

P12.5 ~~Problem~~) By evaluating the appropriate integral, show that the normalization constant for the H₂ VB wave function is $N = \frac{1}{\sqrt{2 + 2S_{ab}^2}}$.

The VB wave function is given by

$$\psi_{\text{bonding}}^{VB}(1, 2) = N \left[\phi_{H1s_a}(1) \phi_{H1s_b}(2) + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \right] \left[\frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \right]$$

In normalizing this function we consider only the spatial part, because the spin part is already normalized.

$$1 = \int (\psi_{\text{bonding}}^{VB})^* \psi_{\text{bonding}}^{VB} d\tau$$

$$1 = N^2 \int \left[\phi_{H1s_a}(1) \phi_{H1s_b}(2) + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \right]^2 d\tau$$

$$1 = N^2 \left\{ \int \phi_{H1s_a}(1) \phi_{H1s_b}(2) \phi_{H1s_a}(1) \phi_{H1s_b}(2) d\tau + \int \phi_{H1s_a}(1) \phi_{H1s_b}(2) \phi_{H1s_b}(1) \phi_{H1s_a}(2) d\tau \right. \\ \left. + \int N^2 \left\{ \int \phi_{H1s_b}(1) \phi_{H1s_a}(2) \phi_{H1s_a}(1) \phi_{H1s_b}(2) d\tau + \int \phi_{H1s_b}(1) \phi_{H1s_a}(2) \phi_{H1s_b}(1) \phi_{H1s_a}(2) d\tau \right\} \right\}$$

Because the second and third integrals and the first and fourth give the same result

$$1 = 2N^2 \left\{ \int \phi_{H1s_a}(1) \phi_{H1s_b}(2) \phi_{H1s_a}(1) \phi_{H1s_b}(2) d\tau + \int \phi_{H1s_a}(1) \phi_{H1s_b}(2) \phi_{H1s_b}(1) \phi_{H1s_a}(2) d\tau \right\}$$

$$1 = 2N^2 \left\{ \int \phi_{H1s_a}(1) \phi_{H1s_a}(1) d\tau_1 \int \phi_{H1s_b}(2) \phi_{H1s_b}(2) d\tau_2 + \int \phi_{H1s_a}(1) \phi_{H1s_b}(1) d\tau_1 \int \phi_{H1s_a}(2) \phi_{H1s_b}(2) d\tau_2 \right\}$$

These integrals can be simplified because $\int \phi_{H1s_a}(1) \phi_{H1s_a}(1) d\tau_1 = 1$ and $\int \phi_{H1s_a}(1) \phi_{H1s_b}(1) d\tau_1 = S_{ab}$

$$1 = 2N^2 (1 + S_{ab}^2)$$

$$N = \frac{1}{\sqrt{2 + 2S_{ab}^2}}$$

P12.6 ~~Problem~~) By simplifying Equation (23.23), show that $\langle E_{\text{electronic}} \rangle = \frac{1}{1 + S_{ab}^2} [2E_{1s}(1 + S^2) + J + K]$

for H₂ in the VB model.

$$\begin{aligned}
\langle E_{\text{electronic}} \rangle &= \frac{1}{2 + 2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\hat{H}_a(1) + \hat{H}_b(2) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau \\
&= \frac{1}{2 + 2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\hat{H}_a(1) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau \\
&+ \frac{1}{2 + 2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\hat{H}_b(2) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau \\
&- \frac{1}{2 + 2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau
\end{aligned}$$

Because $\phi_{H1s_a}(1,2)$ is an eigenfunction of $\hat{H}_a(1,2)$ with eigenvalue E_{1s} ,

