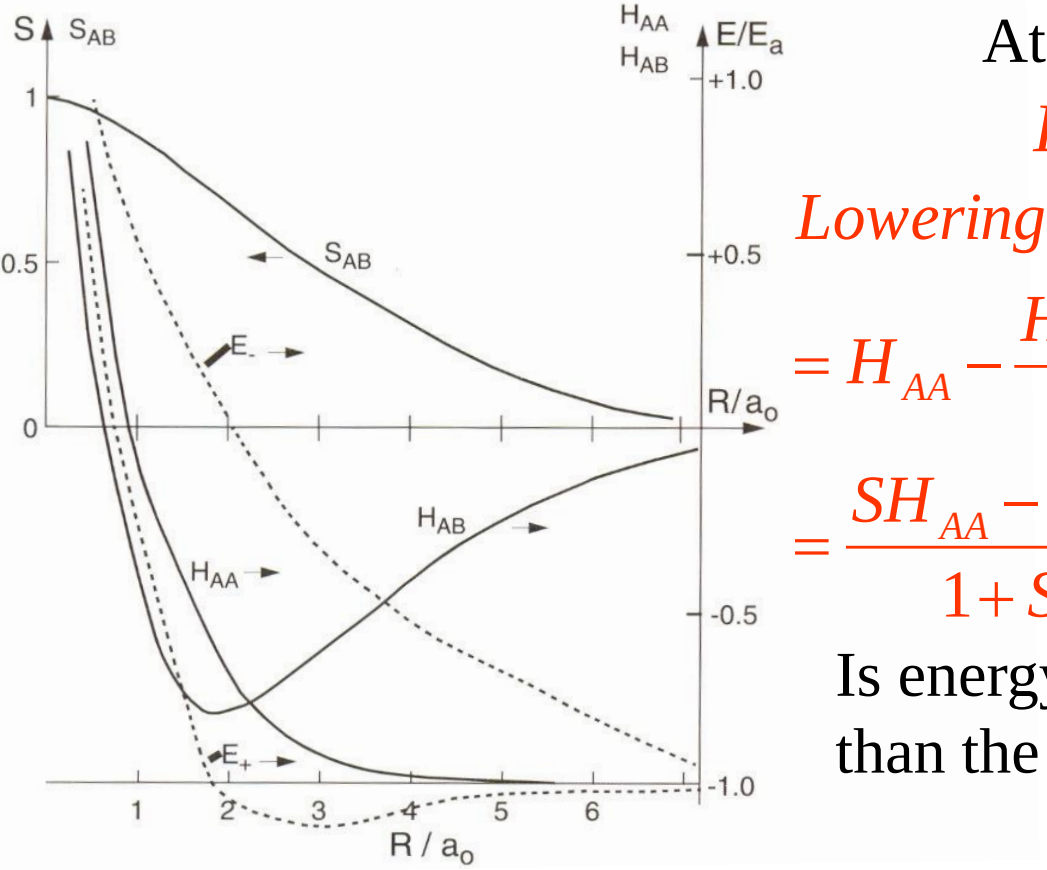
$$E_{\pm}(R) = \frac{H(R)_{AA} \pm H(R)_{AB}}{1 \pm S(R)}$$

