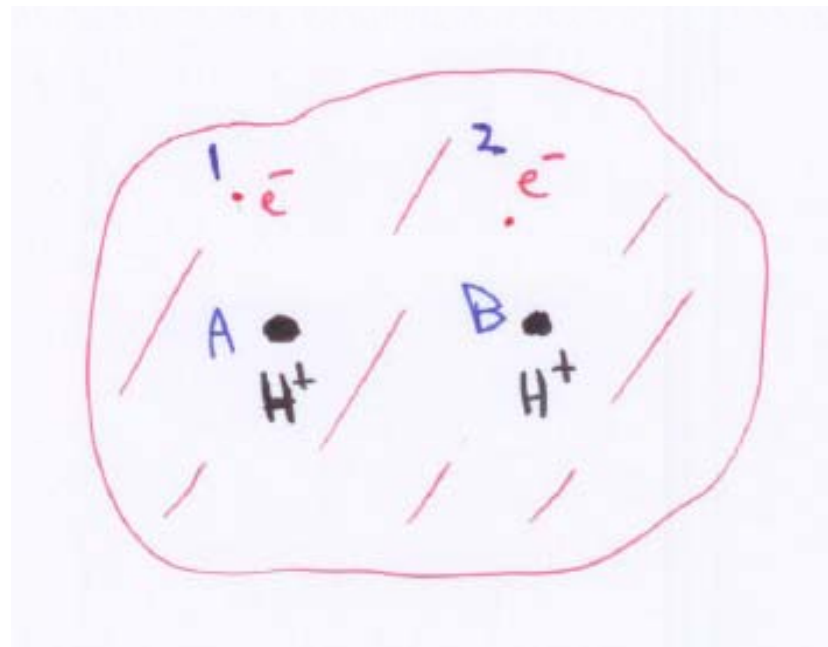


## The Born Oppenheimer (BO) Approximation for Molecular Structure [Atkins, Chapt. 8]

Consider the hydrogen ( $H_2$ ) Molecule:



The full electro-nuclear Schrodinger Eq. reads:

$$H\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) = E\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B)$$

$$H = \sum_{\alpha=A,B} \frac{-\hbar^2}{2m_p} \nabla_{\alpha}^2 + \sum_{j=1,2} \frac{-\hbar^2}{2m_e} \nabla_j^2 - \frac{e_0^2}{4\pi\epsilon_0 r_{1A}} - \frac{e_0^2}{4\pi\epsilon_0 r_{1B}} - \frac{e_0^2}{4\pi\epsilon_0 r_{2A}} - \frac{e_0^2}{4\pi\epsilon_0 r_{2B}} + \frac{e_0^2}{4\pi\epsilon_0 r_{12}} + \frac{e_0^2}{4\pi\epsilon_0 R_{AB}}$$

According to the Born-Oppenheimer Approx.:

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) \cong \psi_j(\vec{r}_1, \vec{r}_2; \vec{R}_A, \vec{R}_B) \chi_n^{(j)}(\vec{R}_A, \vec{R}_B)$$

Here:

$$H_{el} \psi_j(\vec{r}_1, \vec{r}_2; \vec{R}_A, \vec{R}_B) = E_{el}^{(j)}(\vec{R}_A, \vec{R}_B) \psi_j(\vec{r}_1, \vec{r}_2; \vec{R}_A, \vec{R}_B)$$

$$H_{el} = \sum_{j=1,2} \frac{-\hbar^2}{2m_e} \nabla_j^2 - \frac{e_0^2}{4\pi\epsilon_0 r_{1A}} - \frac{e_0^2}{4\pi\epsilon_0 r_{1B}} - \frac{e_0^2}{4\pi\epsilon_0 r_{2A}} - \frac{e_0^2}{4\pi\epsilon_0 r_{2B}} + \frac{e_0^2}{4\pi\epsilon_0 r_{12}} + \frac{e_0^2}{4\pi\epsilon_0 R_{AB}}$$