and the same holds for $\phi_{H1s_b}(1,2)$ and $\hat{H}_b(1,2)$,

$$\begin{aligned}
\langle E_{\text{electronic}} \rangle &= \frac{2E_{1s}}{2 + 2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau \\
&- \frac{1}{2 + 2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau \\
\langle E_{\text{electronic}} \rangle &= \frac{2E_{1s}}{2 + 2S_{ab}^2} \left\{ \begin{array}{l} \int \left[\phi_{H1s_a}(1)\phi_{H1s_a}(1) \right] d\tau_1 \int \left[\phi_{H1s_b}(2)\phi_{H1s_b}(2) \right] d\tau_2 \\ + \int \left[\phi_{H1s_a}(1)\phi_{H1s_b}(1) \right] d\tau_1 \int \left[\phi_{H1s_a}(2)\phi_{H1s_b}(2) \right] d\tau_2 \\ \int \left[\phi_{H1s_b}(1)\phi_{H1s_a}(1) \right] d\tau_1 \int \left[\phi_{H1s_b}(2)\phi_{H1s_a}(2) \right] d\tau_2 \\ + \int \left[\phi_{H1s_b}(1)\phi_{H1s_b}(1) \right] d\tau_1 \int \left[\phi_{H1s_a}(2)\phi_{H1s_a}(2) \right] d\tau_2 \end{array} \right\} \\
&- \frac{1}{2 + 2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau
\end{aligned}$$

The first and fourth integrals have the value 1, and the second and third integrals have the value S_{ab}^2 .

$$\begin{aligned}
\langle E_{\text{electronic}} \rangle &= \frac{4E_{1s}(1 + S_{ab}^2)}{2 + 2S_{ab}^2} \\
&- \frac{1}{2 + 2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau
\end{aligned}$$

$$\langle E_{\text{electronic}} \rangle = \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2}$$

$$- \frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau$$

$$\langle E_{\text{electronic}} \rangle = \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2}$$

$$- \frac{1}{2+2S_{ab}^2} \left\{ \begin{array}{l} \int \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] d\tau \\ + \int \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] d\tau \\ + \int \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] d\tau \\ + \int \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] d\tau \end{array} \right\}$$

The first and fourth as well as the second and third integrals give the same value because the *a* and *b* orbitals are identical.

$$\langle E_{\text{electronic}} \rangle = \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2}$$

$$- \frac{1}{2+2S_{ab}^2} \left\{ \begin{array}{l} 2 \int \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] d\tau \\ + 2 \int \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] d\tau \end{array} \right\}$$

Using the definitions of *J* and *K* in Equation (23.25),

$$\langle E_{\text{electronic}} \rangle = \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2} + \frac{1}{2+2S_{ab}^2} (2J+2K)$$

$$\langle E_{\text{electronic}} \rangle = \frac{1}{1+S_{ab}^2} \left[2E_{1s}(1+S_{ab}^2) + J+K \right]$$

P13.2 ~~13.2~~) Evaluate the energy for the two MOs generated by combining a $1s$ and a $2p$ AO. Use Equation (24.11) and carry out the calculation for $S_{12} = 0.1, 0.2,$ and 0.6 to mimic the effect of increasing the atomic separation in the molecule. Use the parameters $H_{11} = -13.6$ eV, $H_{22} = -18.6$ eV, and $H_{12} = -1.75 S_{12} \sqrt{H_{11} H_{22}}$. Explain the trend that you observe in the results.

$$E = \frac{1}{2 - 2S_{12}^2} [H_{11} + H_{22} - 2S_{12}H_{12}]$$

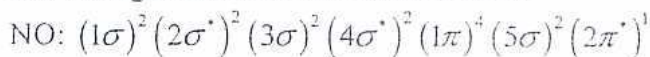
$$\pm \frac{1}{2 - 2S_{12}^2} \left[\sqrt{(H_{11}^2 + 4H_{12}^2 + H_{22}^2 - 4S_{12}H_{12}H_{22} - 2H_{11}(H_{22} + 2S_{12}H_{12} - 2S_{12}^2H_{22}))} \right]$$

S_{12}	H_{12} (eV)	$\epsilon_{\text{antibonding}}$ (eV)	$\epsilon_{\text{bonding}}$ (eV)
0.1	-2.78	-13.2	-18.8
0.2	-5.57	-12.1	-19.1
0.6	-16.7	+1.94	-20.9

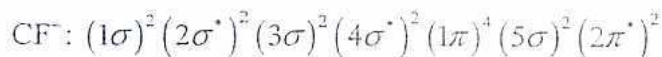
As the overlap increases, mimicking the atoms getting closer, the interaction of the AOs increases, and the difference between the MO and the AO energies increases. For small values of the overlap, the energy of the bonding MO is only slightly lower than that of the lower AO, and the energy of the antibonding MO is only slightly higher than that of the higher AO. As the overlap increases, these differences become greater, and the difference between the MO energies becomes greater. The change in the energy change of the bonding MO is greater than that of the antibonding MO.