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





Energy Lowering and Rising



At equilibrium of E_+

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

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

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

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

Is energy of lowering much more than the energy of rising? ΔE

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

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

Bonding Orbital Compare With Exact

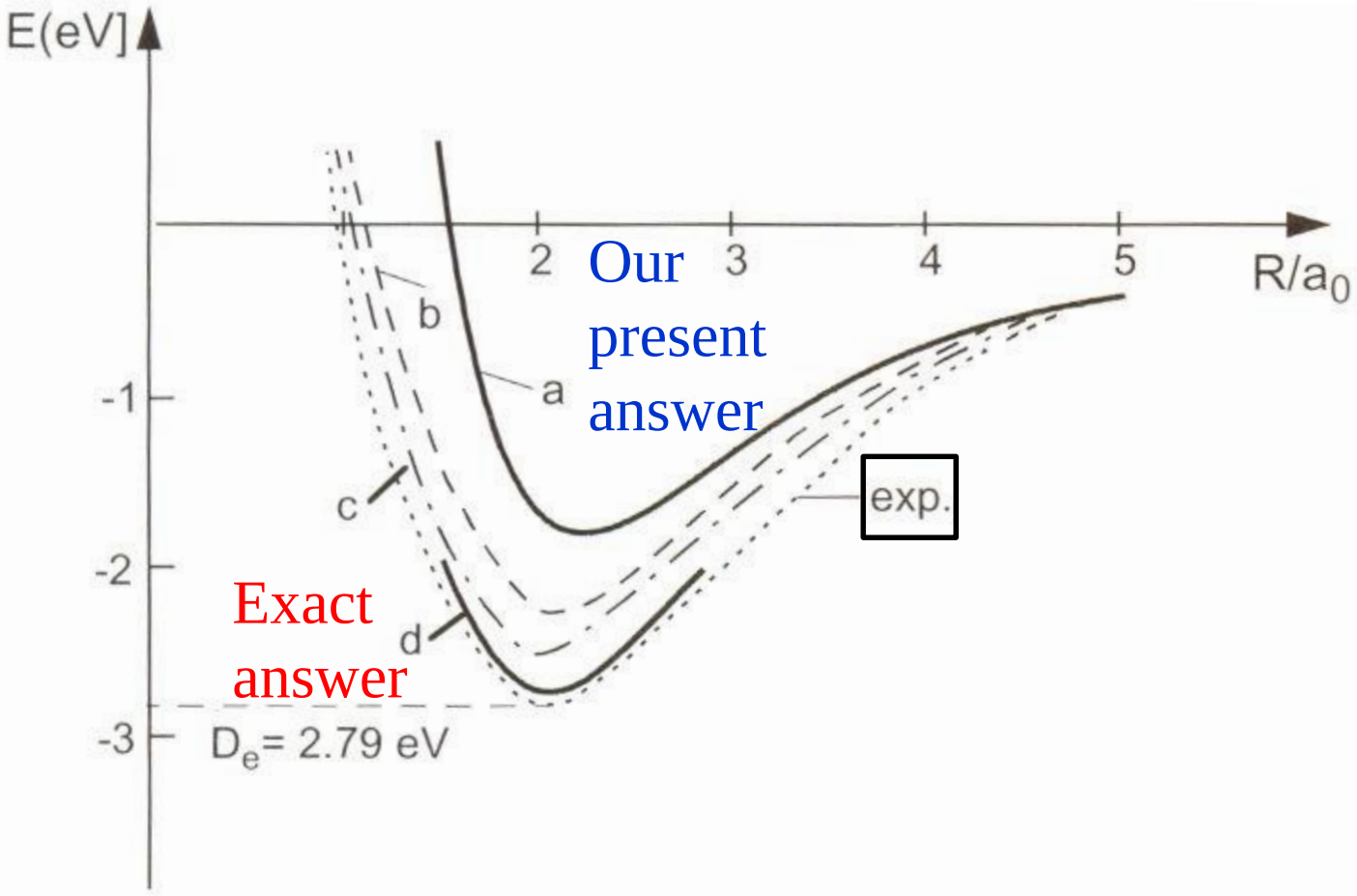
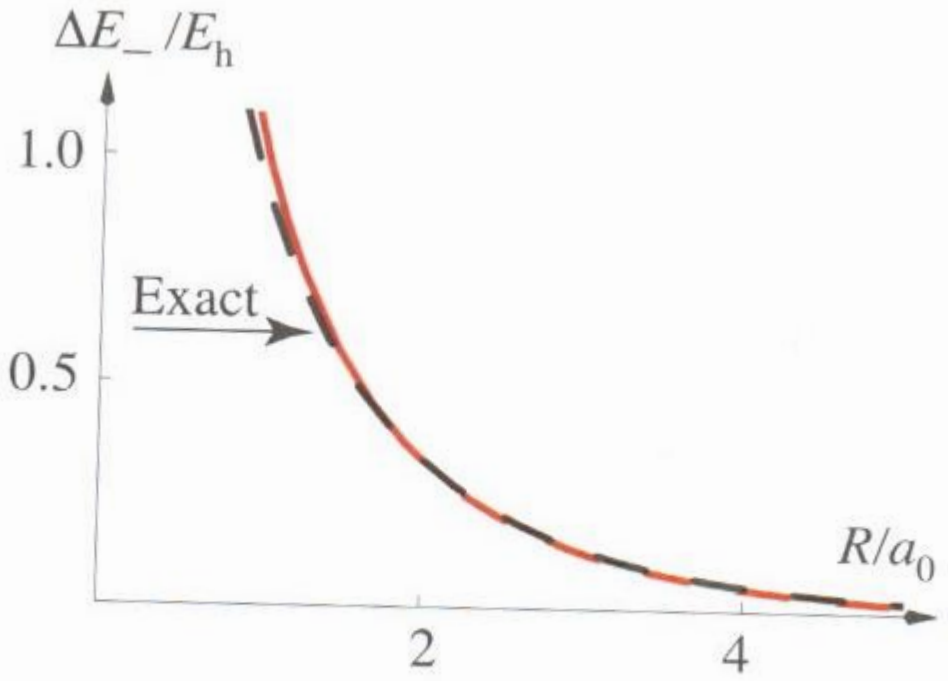


