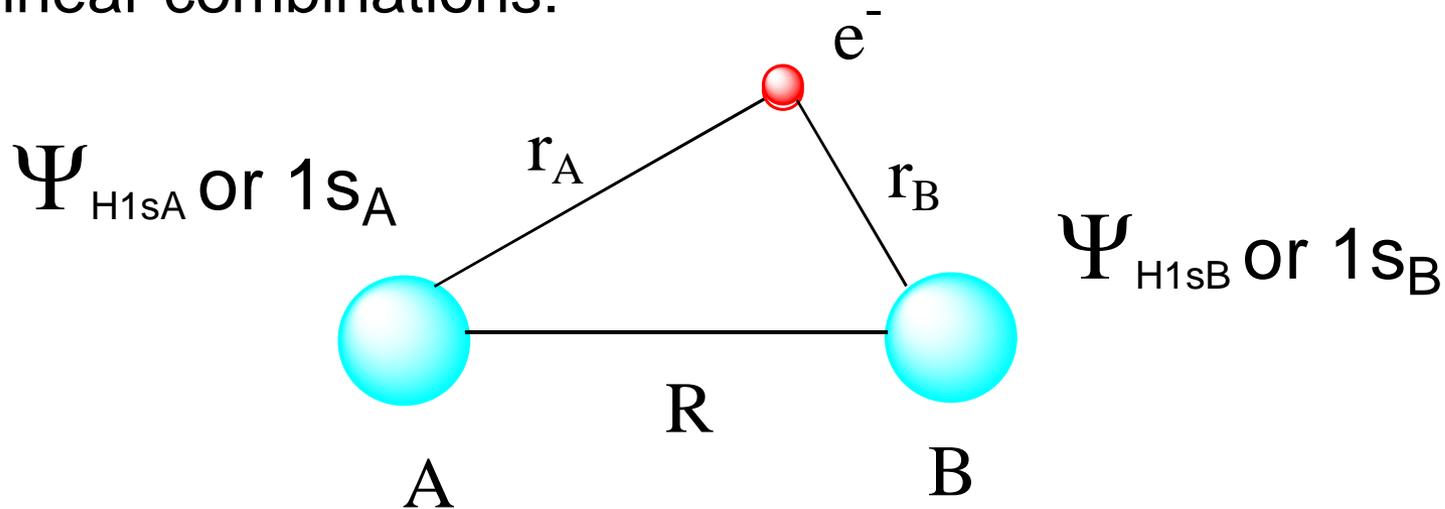# Hydrogen molecule ion wave functions

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

Ψ_{H1sA} or $1s_A$

r_A

e^-

r_B

Ψ_{H1sB} or $1s_B$

R

A

B

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

$$\Psi_\pm = 1s_A \pm 1s_B$$

The hamiltonian for H_2^+

The hamiltonian for H_2^+ is:

$$H = -\frac{\hbar^2}{2M}\left(\nabla_A^{\;2} + \nabla_B^{\;2}\right) - \frac{\hbar^2}{2m_e}\nabla_e^{\;2} - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R}$$

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.

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

• 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:

$$H = -\frac{\hbar^2}{2m_e}\nabla_e{}^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R}$$

In atomic energy units we set

$$\hbar = 1 \, ; e = 1 \, ; m_e = 1 \, ; 4\pi\varepsilon_0 = 1$$

in the above equations. The atomic unit of distance is the Bohr radius $a_0 = 0.529$ Å. 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

$$E_h = \frac{e^2}{4\pi\varepsilon_0 a_0}$$

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.

$$\Psi_\pm = c_1 A \pm c_2 B$$

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.

$$\int \Psi^* \Psi d\tau = \int \left(1s_A^* + 1s_B^*\right)\left(1s_A + 1s_B\right) d\tau$$

$$= \int 1s_A^* 1s_A d\tau + \int 1s_A^* 1s_B d\tau + \int 1s_B^* 1s_B d\tau + \int 1s_B^* 1s_A d\tau$$

$$= 1 + S + 1 + S, \; where \int 1s_A^* 1s_A d\tau = 1 \; and \int 1s_A^* 1s_B d\tau = S$$

Normalized LCAO wave functions

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

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

and

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

These wave functions are orthogonal and normalized.