P 13.5 ~~13.5~~) The bond dissociation energies of the species NO , CF^- and CF^+ follow the trend $\text{CF}^+ > \text{NO} > \text{CF}^-$. Explain this trend using MO theory.

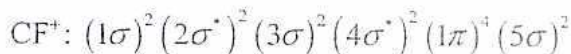
The configurations for the molecules are



$$\text{Bond Order} = \frac{10 - 5}{2} = 2.5$$



$$\text{Bond Order} = \frac{10 - 6}{2} = 2$$



$$\text{Bond Order} = \frac{10 - 4}{2} = 3$$

We see that the calculated bond orders account for the relative bond strengths.

P13.8 ~~Calculate~~ Calculate the bond order in each of the following species. Which of the species in parts (a-d) do you expect to have the smaller bond length?

- a) Li_2 or Li_2^+ b) C_2 or C_2^+ c) O_2 or O_2^+ d) F_2 or F_2^- ?

$$\text{Li}_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2$$

$$\text{Bond Order} = \frac{4-2}{2} = 1$$

$$\text{Li}_2^+: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^1$$

$$\text{Bond Order} = \frac{3-2}{2} = 0.5$$

$$\text{C}_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (1\pi_u)^4$$

$$\text{Bond Order} = \frac{8-4}{2} = 2$$

$$\text{C}_2^+: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (1\pi_u)^3$$

$$\text{Bond Order} = \frac{7-4}{2} = 1.5$$

$$\text{O}_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^1 (1\pi_g^*)^1$$

$$\text{Bond Order} = \frac{10-6}{2} = 2$$

$$\text{O}_2^+: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^1$$

$$\text{Bond Order} = \frac{10-5}{2} = 2.5$$

$$\text{F}_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^2 (1\pi_g^*)^2$$

$$\text{Bond Order} = \frac{10-8}{2} = 1$$

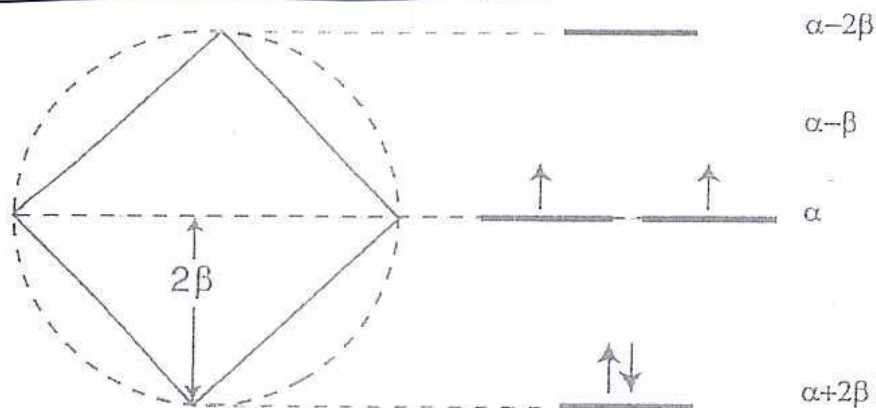
$$\text{F}_2^-: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^3 (1\pi_g^*)^2$$

$$\text{Bond Order} = \frac{10-9}{2} = 0.5$$

Because the bond length is shorter for a greater bond order, the answers are Li_2 , C_2 , O_2^+ ,

F_2 .

P14.15)