Fig. 2.30 Potential curve of the H_2^+ ground state as computed with a) simple LCAO, b) optimized parameter η, c) polarization term, and d) exact treatment.

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.

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

Larger coefficient means smaller orbital

. 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).

Bonding Orbital Compare With Exact

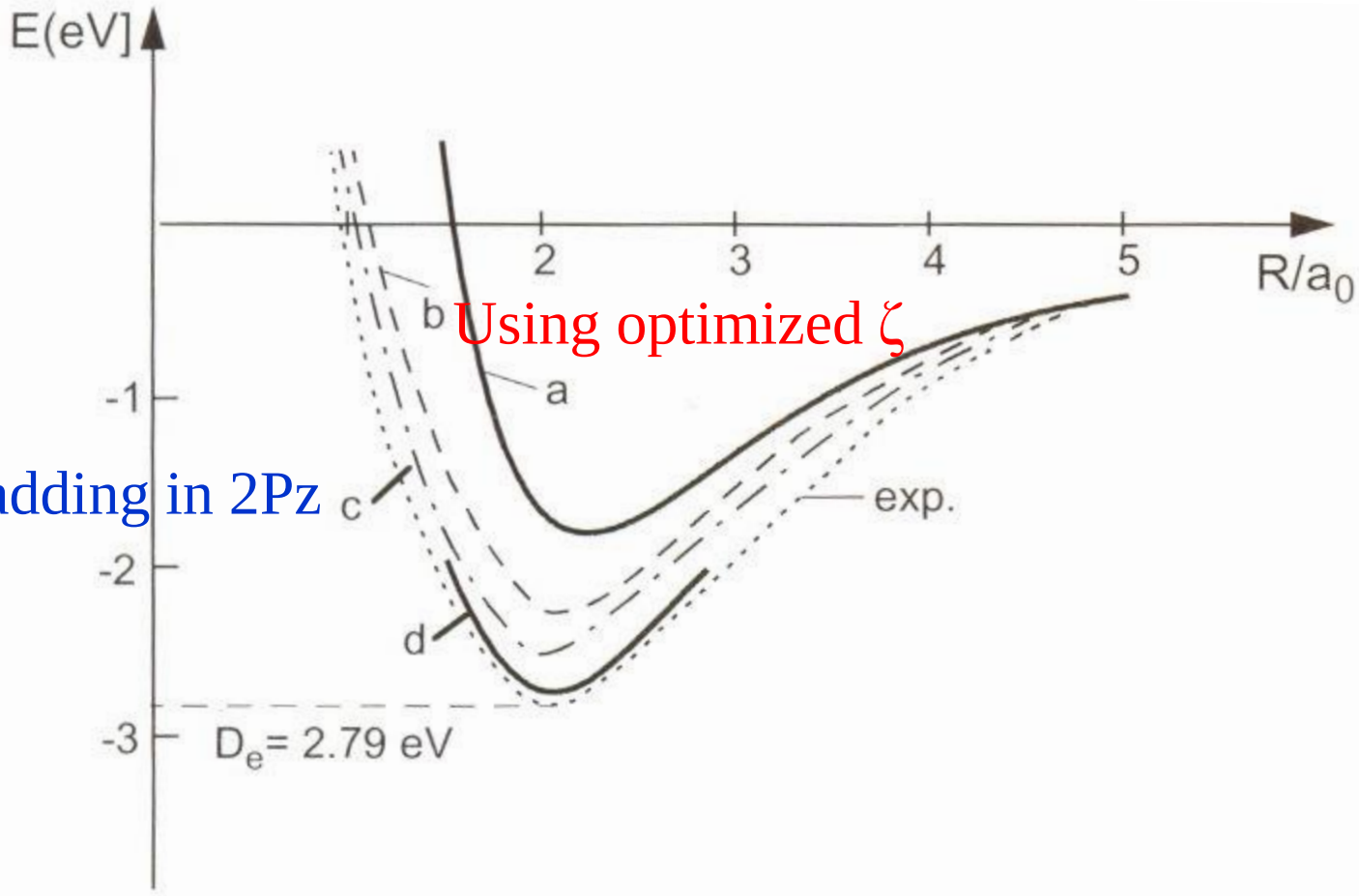


Fig. 2.30 Potential curve of the H_2^+ ground state as computed with a) simple LCAO, b) optimized parameter η, c) polarization term, and d) exact treatment.

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.
- Changing coefficient on basis set is also important

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 $2p_z$

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

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

Questions

- Why does using a smaller atomic wavefunction help?
- Why does adding a 2p orbital help in making the energy lower, but adding the 2s orbital does not help much?

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 ?

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

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

Spin Orbital and Spacial Orbitals

When you consider more than one electron you have to consider not only the ? but also the spin ?
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 ?
Exchange of electron leads to asymmetric wave function

?

Slater Determinant

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

$$\Psi(\mathbf{x}_2,\mathbf{x}_1)=?$$

Asymmetric wavefunction after exchange of electron coordinate

Generalization for n electron system: Slater Determinant

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

As an educator and advisor [edit]

Slater's concern for the well being of others is well illustrated by the following dialog that Richard Feynman relates. It took place at the end of his undergraduate days at MIT, when he wanted to stay on to do a Ph.D.[81] "When I went to Professor Slater and told him of my intentions he said: 'We will not have you here'. I said 'What?' Slater said 'Why do you think you should go to graduate school at MIT?' 'Because it is the best school for science in the country' ... 'That is why you should go to some other school. You should find out how the rest of the world is.' So I went to Princeton. ... Slater was right. And I often advise my students the same way. Learn what the rest of the world is like. The variety is worth while."

Summary [edit]

From the memoir by Philip Morse: "He contributed significantly to the start of the quantum revolution in physics; he was one of the very few American-trained physicists to do so. He was exceptional in that he persisted in exploring atomic, molecular and solid state physics, while many of his peers were coerced by war, or tempted by novelty, to divert to nuclear mysteries. Not least, his texts and his lectures contributed materially to