Energy levels in H_2^+

Explicit substitution of the hamiltonian gives

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

$$= \int 1s_A^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A d\tau$$

$$+ \int 1s_A^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B d\tau$$

$$+ \int 1s_B^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B d\tau$$

$$+ \int 1s_B^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A d\tau$$

Energy levels in H$_2^+$

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

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

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$_2^+$

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

$$+ E_{1s}\left(1+S\right) + \int 1s_B^*\left(-\tfrac{1}{r_A}+\tfrac{1}{R}\right)1s_B d\tau + \int 1s_B^*\left(-\tfrac{1}{r_B}+\tfrac{1}{R}\right)1s_A d\tau$$

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

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

and the exchange integral

$$K = \int 1s_B^*\left(-\tfrac{1}{r_B}+\tfrac{1}{R}\right)1s_A d\tau = -\int \frac{1s_B^* 1s_A}{r_B} d\tau + \frac{S}{R}$$
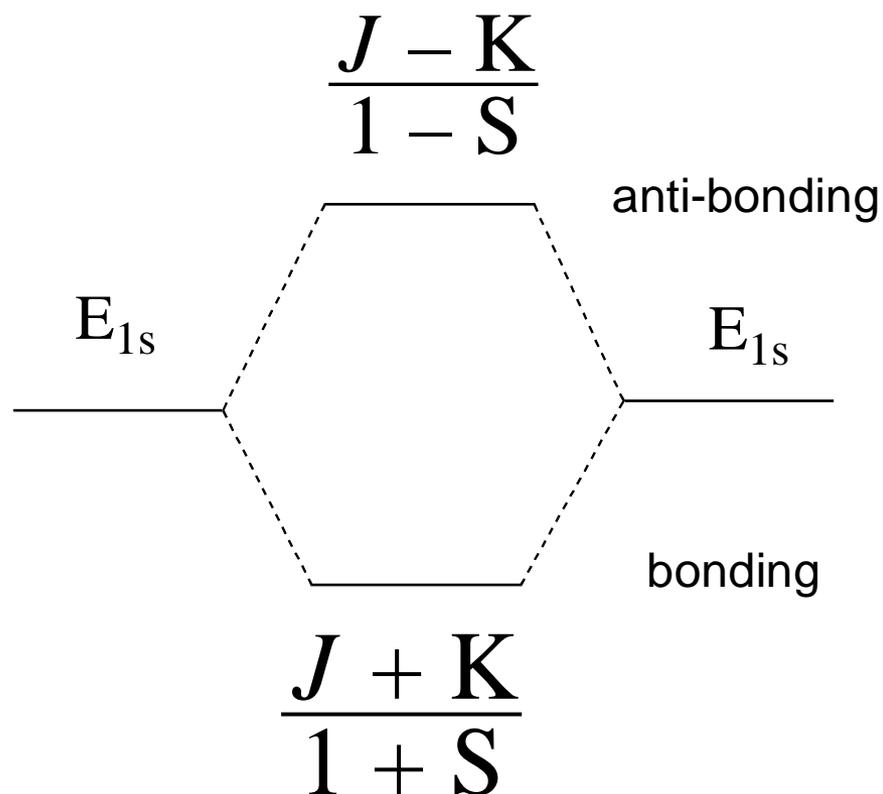
Energy levels in H$_2^+$

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

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

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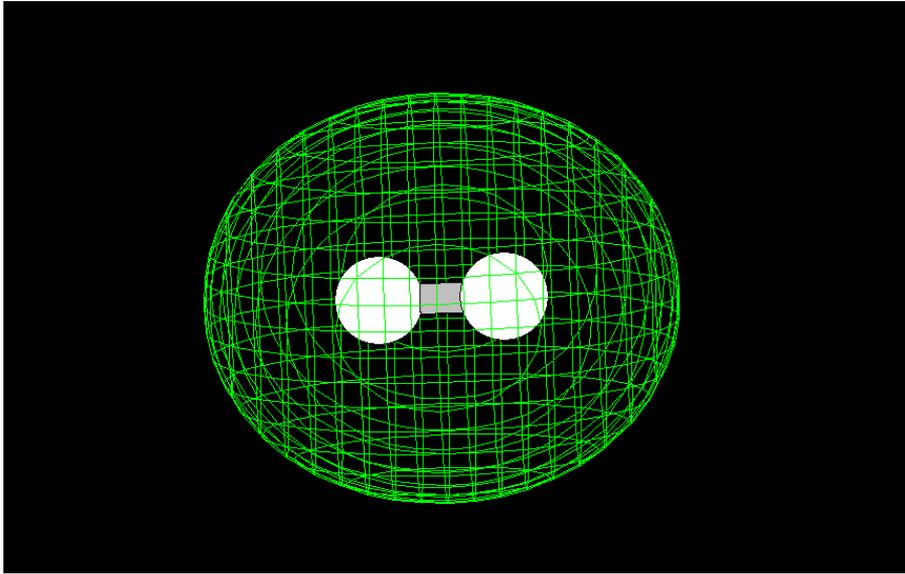
$$E_-' = E_{1s} + \frac{J-K}{1-S}$$