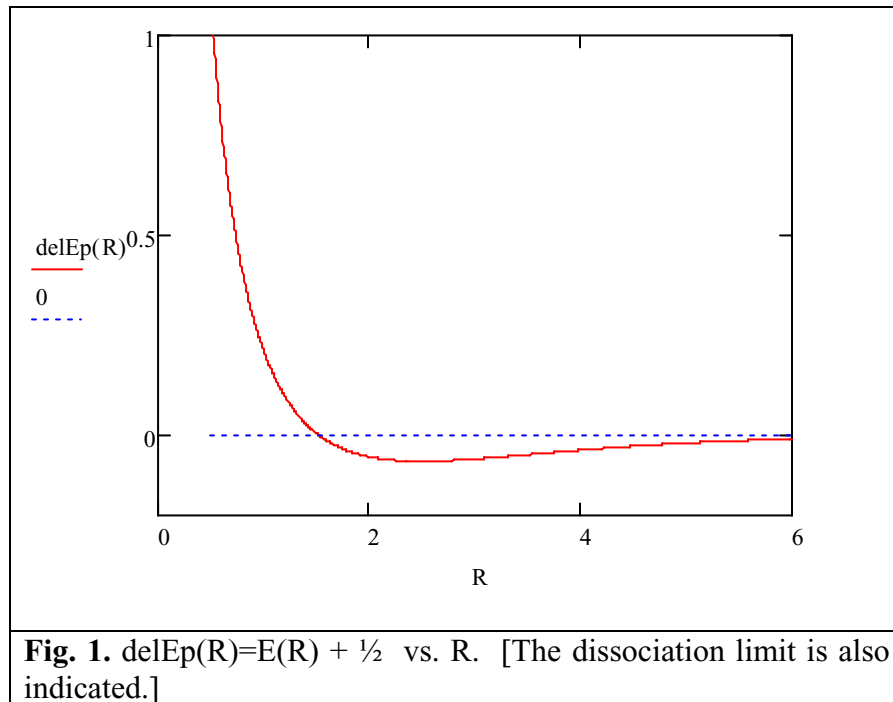


There are 2 unpaired electrons.

The total π energy is $E_\pi = 2(\alpha + 2\beta) + 2(\alpha) = 4\alpha + 4\beta$

Problem Set 10: solution to Problem 2

a) Using the given functions $S(R), J'(R), K'(R)$, a plot of $E(R)+1/2$ (which reaches the asymptotic value of 0 as $R \rightarrow \infty$) vs. R is shown in Fig. 1.

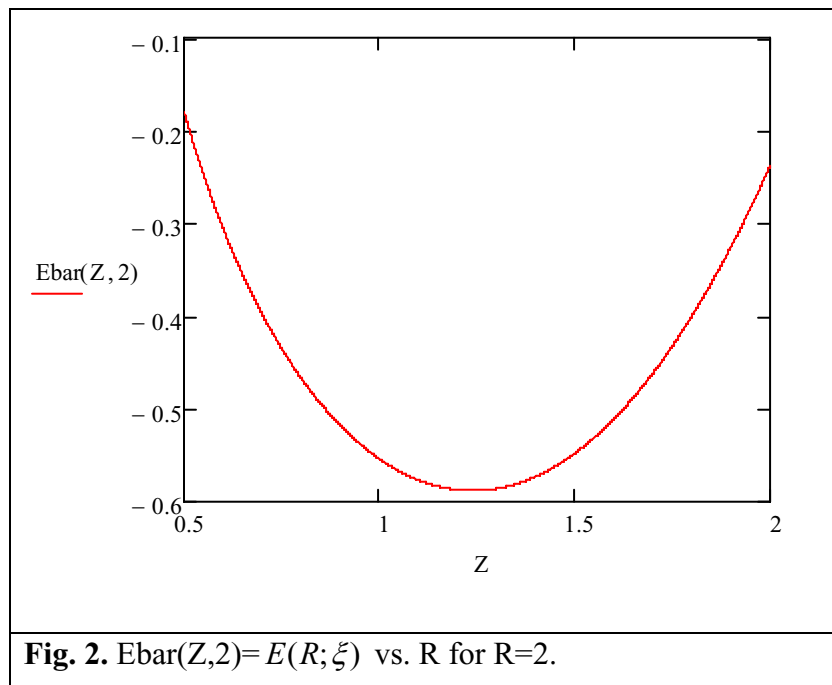


As can be gleaned from Fig. 1, this curve has a minimum at $R \cong 2.5 \text{ a.u.}$ or $2.5 * 0.53 = 1.33 \text{ \AA}$, at which the energy of the ground state relative to the dissociation limit is ca. 0.065 a.u. or $0.065 * 27.2 = 1.77 \text{ eV}$.

b) i) Using the ξ dependent functions provided in the statement of the problem, a plot of $E(R=2, \xi)$ is shown in Fig. 2. The function clearly shows a unique minimum, corresponding to the value $\xi \cong 1.24$, and that $E(2; 1.24) \cong -0.588 \text{ a.u.}$

ii) Repeating the exercise in part i) for each of the requested values of R , we obtain the plot of $E(R)+1/2$ shown in Fig. 3. As expected, the value of E obtained at a given value of R is always lower for the “optimized ξ ” version of the calculation (part b) than for the simpler version corresponding to $\xi = 1$ (hydrogen 1s orbitals).