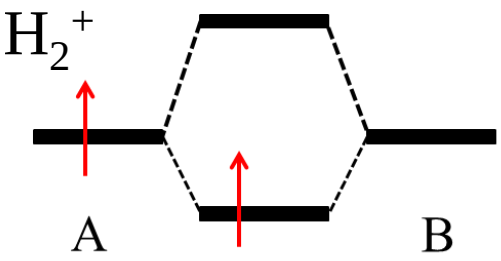
What Happens if we use direct product of H_2^+ solutions

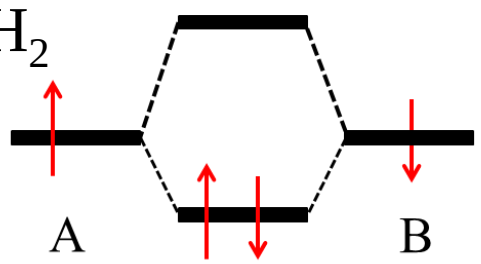
$$|+\rangle = \frac{|A\rangle + |B\rangle}{\sqrt{2+2S}}$$

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

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

?





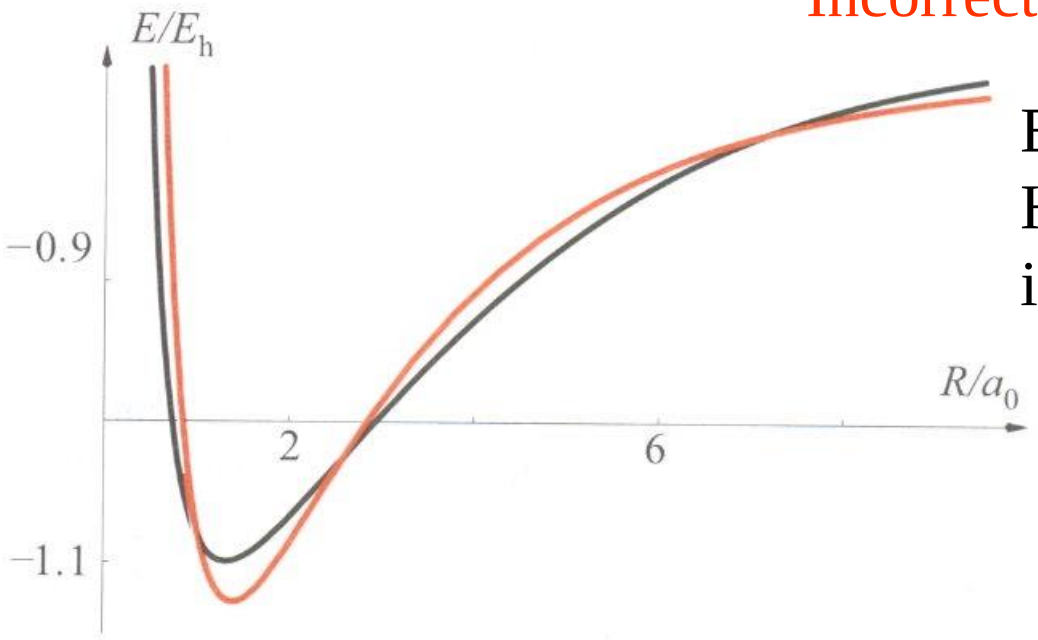
Hamiltonian does not include any spin terms so we could obtain the R dependence of the energy using only the spatial part of the electronic wavefunction

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

Potential Energy Curve

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

Incorrect Dissociation!



Energy of Hydrogen atom in Hartree is ?

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:
bonding and antibonding!

Why not use the two and make combinations

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

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

2e- in bond

2e- in antibond

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

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

1e- in bond; 1e- in antibond

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

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

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

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

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

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

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

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

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 of electron 1 and electron 2

$|\Psi_1\rangle$ and $|\Psi_2\rangle$?

$|\Psi_3\rangle$ and $|\Psi_4\rangle$ and $|\Psi_5\rangle$ and $|\Psi_6\rangle$?

Hamiltonian is ?

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

Solution: Configuration Interaction

Using an wavefunction with two electrons in bonding orbital as well as two electrons in antibonding orbital

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

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

Configuration 1: ?

