

Quantum Chemistry

Lecture 9

Diatomic Molecules

Molecular Electronic Structure Calculations Applied to Diatomic Molecules

NC State University

Molecular Structure

- Born-Oppenheimer approximation
- LCAO-MO application to H_2^+
- The potential energy surface
- Hartree-Fock theory
- MOs for diatomic molecules
- Post Hartree-Fock
(Configuration Interaction)

Born-Oppenheimer approximation

- Molecular motion includes the motion of both nuclei and electrons.
- The time scale of the motion of the nuclei is orders of magnitude slower than electron motion due to the difference in mass:

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

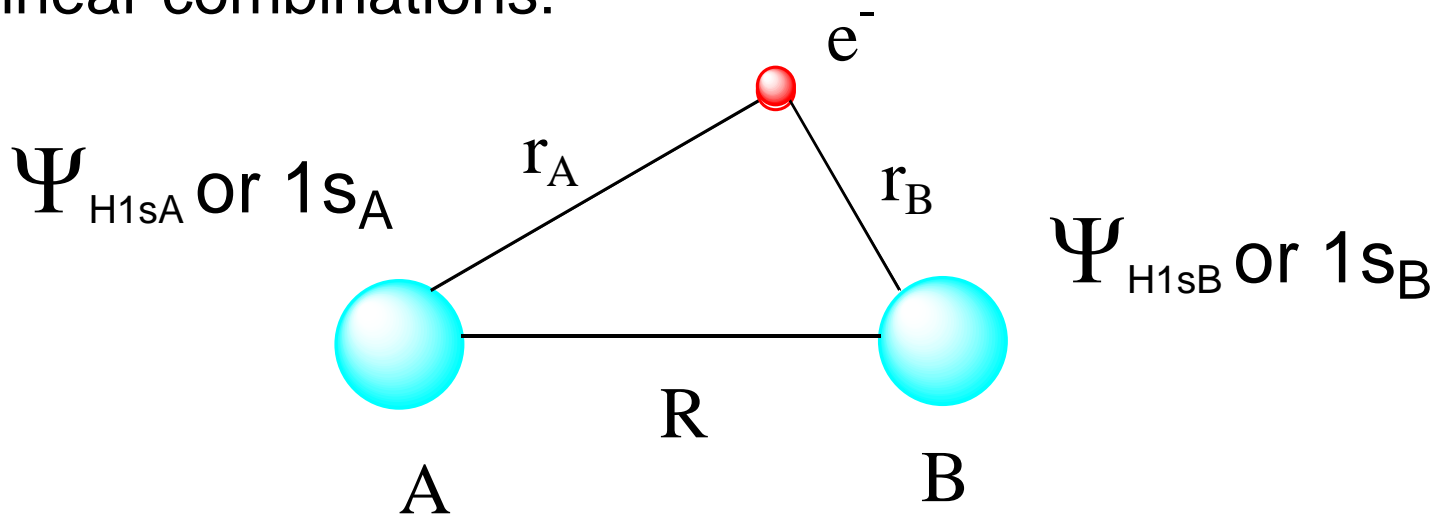
$$m_p = 1.672 \times 10^{-27} \text{ kg}$$

The potential energy surface

- The idea that nuclear and electronic motions can be separated implies that there is a nuclear potential energy surface $U(R)$ where R is the internuclear distance.
- The potential surface has an equilibrium geometry R_e and well depth D_e .

Hydrogen molecule ion wave functions

We use this example because it can be solved exactly.
The spatial wavefunction on each of two H atoms forms linear combinations:



The atomic wave functions form linear combinations to make molecular orbital wave functions.

$$\Psi_{\pm} = 1s_{\text{A}} \pm 1s_{\text{B}}$$

The hamiltonian for H_2^+

The hamiltonian for H_2^+ is:

$$H = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}$$

Given above are the kinetic energy operators for the nuclei A and B and for the electron e. Also there are three potential energy terms, two attractive potential terms between the nuclei (A and B) and the electron and one repulsive term involving A and B only. In order to proceed we will:

- Separate nuclear and electronic motion (Born-Oppenheimer approximation)
- Convert to atomic units.

Separation of electronic and nuclear motion

The Born-Oppenheimer approximation states that electronic motion is much more rapid than nuclear motion and therefore the electrons see a static nuclear configuration. This means:

- We can separate the nuclear kinetic energy terms in a separate Schrödinger equation.

$$H_{nuclear} = -\frac{\hbar^2}{2M} (\nabla_A^2 + \nabla_B^2)$$

- We can solve the electronic Schrödinger equation at fixed values of R. For each value of R we will obtain a set of energy values for the various states of H_2^+ . The plot of these energy values against R produces a potential energy surface for the molecule.