iii) The minimum of the “optimized ξ ” $E(R)$ curve occurs at $R \cong 2a.u.$ or $2*0.53=1.06\text{\AA}$, and corresponds to a dissociation energy of $0.088a.u.$ or $0.088*27.2=2.394\text{eV}$.



iv) According to the Variational Principle, the exact solution of the Schrödinger Eq. (which corresponds to experimental reality!) gives an $E(R)$ curve which is everywhere lower in energy than the “optimized ξ ” result plotted in Fig. 3. Thus, the experimentally measured dissociation energy for H_2^+ should be larger than 2.394eV . (In fact, the measured value of this dissociation energy is 2.78eV .)

N.B.: A printout of the .xmcd worksheet used to generate the numerical results presented above is attached below.

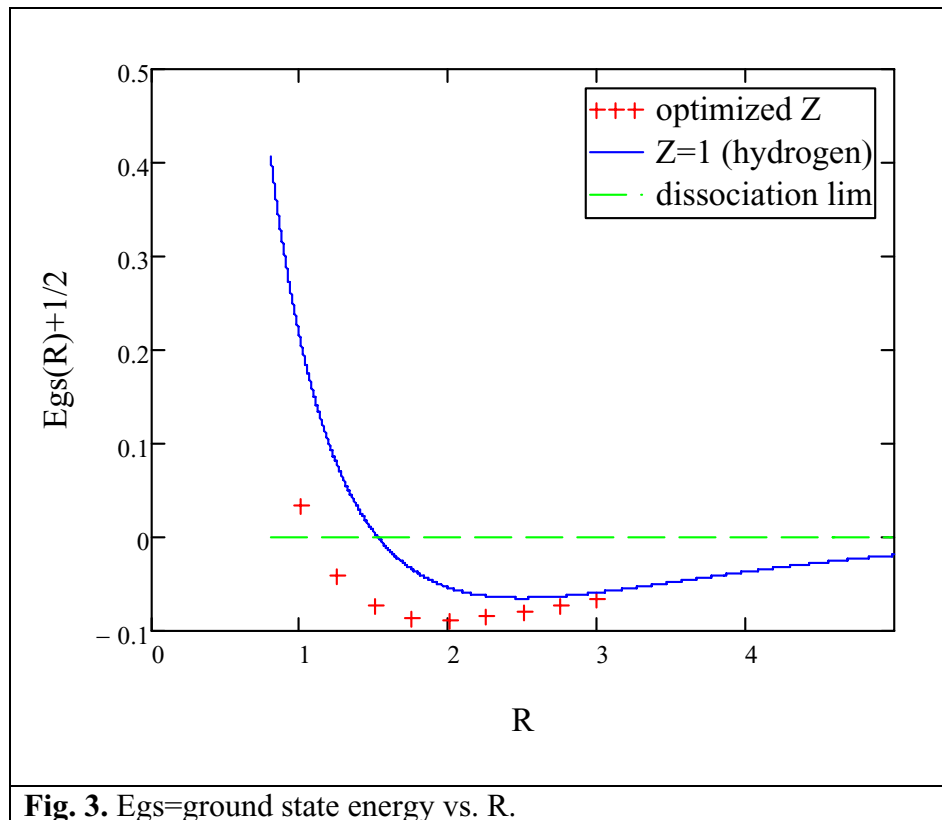


Fig. 3. E_{gs} =ground state energy vs. R .

Study of electronic structure of H₂⁺.

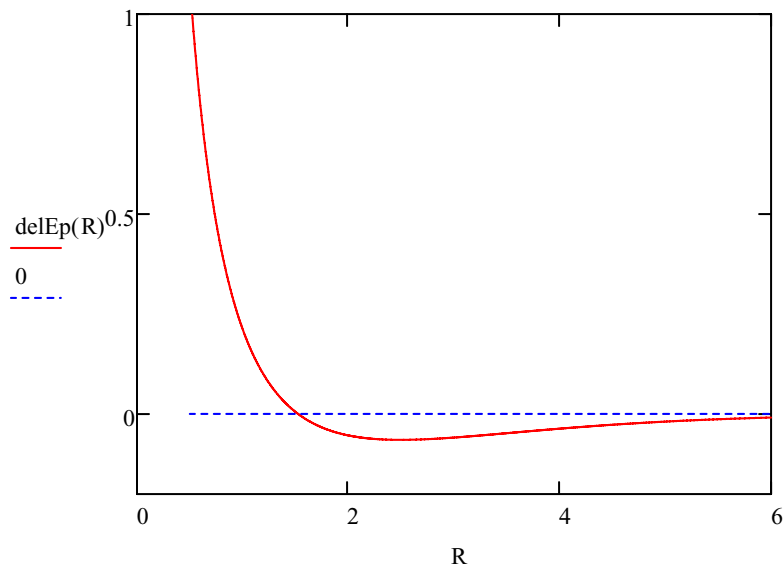
Focus on g.s. energy (and eigenfunction): Begin with the simplest version (using 1:1 linear combo of standard [Z=1] hydrogen 1s orbitals):