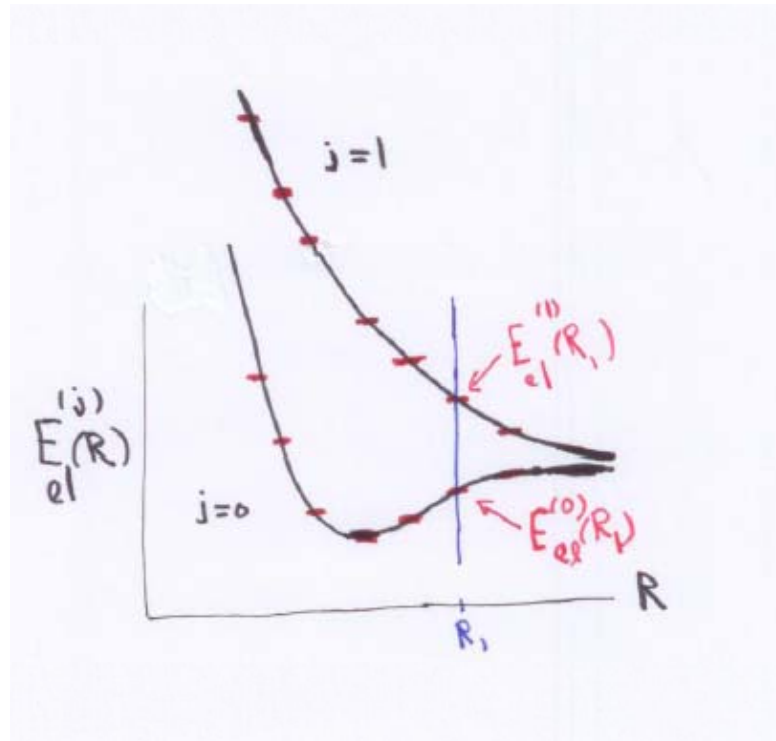
$$\text{Then: } H_{nuc} \chi(\vec{R}_A, \vec{R}_B) = E_n^{(j)} \chi(\vec{R}_A, \vec{R}_B)$$

$$\text{with: } H_{nuc} = \sum_{\alpha=A,B} \frac{-\hbar^2}{2m_p} \nabla_\alpha^2 + E_{el}^{(j)}(\vec{R}_A, \vec{R}_B)$$

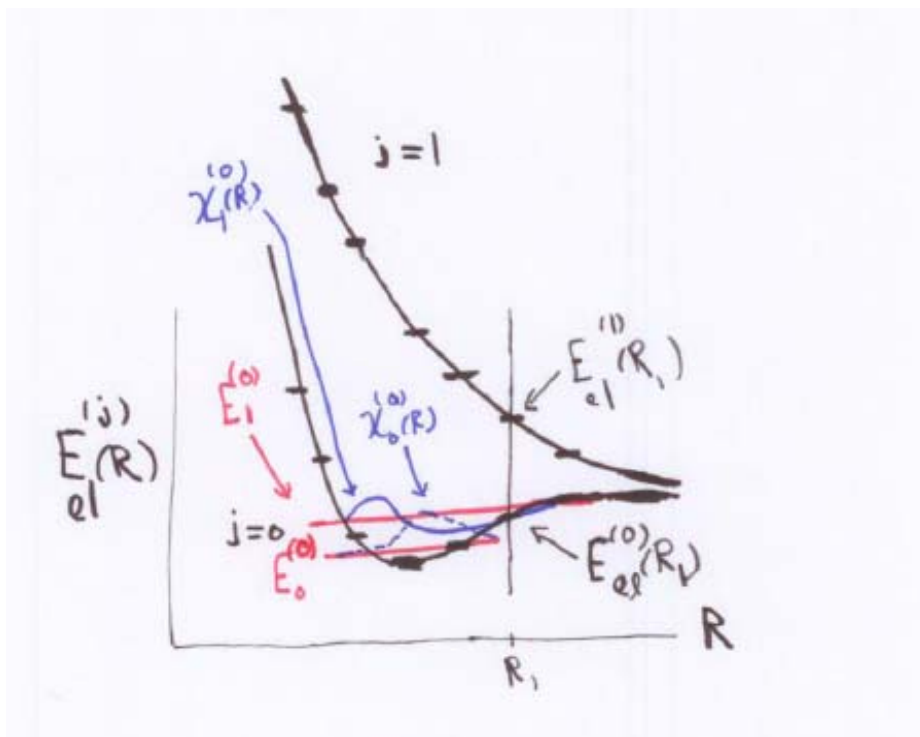
For the hydrogen molecule (or any diatomic):

$$E_{el}^{(j)}(\vec{R}_A, \vec{R}_B) = E_{el}^{(j)}(|\vec{R}_A - \vec{R}_B|)$$

Plotting, schematically:



Then, the total energy (eigenvalue) of the molecule (excluding translation of the molecular center of mass) is given by:



Atkins' "derivation" of the BO approximation  
(Sect. 8.1):

$$H = -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z^2} - \sum_{j=1,2} \frac{\hbar^2}{2m_j} \frac{\partial^2}{\partial Z_j^2} + V(z, Z_1, Z_2)$$

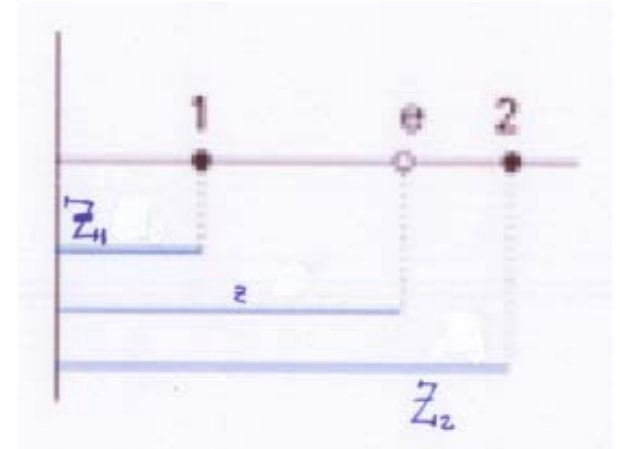
$$H = T_e + T_N + V \quad \text{Full electro-nuclear Hamiltonian (collinear reduction)}$$

$$H\Psi(z, Z_1, Z_2) = E\Psi(z, Z_1, Z_2) \quad \text{Full electro-nuclear Schrodinger Eq.}$$

$$\Psi(z, Z_1, Z_2) = \psi(z; Z_1, Z_2)\chi(Z_1, Z_2) \quad \text{Presumed Born-Oppenheimer (BO) factorization of the wavefunction.}$$

$$H\psi\chi = \chi T_e \psi + \psi T_N \chi + V\psi\chi + W = E\psi\chi \quad \text{Substitution of BO wavefunction Ansatz into (full) SE.}$$

$$W = \sum_{j=1,2} \frac{\hbar^2}{2m_j} \left( 2 \frac{\partial \psi}{\partial Z_j} \frac{\partial \chi}{\partial Z_j} + \frac{\partial^2 \psi}{\partial Z_j^2} \chi \right) \quad \text{Non-adiabatic coupling terms..}$$



Assuming that the non-Born Oppenheimer terms (i.e., W) are tiny:

$$\chi T_e \psi + \psi T_N \chi + V \psi \chi = E \psi \chi \quad [1]$$

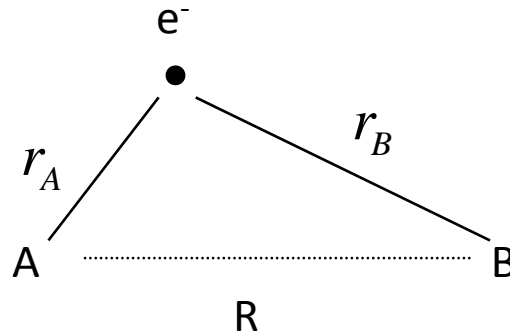
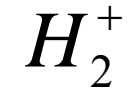
$$\psi T_N \chi + (T_e \psi + V \psi) \chi = E \psi \chi \quad \text{Rearrange Eq. [1]}$$

$$T_e \psi + V \psi = E_e(Z_1, Z_2) \psi \quad \text{Solve the electronic SE for fixed ("frozen")}$$

$$\psi T_N \chi + E_e \psi \chi = E \psi \chi \quad \text{Substitute the solution for the electronic SE into Eq. [1]}$$

$$T_N \chi + E_e \chi = E \chi \quad \text{This implies the indicated nuclear coordinate Schrod. Eq.}$$

A (semi)quantitative example of chemical bonding:



For nuclei A,B clamped at internuclear separation R \*\*, the electronic Hamiltonian reads:

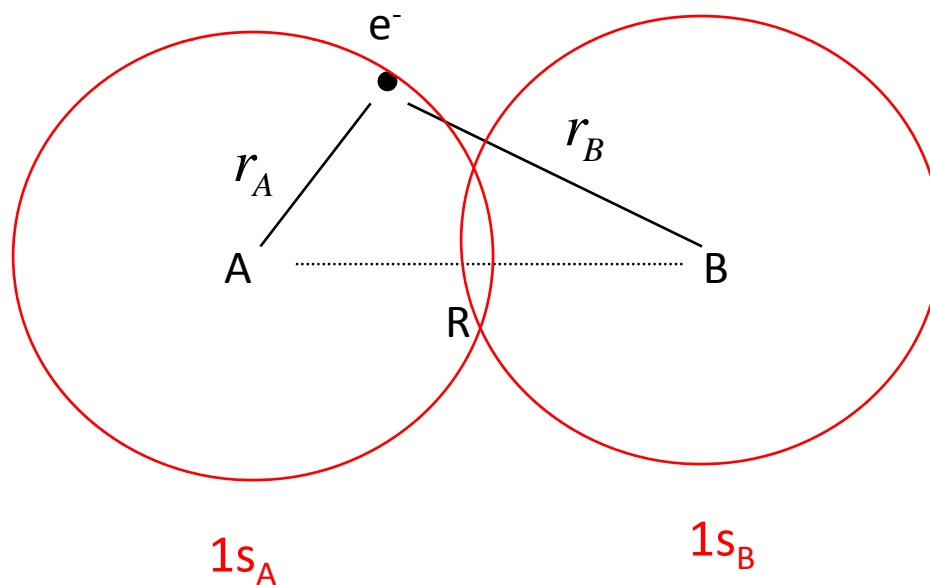
$$\hat{H} = \frac{-\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0 R} - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}$$

\*\* i.e., within the Born-Oppenheimer approx.



A reasonable approximation to the (unnormalized) ground electronic state energy eigenfunction turns out to be:

$$\psi_{gs}(\vec{r}) = 1s_A(\vec{r}) + 1s_B(\vec{r})$$

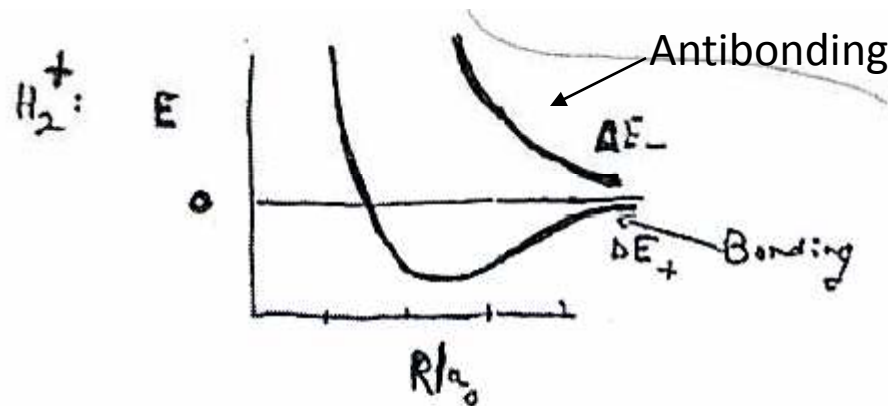


Thus:

$$E_{gs}(R) \cong \frac{\int d\vec{r} \psi_{gs}(\vec{r}) \hat{H} \psi_{gs}(\vec{r})}{\int d\vec{r} \psi_{gs}^2(\vec{r})} = -\frac{1}{2} + \frac{\overbrace{J'(R) + K'(R)}^{\Delta E_+(R)}}{1 + S(R)}$$

where  $R$  is in units of the Bohr radius  $a_0$ ;  $E$  is in units of Hartrees:  
 1 Hartree =  $2 \cdot 13.6 \text{ eV} = 27.2 \text{ eV}$ .

Furthermore,  $J'(R)$ ,  $K'(R)$ ,  $S(R)$  are simple (known!) functions, all of which vanish as  $R \rightarrow \infty$ .