Atomic Units

After application of the B-O approximation the electronic hamiltonian becomes:

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

In atomic energy units we set

$$\hbar = 1 ; e = 1 ; m_e = 1 ; 4\pi\epsilon_0 = 1$$

in the above equations. The atomic unit of distance is the Bohr radius $a_0 = 0.529 \text{ \AA}$. The atomic unit of energy is the Hartree which is equal to the twice the ionization energy of the hydrogen atom. The Hartree is defined as

$$E_h = \frac{e^2}{4\pi\epsilon_0 a_0}$$

In atomic units the hamiltonian takes on a simple form.

$$H = -\frac{1}{2}\nabla_e^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

where r_A and r_B are the distances of the electron from nucleus A and B, respectively. The Schrödinger equation for H_2^+ is:

$$H\Psi(r_A, r_B; R) = E\Psi(r_A, r_B; R)$$

We can use linear combinations of atomic wavefunctions for our molecular wavefunctions.

$$\Psi_{\pm} = c_1A \pm c_2B$$

where A and B represent the $1s_A$ and $1s_B$ wave functions, respectively. Given that the nuclei are identical we must have $|c_1| = c_2$. Thus, our linear combination becomes:

$$\Psi_+ = A + B$$

for the bonding and

$$\Psi_- = A - B$$

For the anti-bonding orbital.

The hamiltonian for H_2^+

The potential involves three particles, one electrons and two protons. In atomic units it is given by

$$V = - \left(\frac{1}{r_A} + \frac{1}{r_B} \right) + \frac{1}{R}$$

The hamiltonian includes the kinetic energy terms for the electron only since the Born-Oppenheimer approximation allows separation of nuclear and electronic motion. The internuclear distance R is fixed and the nuclear kinetic energy is zero.

$$H = -\frac{1}{2} \nabla^2 + V$$

Setting up the energy calculation for H_2^+

The average energy is obtained by evaluating the expectation value:

$$E' = \frac{\int \Psi^* H \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

The denominator gives the required normalization.

$$\begin{aligned} \int \Psi^* \Psi d\tau &= \int (1s_A^* + 1s_B^*)(1s_A + 1s_B) d\tau \\ &= \int 1s_A^* 1s_A d\tau + \int 1s_A^* 1s_B d\tau + \int 1s_B^* 1s_B d\tau + \int 1s_B^* 1s_A d\tau \\ &= 1 + S + 1 + S, \text{ where } \int 1s_A^* 1s_A d\tau = 1 \text{ and } \int 1s_A^* 1s_B d\tau = S \end{aligned}$$

Normalized LCAO wave functions

The LCAO wave functions for the H_2^+ molecule ion are

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B)$$

and

$$\psi_- = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B)$$

These wave functions are orthogonal and normalized.

Energy levels in H_2^+

Explicit substitution of the hamiltonian gives

$$\begin{aligned} E &= \int \Psi^* H \Psi d\tau = \int \Psi^* \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) \Psi d\tau \\ &= \int 1s_A^* \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A d\tau \\ &+ \int 1s_A^* \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B d\tau \\ &+ \int 1s_B^* \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B d\tau \\ &+ \int 1s_B^* \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A d\tau \end{aligned}$$

Energy levels in H_2^+

$$\begin{aligned} &= \int 1s_A^* \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A d\tau + \int 1s_A^* \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B d\tau \\ &+ \int 1s_B^* \left(E_{1s} - \frac{1}{r_A} + \frac{1}{R} \right) 1s_B d\tau + \int 1s_B^* \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A d\tau \end{aligned}$$

Since

$$\left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} \right) 1s_A = E_{1s} 1s_A$$

$$\left(-\frac{1}{2} \nabla^2 - \frac{1}{r_B} \right) 1s_B = E_{1s} 1s_B$$

These are just
hydrogen atom
Schrödinger
equations

Energy levels in H_2^+

$$\begin{aligned} &= E_{1s}(1+S) + \int 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A d\tau + \int 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_B d\tau \\ &+ E_{1s}(1+S) + \int 1s_B^* \left(-\frac{1}{r_A} + \frac{1}{R}\right) 1s_B d\tau + \int 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A d\tau \end{aligned}$$