Diagram of H_2^+ energy levels

$$\frac{J - K}{1 - S}$$

anti-bonding

E_{1s} E_{1s}
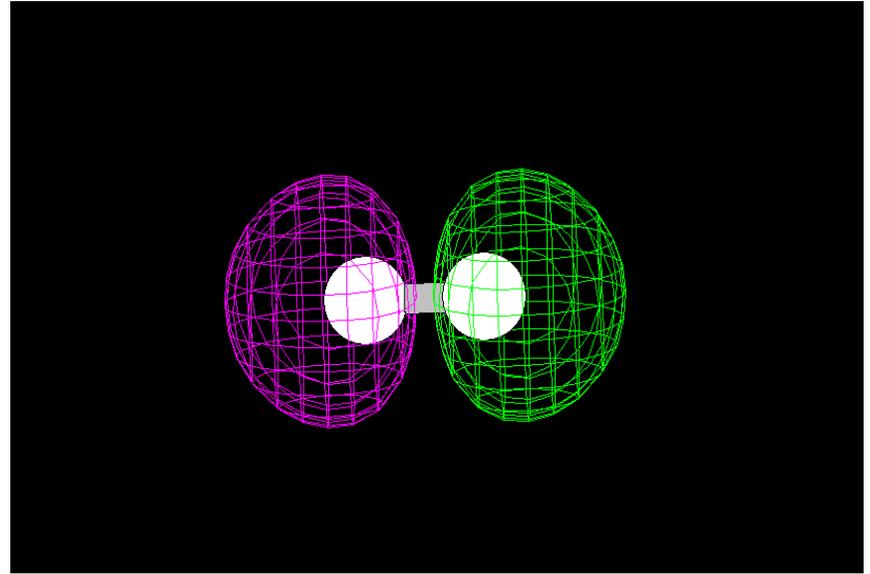
bonding

$$\frac{J + K}{1 + S}$$

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

Bonding and anti-bonding orbitals

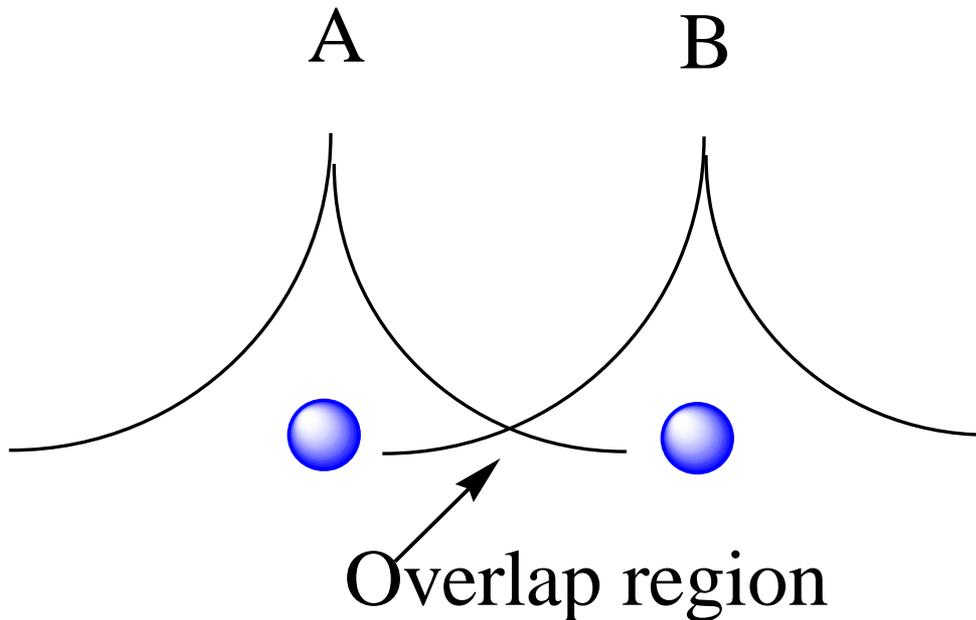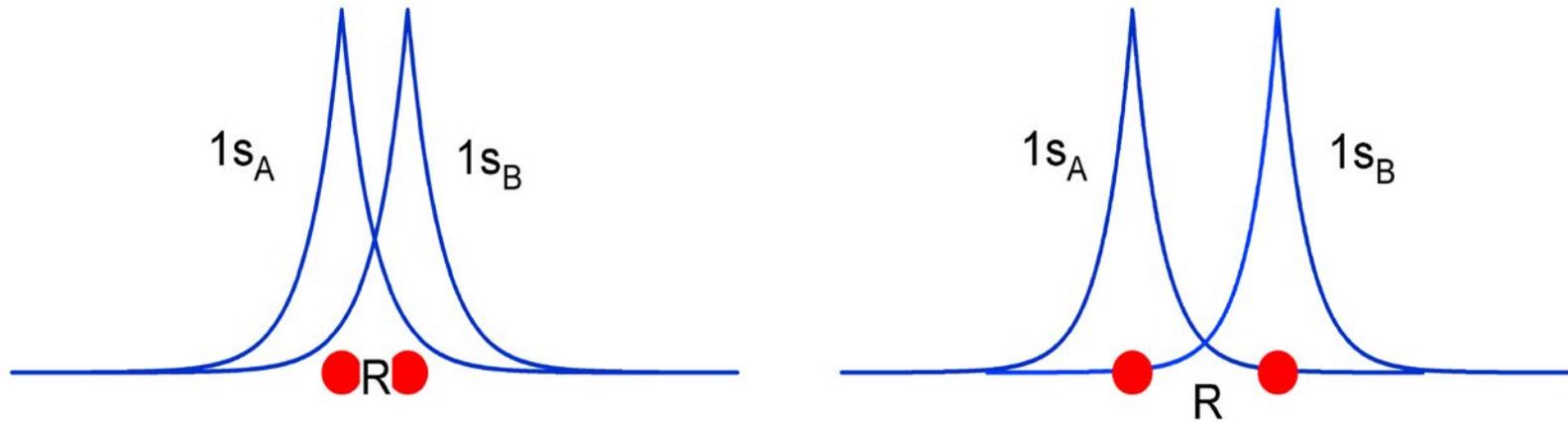$$\Psi_+ = \frac{1}{\sqrt{2(1+S)}}\left(1s_A + 1s_B\right)$$