S, J',K' represent the integrals:

$$S = \int d\vec{r} 1s_A 1s_B$$

$$J' = \int d\vec{r} 1s_A \left( -\frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$

$$K' = \int d\vec{r} 1s_A \left( -\frac{1}{r_A} + \frac{1}{R} \right) 1s_B$$

These integrals evaluate to:

$$S(R) = e^{-R} (1 + R + R^2 / 3)$$

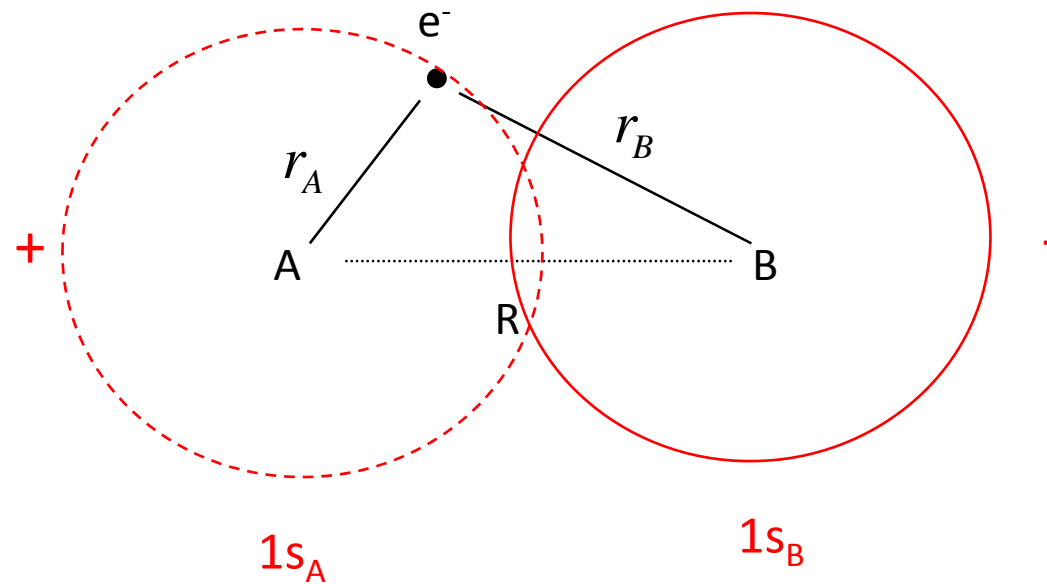
$$J'(R) = e^{-2R} \left( 1 + \frac{1}{R} \right)$$

$$K'(R) = \frac{S(R)}{R} - e^{-R} (1 + R)$$

where R is measured in units of the Bohr radius,  $a_0=0.53 \text{ \AA}$ , and J', K' are measured in terms of the Hartree (or atomic unit = a.u. of energy), 1 Hartree = 27.2 eV.

Finally, a reasonable approximation to the (unnormalized) 1<sup>st</sup> excited electronic state energy eigenfunction turns out to be:

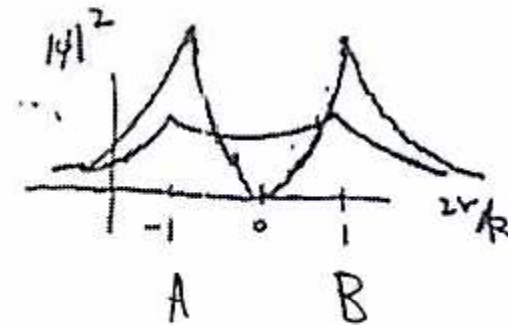
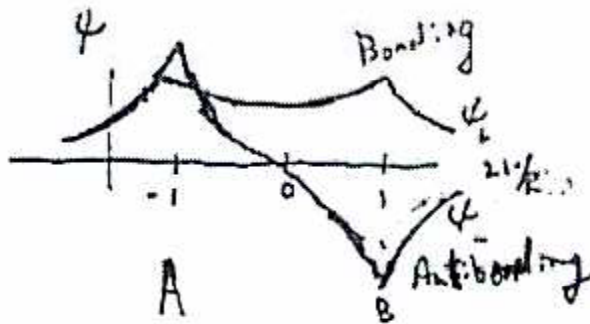
$$\psi_{es}(\vec{r}) = 1s_A(\vec{r}) - 1s_B(\vec{r})$$



One then evaluates:

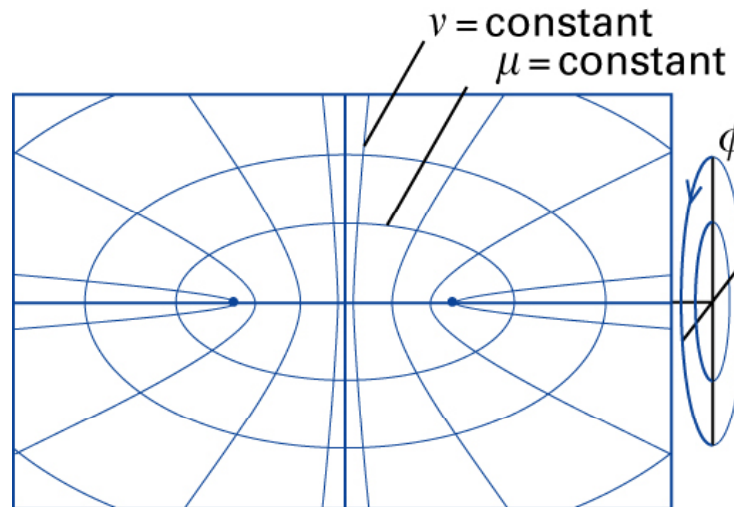
$$E_{es}(R) \cong \frac{\int d\vec{r} \psi_{es}(\vec{r}) \hat{H} \psi_{es}(\vec{r})}{\int d\vec{r} \psi_{es}^2(\vec{r})} = -\frac{1}{2} + \frac{\overbrace{J'(R) - K'(R)}^{\Delta E_-(R)}}{1 - S(R)}$$

Finally, w.f. is:  
for  $H_2^+$



## Additional Comments on the $H_2^+$ molecule ion:

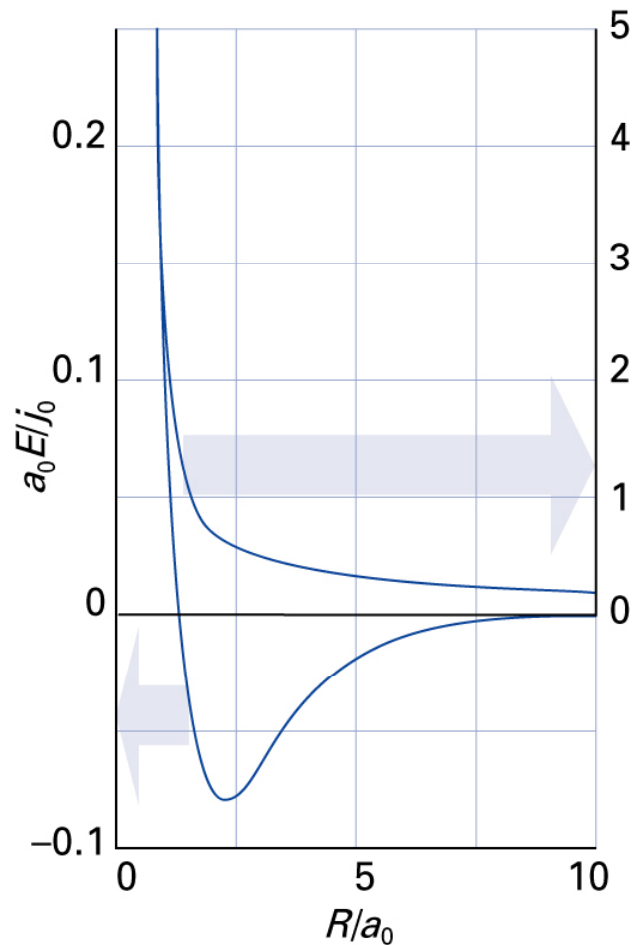
- 1) The Schrodinger Eq. for this problem can be solved analytically in elliptical coordinates:



The analytical expressions for  $\psi, E$  are “too complicated” to present here. (The same essential content is contained in the simple  $1s_A, 1s_B$  molecular orbital analysis given above.)

However, the elliptical coordinate transformation can be used to evaluate  $S(R), J'(R), K'(R)$  analytically (see above).

2) Here is a more quantitative diagram of the bonding (ground state) and anti-bonding (excited state) nuclear potential energy curves obtained from the simple  $1s_A, 1s_B$  MO treatment above:



These curves are in semi-quantitative agreement with exact solutions of  $H_2^+$  molecule Schrodinger Eq. ( $\leftarrow$  which agree well with spectroscopic data).