To further evaluate these two-center integrals we define the Coulomb integral

$$J = \int 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A d\tau = - \int \frac{1s_A^* 1s_A}{r_B} d\tau + \frac{1}{R}$$

and the exchange integral

$$K = \int 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A d\tau = - \int \frac{1s_B^* 1s_A}{r_B} d\tau + \frac{S}{R}$$

Energy levels in H_2^+

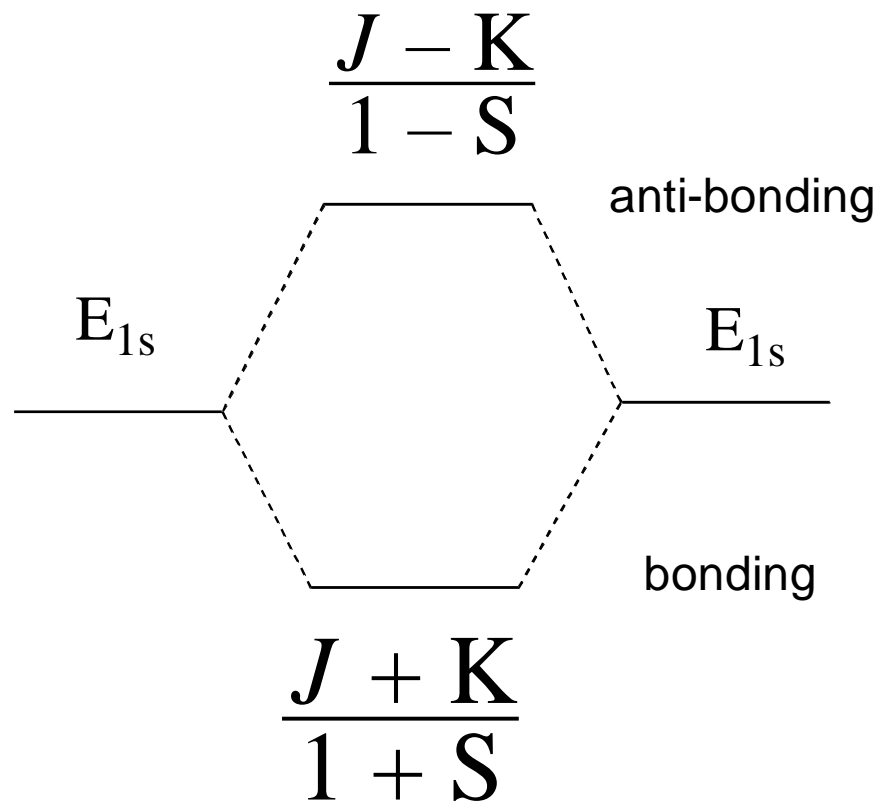
$$E'_+ = \frac{\int \Psi_+^* H \Psi_+ d\tau}{\int \Psi_+^* \Psi_+ d\tau} = \frac{E_{1s} 2(1+S) + 2(J+K)}{2(1+S)}$$

$$E'_+ = E_{1s} + \frac{J+K}{1+S}$$

$$E'_- = \frac{\int \Psi_-^* H \Psi_- d\tau}{\int \Psi_-^* \Psi_- d\tau} = \frac{E_{1s} 2(1-S) + 2(J-K)}{2(1-S)}$$