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

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.

A   B

Overlap region

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.
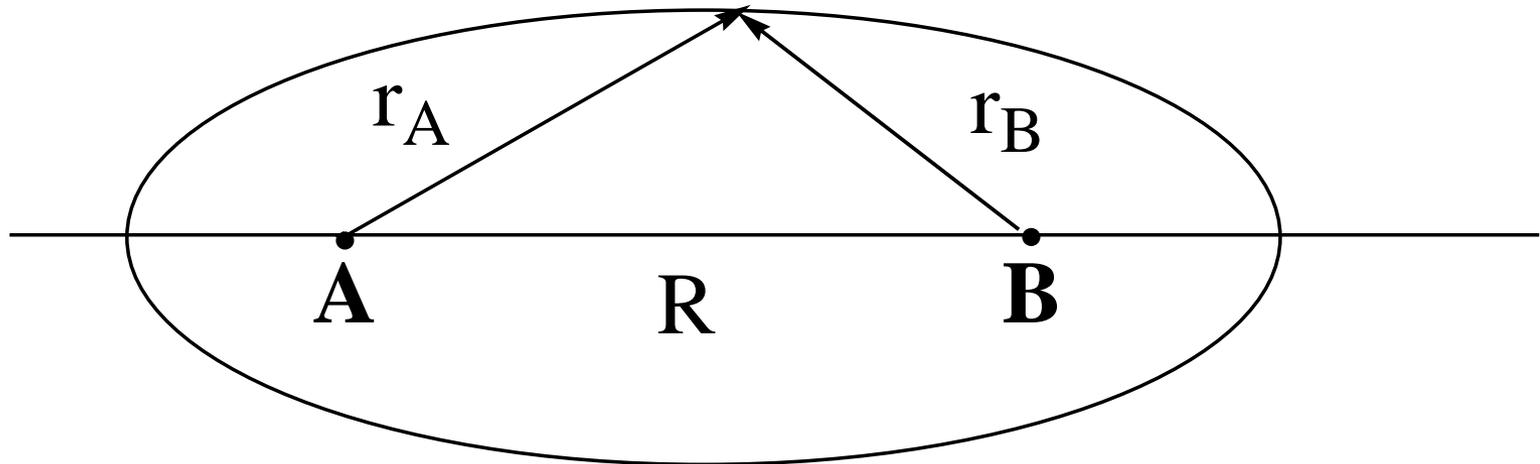
To transform the coordinates we use the following

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

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 Å) the hydrogen atom 1s wave function is:

for atom A $\qquad f_A = \dfrac{1}{\sqrt{\pi}} e^{-r_A}$ $\qquad$ and $\qquad f_B = \dfrac{1}{\sqrt{\pi}} e^{-r_B}$

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.

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

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

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

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 = -Rλ then du = -Rdλ and dλ = -du/R.

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

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

$$\int e^u u^2\, du = e^u u^2 - 2 \int e^u u\, du$$

$$= e^u u^2 - 2(e^u u - e^u)$$
$$= e^u(u^2 - 2u + 2)$$

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.

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

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

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