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

$$Kp(R) := \frac{S(R)}{R} - e^{-R} \cdot (1 + R)$$

$$\text{delEp}(R) := \frac{Jp(R) + Kp(R)}{1 + S(R)} \quad \text{Note: } E_{\text{gs}} = -1/2 + \text{delEp}(R)$$

$$R := 0.5, 0.505.. 6$$



Note: binding curve has $\text{delEp}_{\text{min}} = -0.065$, at $R_{\text{min}}=2.5$ (approximately).

$2.5 \cdot 0.53 = 1.325$ Angst., $0.065 \cdot 27.2 = 1.77$ eV.

Now, define analogs of S, Jp, Kp which are valid for hydrogenic 1s orbitals with effective nuclear charge Z:

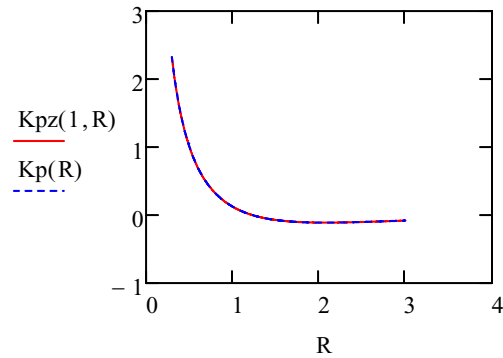
$$S_z(Z, R) := e^{-Z \cdot R} \cdot \left[1 + Z \cdot R + \frac{(Z \cdot R)^2}{3} \right]$$

$$J_{pz}(Z, R) := (Z - 1) \cdot Z + \left(1 + \frac{1}{Z \cdot R} \right) \cdot e^{-2 \cdot Z \cdot R}$$

$$K_{pz}(Z, R) := \frac{S_z(Z, R)}{R} + (Z - 2) \cdot Z \cdot (1 + Z \cdot R) \cdot e^{-Z \cdot R}$$

R := 0.3, 0.31 .. 3

Option to check Sz, Jpz, Kpz vs the standard S, J, K (i.e., with Z=1):

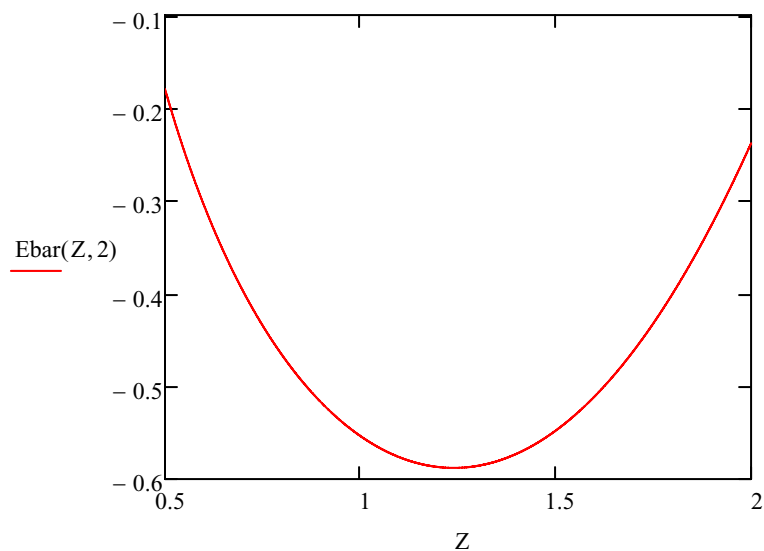


Ebar(Z, R) = expectation of H in LCAO of 1s orbitals with effective nuclear charge Z at separation R (in a.u.):

$$E_{\text{bar}}(Z, R) := \frac{-Z^2}{2} + \frac{J_{pz}(Z, R) + K_{pz}(Z, R)}{1 + S_z(Z, R)}$$