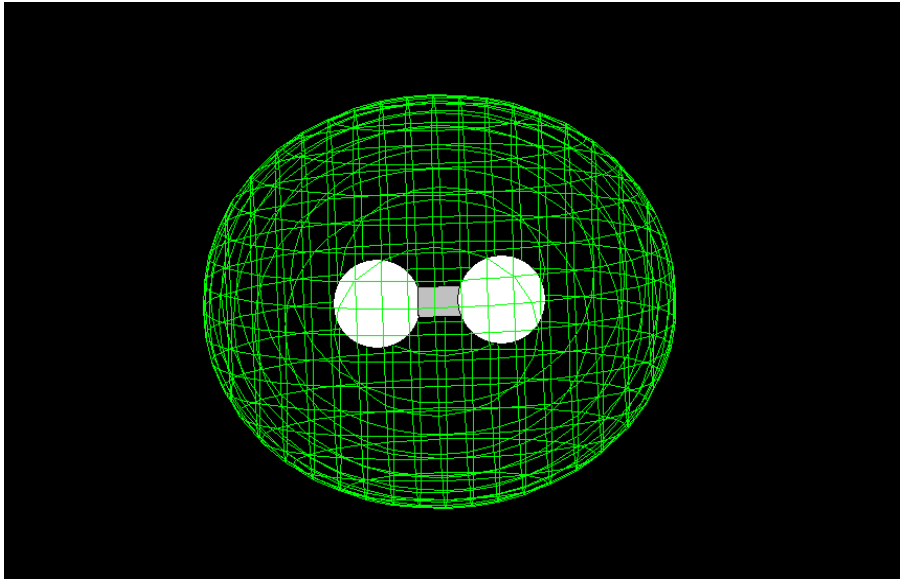
$$E'_- = E_{1s} + \frac{J-K}{1-S}$$

Diagram of H_2^+ energy levels

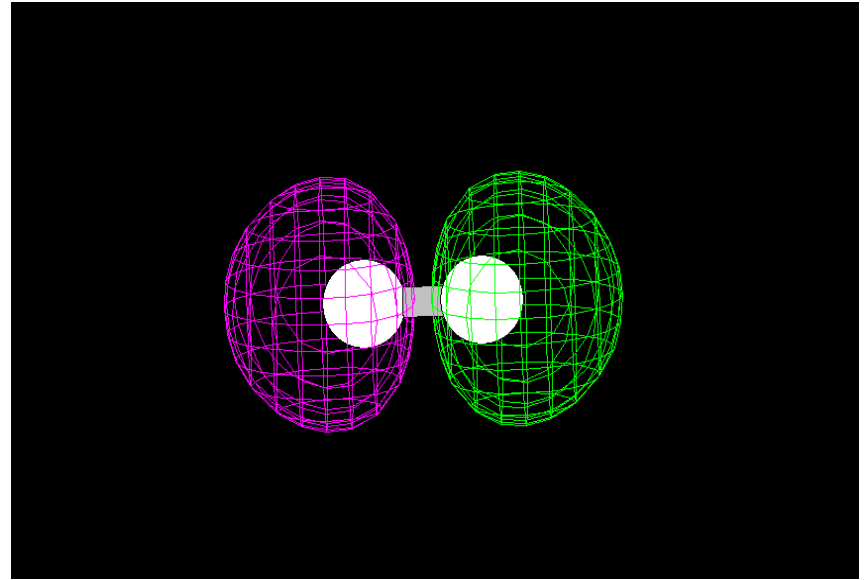


Note that the anti-bonding level is more destabilizing than the bonding level is stabilizing.

Bonding and anti-bonding orbitals



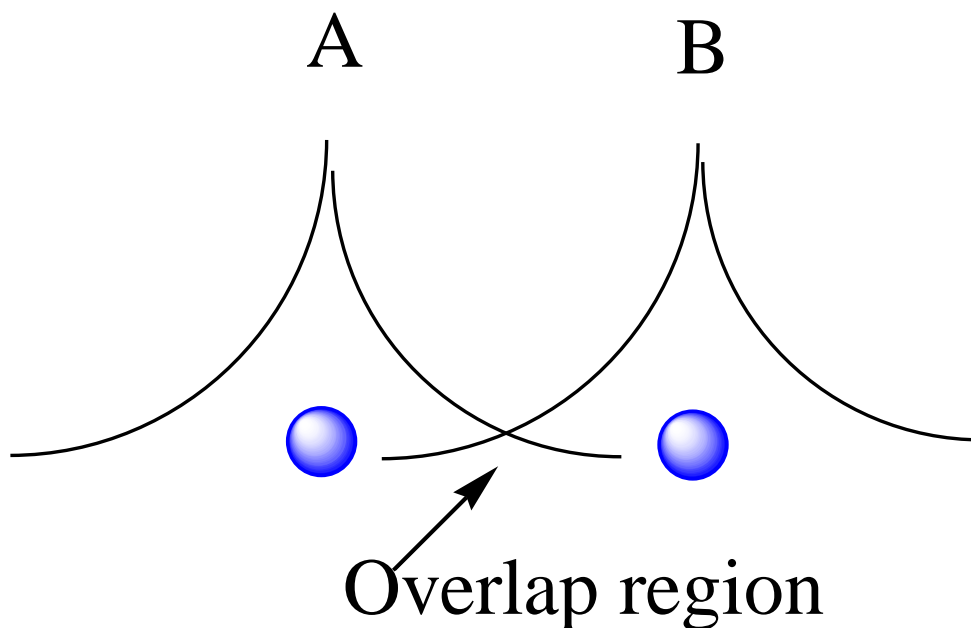
$$\Psi_+ = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B)$$