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

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

Configuration 2: ?

Configuration Interaction

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

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

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

?

H2 Potential Curve Revisited

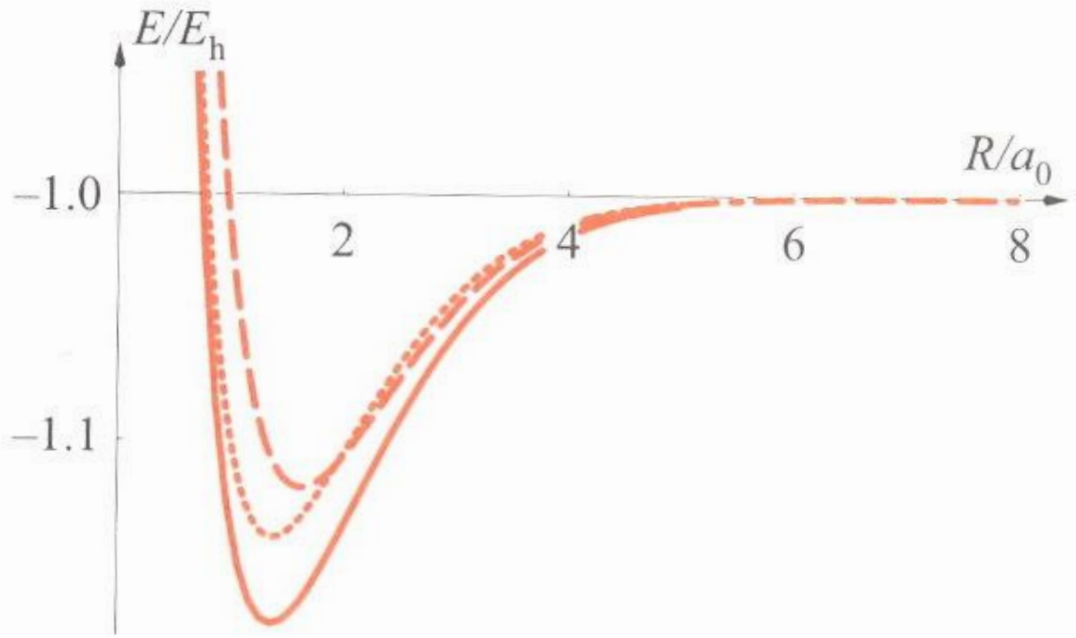


FIGURE 10.25
The configuration-interaction energy E_{CI} of the ground-state energy of H_2 for $\zeta = 1$ (dashed curve) and for an optimized value of ζ (dotted curve) plotted against R. The "exact" results of Kolos and Wolniewicz (solid curve) are shown for comparison.