Z := .5, .501 .. 2

Note: Fix R, scan Z=effective nuclear charge



Note: For $R=2.0$, find minimum at $Z=1.24$, with value for $E_{\text{bar}}=-0.588$

To determine the ground state potential energy curve by applying the variational principle at each nuclear separation R , it is simplest to simply plot $E_{\text{bar}}(Z, R)$ vs Z for fixed R (above), read off the minimum value of E_{bar} ** (this is the variational estimate of the g.s. energy), make a table (below), and plot it.

** Note: right-click on graph; choose Trace (<-- click on curve, Trace will determine numerical values).

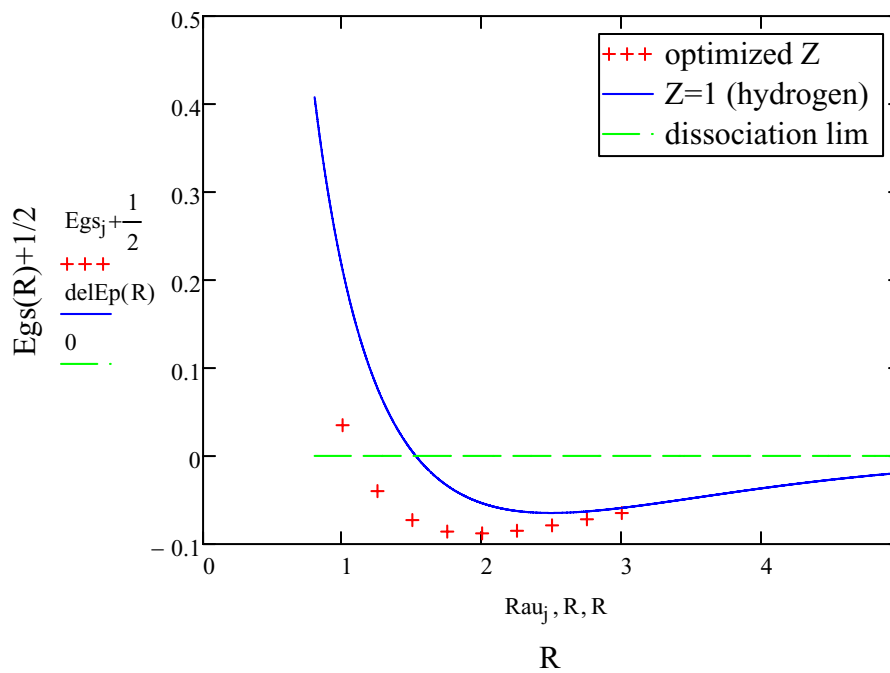
RESULTS:

$R_{\text{au}}_0 := 1$	$E_{\text{gs}}_0 := -0.465$
$R_{\text{au}}_1 := 1.25$	$E_{\text{gs}}_1 := -0.540$
$R_{\text{au}}_2 := 1.5$	$E_{\text{gs}}_2 := -0.573$
$R_{\text{au}}_3 := 1.75$	$E_{\text{gs}}_3 := -0.586$
$R_{\text{au}}_4 := 2$	$E_{\text{gs}}_4 := -0.588$
$R_{\text{au}}_5 := 2.25$	$E_{\text{gs}}_5 := -0.585$

$R_{au_6} := 2.5$ $E_{gs_6} := -0.579$
 $R_{au_7} := 2.75$ $E_{gs_7} := -0.572$
 $R_{au_8} := 3$ $E_{gs_8} := -0.565$

$j := 0..8$ $R := 0.8, 0.802..5$

Note: plot here $E_{gs}(R) + 1/2$, so that the dissociation limit ($R \rightarrow$ infinity), corresponds to $E_{gs} = 0$



NB: Minimum in E_{gs} ("variationally optimized) is approximately at $R=2.0$ a.u. = $2.0 \cdot 0.53 = 1.06$ Angst. The corresponding dissociation energy is $E_{dis} = 0.588 - 0.5 = 0.088$ a.u. = $0.088 \cdot 27.2 = 2.394$ eV.

Note: Experimentally measured dissociation E for $H_2^+ = 2.78$ eV.