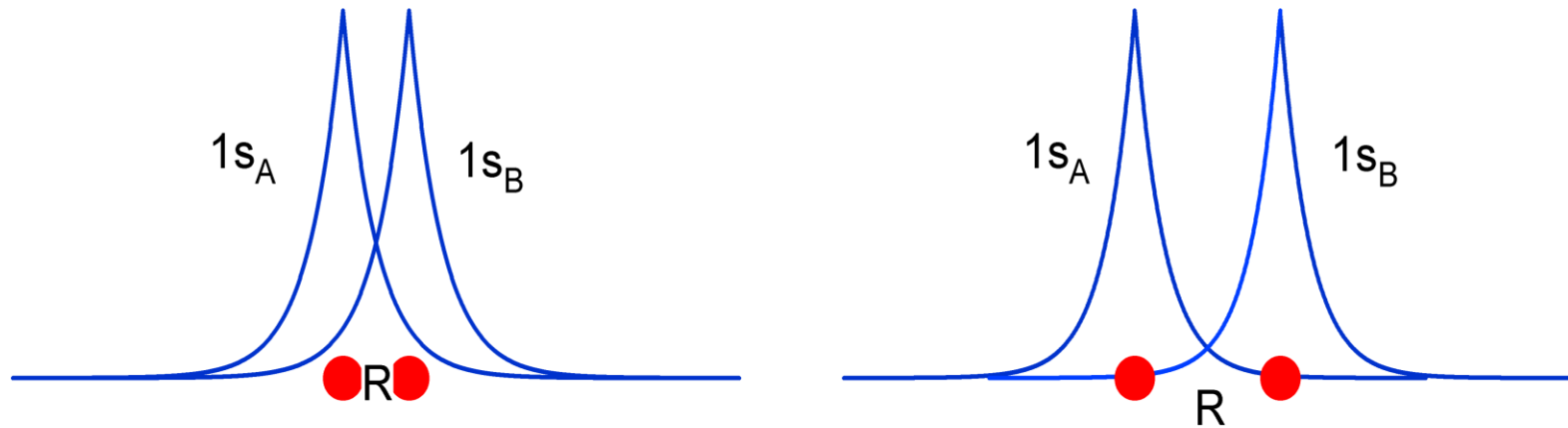
$$\Psi_- = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B)$$

Significance of the overlap integral

The wave functions $1s_A$ and $1s_B$ are not orthogonal since they are centered on different nuclei. The overlap integral S is a function of the internuclear distance.



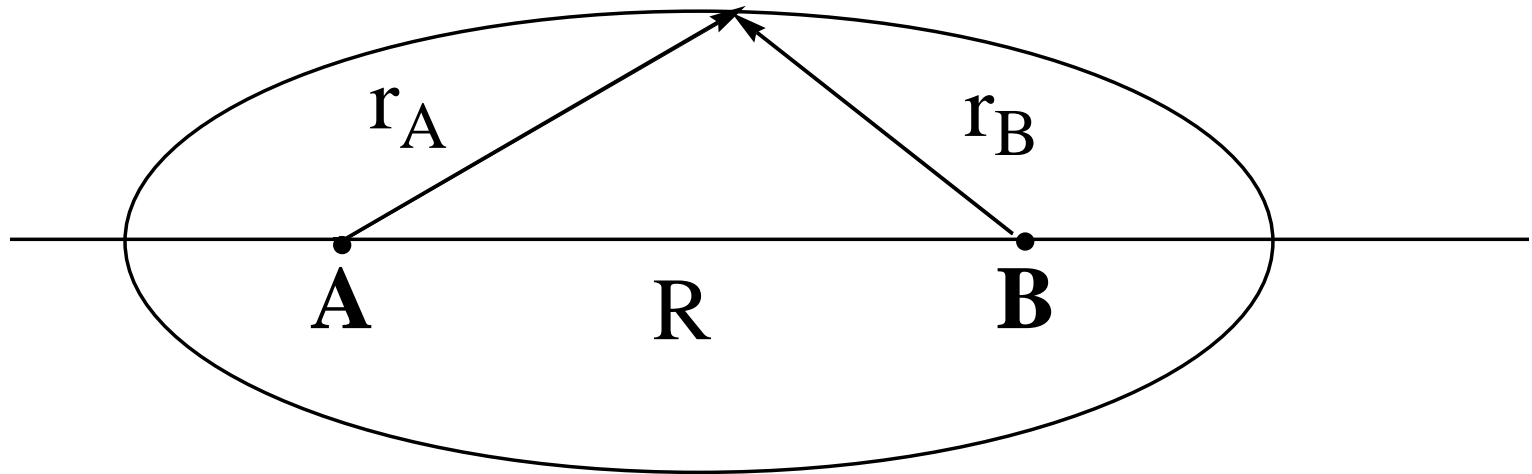
Distance dependence of terms that make up the energy



The energy, overlap and other integrals that describe the system are all a function of distance. $E(R)$ is the distance dependent energy (surface) $S(R)$ is the distance dependent overlap $J(R)$ is the distance dependent Coulomb integral $K(R)$ is the distance dependent exchange integral

Elliptical coordinate system

In order to solve the H_2^+ ion analytically we can use integration in elliptical coordinates. This is shown schematically below.