R Dependence of Expanstion Coefficients

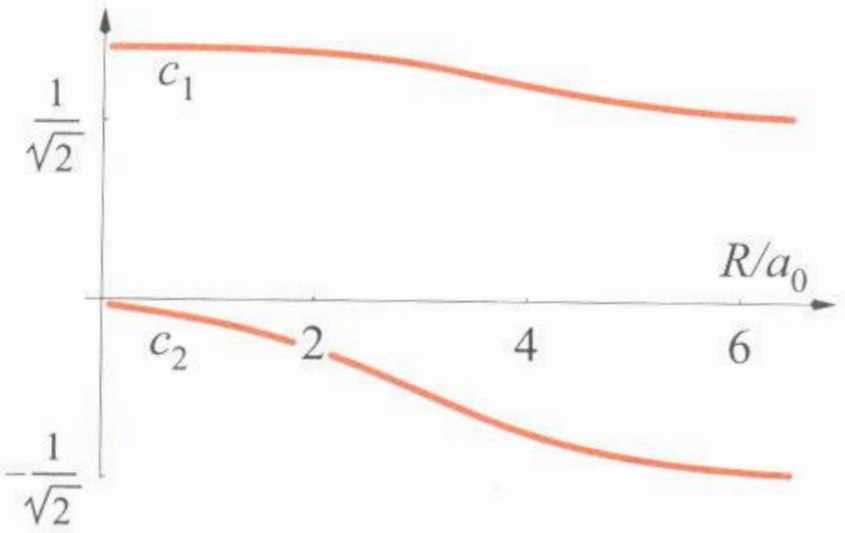


FIGURE 10.27
A plot of c_1 and c_2 for the optimized value of ζ in Equation 10.53 against R. Note that $c_1 \to 1/\sqrt{2}$ and $c_2 \to -1/\sqrt{2}$ as $R \to \infty$.

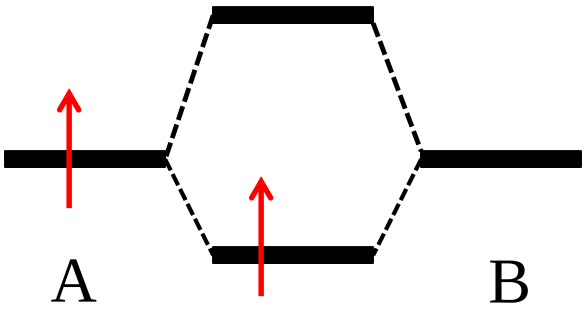
Use of more orbitals

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

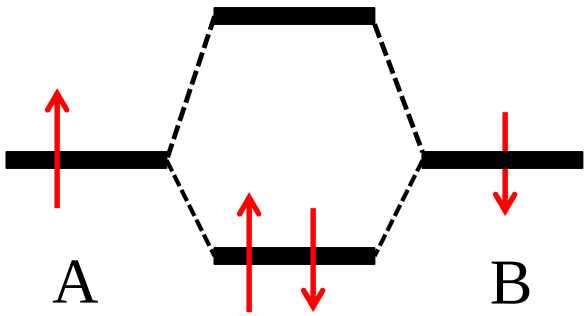
TABLE 10.4
Results of Various Calculations of the Ground-State Energy of H_2

	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

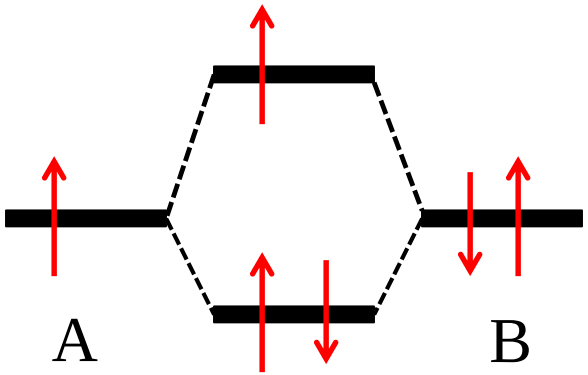
H_2^+, H_2, He_2^+, He_2



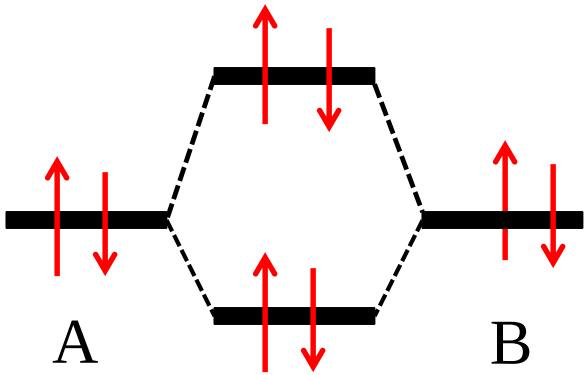
H_2^+ R_{eq}=1.06 Angstrom
Binding Energy 61 kcal/mol



H_2 R_{eq}=? Angstrom
Binding Energy ? kcal/mol



He_2^+ R_{eq}=? Angstrom
Binding Energy ? kcal/mol



He_2 R_{eq}= Infinity not bound
Binding Energy 0 Kcal mol