To transform the coordinates we use the following

$$\lambda = \frac{r_A + r_B}{R}, \mu = \frac{r_A - r_B}{R}$$

within the following limits

$$1 \leq \lambda \leq \infty, -1 \leq \mu \leq 1, 0 \leq \phi \leq 2\pi$$

Wave functions and variables

If the radius is given in units of Bohr radii ($a_0 = 0.529 \text{ \AA}$) the hydrogen atom 1s wave function is:

$$\text{for atom A} \quad f_A = \frac{1}{\sqrt{\pi}} e^{-r_A} \quad \text{and} \quad f_B = \frac{1}{\sqrt{\pi}} e^{-r_B}$$

for atom B in spherical polar coordinates. To solve the following integrals, we can solve for r_A and r_B in terms of λ and μ .

$$r_A = R\lambda - r_B, \quad r_B = r_A - R\mu$$

$$r_A = R\lambda - r_A + R\mu$$

$$2r_A = R(\lambda + \mu), \quad 2r_B = R(\lambda - \mu)$$

The volume element is

$$d\tau = \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\phi$$

Normalization

The normalization constant in elliptical coordinates is determined from the integral:

$$1 = N^2 \int f_A f_A d\tau = \frac{N^2}{\pi} \int e^{-2r_A} d\tau$$

Since $2r_A = (\lambda + \mu)R$ we have

$$1 = \frac{N^2 R^3}{8\pi} \int_0^{2\pi} d\phi \left(\int_{-1}^1 e^{-R\mu} d\mu \int_1^{\infty} e^{-R\lambda} \lambda^2 d\lambda - \int_{-1}^1 e^{-R\mu} \mu^2 d\mu \int_1^{\infty} e^{-R\lambda} d\lambda \right)$$

The result is:

$$1 = N^2 (2\pi) \left(\frac{4}{R^3} \right)$$

so that,

$$N = \sqrt{\frac{R^3}{8\pi}}$$

The overlap integral $S(R)$

The overlap integral is distance dependent. In the elliptical coordinate system it can be solved for an analytical expression in terms of the internuclear distance, R .

The wave functions are normalized. The overlap integral S is

$$S(R) = \frac{1}{\pi} \int f_A f_B d\tau$$

where

$$\int f_A f_B d\tau = \int e^{-r_A} e^{-r_B} d\tau = \int e^{-(r_A+r_B)} d\tau$$

Using the above definitions this integral can be recast as

$$S(R) = \frac{R^3}{8\pi} \int_0^{2\pi} d\phi \left(\int_{-1}^1 d\mu \int_1^{\infty} e^{-R\lambda} \lambda^2 d\lambda - \int_{-1}^1 \mu^2 d\mu \int_1^{\infty} e^{-R\lambda} d\lambda \right)$$

Let $u = -R\lambda$ then $du = -Rd\lambda$ and $d\lambda = -du/R$.

$$S(R) = \frac{R^3}{8\pi} 2\pi \left(-\frac{2}{R^3} \int_{-R}^{-\infty} e^u u^2 du - \frac{2}{3R} \int_{-R}^{-\infty} e^u du \right)$$

The second term integrates to $-e^{-R}$, but the first requires integration by parts.

$$\begin{aligned} \int e^u u^2 du &= e^u u^2 - 2 \int e^u u du \\ &= e^u u^2 - 2(e^u u - e^u) \\ &= e^u (u^2 - 2u + 2) \end{aligned}$$

The integral is evaluated at minus infinity (it is zero there) and at $-R$.

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

The Coulomb integral J(R)

The Coulomb integral is:

$$J = - \int \frac{1s_B 1s_B}{r_A} d\tau + \int \frac{1s_B 1s_B}{R} d\tau$$

which can be resolved to

$$J(R) = - \frac{1}{\pi} \int \frac{e^{-r_B} e^{-r_B}}{r_A} d\tau + \frac{1}{\pi} \int \frac{e^{-r_B} e^{-r_B}}{R} d\tau$$

$$= - \frac{1}{\pi} \int \frac{e^{-2r_B}}{r_A} d\tau + \frac{1}{R}$$

and then cast into the elliptical coordinate system

$$- \frac{1}{\pi} \int \frac{e^{-2r_B}}{r_A} d\tau = - \frac{1}{\pi} \int \frac{2e^{-R(\lambda-\mu)}}{R(\lambda+\mu)} \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\phi$$

The Coulomb integral J(R)

Recognizing that $(\lambda^2 - \mu^2) = (\lambda + \mu)(\lambda - \mu)$ we can rewrite this integral as.

$$-\frac{R^2}{4\pi} \int_0^{2\pi} d\phi \int e^{-R(\lambda-\mu)} (\lambda - \mu) d\lambda d\mu$$

which is expanded to

$$-\frac{R^2}{2} \left(\int_{-1}^1 e^{R\mu} d\mu \int_1^{\infty} e^{-R\lambda} \lambda d\lambda - \int_{-1}^1 e^{R\mu} \mu d\mu \int_1^{\infty} e^{-R\lambda} d\lambda \right)$$

Using the fact that integration by parts yields

$$\int e^u u du = e^u u - \int e^u du = e^u (u - 1)$$

The integrals evaluate to

$$\int_{-1}^1 e^{R\mu} d\mu = -\frac{1}{R} \int_{-R}^R e^u du = -\frac{e^R - e^{-R}}{R}$$

$$\int_1^{\infty} e^{-R\lambda} \lambda d\lambda = \frac{1}{R^2} \int_{-R}^{-\infty} e^u u du = e^{-R} \left(1 + \frac{1}{R}\right)$$

$$\int_{-1}^1 e^{R\mu} \mu d\mu = \frac{1}{R^2} \int_{-R}^R e^u u du = \frac{e^R(R-1) - e^{-R}(R+1)}{R^2}$$

$$\int_1^{\infty} e^{-R\lambda} d\lambda = -\frac{1}{R} \int_{-R}^{-\infty} e^u du = \frac{e^{-R}}{R}$$

The Coulomb integral $J(R)$

Therefore

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

The Exchange integral $K(R)$

The exchange integral can likewise be evaluated.

$$K = -\frac{1}{\pi} \int \frac{1s_A 1s_B}{r_A} d\tau + \frac{1}{\pi} \int \frac{1s_A 1s_B}{R} d\tau$$

$$K(R) = -\frac{1}{\pi} \int \frac{e^{-r_A} e^{-r_B}}{r_A} d\tau$$

$$= -\frac{1}{\pi} \int \frac{e^{-(r_A+r_B)}}{r_A} d\tau + \frac{S(R)}{R} + \frac{1}{\pi} \int \frac{e^{-r_A} e^{-r_B}}{R} d\tau$$

$$-\frac{1}{\pi} \int \frac{e^{-(r_A+r_B)}}{r_A} d\tau = -\frac{2}{R\pi} \int \frac{e^{-R\lambda}}{(\lambda + \mu)} \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\phi$$

$$= -\frac{R^2}{4\pi} \int e^{-R\lambda} (\lambda - \mu) d\lambda d\mu d\phi$$

The Exchange integral $K(R)$

The integral that comprises the first term in $K(R)$ is

$$-\frac{R^2}{4\pi} \int_0^{2\pi} d\phi \left(\int_{-1}^1 d\mu \int_1^{\infty} e^{-R\lambda} \lambda d\lambda - \int_{-1}^1 \mu d\mu \int_1^{\infty} e^{-R\lambda} d\lambda \right)$$

Making substitutions as above

$$-\frac{R^2}{2} \left(\frac{2}{R^2} \int_{-R}^{-\infty} e^u u du \right) = -e^{-R}(R + 1)$$

which, when substituted into the initial expression for K gives

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

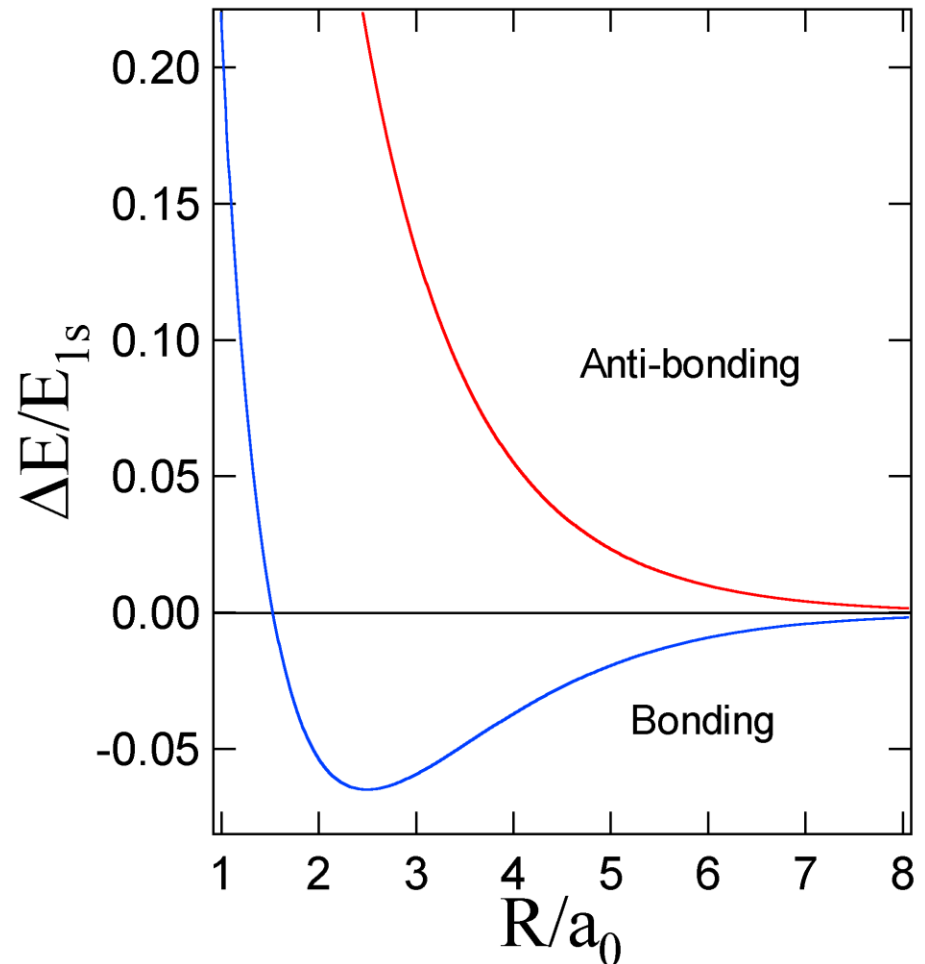
Potential energy surface for H_2^+

Using elliptical integrals that S, J, and K integrals can be solved analytically to yield the following PES.

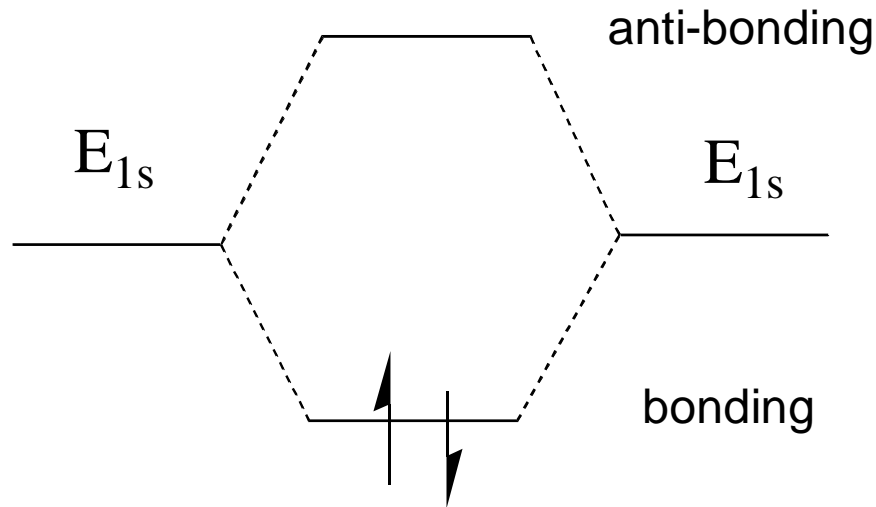
$$S(R) = e^{-R} \left(1 + R + \frac{R^2}{3} \right)$$

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

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



MO treatment of H₂



The two electrons must have opposite spins, α and β .
The wave function must be anti-symmetric with respect to electron exchange.

$$\Psi_{MO} = \Psi_b(1) \Psi_b(2) \left\{ \frac{1}{\sqrt{2}} \left(\alpha(1)\beta(2) - \alpha(2)\beta(1) \right) \right\}$$

Spatial part

Spin part (anti-symmetric)