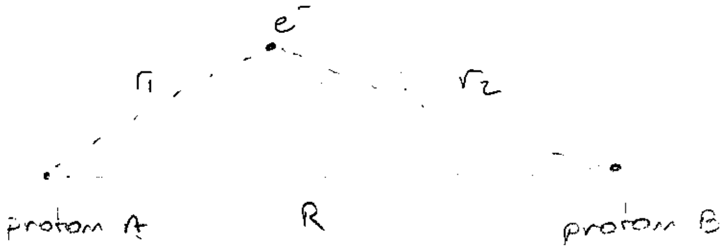
Linear Combination of Atomic Orbitals (LCAO)

The H_2^+ molecule

Consider the H_2^+ molecule



If we assume that the two protons are fixed, the total Hamiltonian becomes

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{q^2}{r_1} - \frac{q^2}{r_2} + \frac{q^2}{R} \qquad (1)$$

where the last term is the proton-proton repulsion.

I want to use the variational principle to treat this problem. If the protons were infinitely far apart we would have the ground state as being either

$$\chi_1(r) = \psi_0(r_1) \qquad (2)$$

or

$$\chi_2(r) = \psi_0(r_2)$$

where ψ_0 is the Hydrogen ground state ($a_0 = 1$);

$$\psi_0(r) = \frac{1}{\sqrt{\pi}} e^{-r} \qquad (3)$$

s a specific parametrization we could use

$$\vec{r}_1 = (x, y, z)$$

$$r_1 = r$$

nd

$$\vec{r}_2 = \vec{r}_1 - \vec{R}$$

r

$$r_2 = \sqrt{r_1^2 + R^2 - 2 r_1 R \cos\theta} \qquad (4)$$

when R is not very large we may try to use as a trial ave function the linear combination

$$\psi = c_1 \chi_1 + c_2 \chi_2 \qquad (5)$$

this is the idea of a linear combination of atomic orbitals (LCAO).

The first thing we do is normalize the wave function:

$$\langle\psi|\psi\rangle = c_1^2 \langle\chi_1|\chi_1\rangle + c_2^2 \langle\chi_2|\chi_2\rangle + 2c_1c_2 \langle\chi_1|\chi_2\rangle \qquad (6)$$

Since χ_1 and χ_2 are real, $\langle\chi_1|\chi_2\rangle = \langle\chi_2|\chi_1\rangle$ and there is no point in choosing $c_{1,2}$ complex

we have

$$\langle\chi_1|\chi_1\rangle = \langle\chi_2|\chi_2\rangle = 1$$

But $\chi_{1,2}$ do not form a basis so the cross term is not zero. Indeed, let us define

$$\boxed{\Delta = \langle\chi_1|\chi_2\rangle} \qquad (7)$$

We will compute this integral later

Hence

$$\boxed{\langle\psi|\psi\rangle = c_1^2 + c_2^2 + 2c_1c_2\Delta} \qquad (8)$$

Next, we need

$$\langle\psi|H|\psi\rangle = c_1^2\langle\chi_1|H|\chi_1\rangle + c_2^2\langle\chi_2|H|\chi_2\rangle$$
$$+\, c_1c_2\left(\langle\chi_1|H|\chi_2\rangle + \langle\chi_2|H|\chi_1\rangle\right)$$

Since H is Hermitian and the χ are real, the last two terms are equal. Define

$$\begin{aligned} H_{11} &= \langle\chi_1|H|\chi_1\rangle \\ H_{22} &= \langle\chi_2|H|\chi_2\rangle \\ H_{12} &= \langle\chi_1|H|\chi_2\rangle \end{aligned} \qquad (9)$$

By symmetry arguments we know that in our problem $H_{22} = H_{11}$. But let us leave it in general for now.

According to the variational principle we should now have

$$F = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{c_1^2H_{11} + c_2^2H_{22} + 2c_1c_2H_{12}}{c_1^2 + c_2^2 + 2c_1c_2\Delta} \geq E_g \qquad (10)$$

Next we minimize F with respect to the free parameters c_1 and c_2, and equate the result to zero nice way to do this is to first write

$$\langle\psi|H|\psi\rangle = F\langle\psi|\psi\rangle$$

$$c_1^2 H_{11} + c_2^2 H_{22} + 2c_1c_2H_{12} = F(c_1^2 + c_2^2 + 2c_1c_2\Delta)$$

ifferentiating with respect to c_1:

$$2c_1H_{11} + 2c_2H_{12} = \frac{\partial F}{\partial c_1}(c_1^2 + c_2^2 + 2c_1c_2\Delta) + F(2c_1 + 2c_2\Delta)$$

But the condition of minimum is $\partial F/\partial c_1 = 0$ so we get

$$c_1H_{11} + c_2H_{12} = F(c_1 + c_2\Delta) \tag{11a}$$

similarly, differentiating with respect to c_2 we get the equation

$$c_2H_{22} + c_1H_{12} = F(c_2 + c_1\Delta) \tag{11b}$$

This is a system of 2 equations for 2 unknowns because one of c_1 or c_2 is actually fixed from the normalization requirement.

We can also write this in matrix notation as

$$\boxed{\begin{bmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = F\begin{bmatrix} 1 & \Delta \\ \Delta & 1 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix}} \tag{12}$$

This looks like an eigenvalue / eigenvector equation. But it is a bit different because there is a matrix on the right-hand side as well. Indeed, this is called a generalized eigenvalue equation (very creative name) the method of solution is the same, however. First we put everything on the left

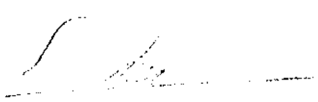
$$\begin{bmatrix} H_{11} - F & H_{12} - F\Delta \\ H_{12} - F\Delta & H_{22} - F \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \qquad (13)$$

This equation will only have a solution if the determinant of this matrix is zero. Thus

$$\begin{vmatrix} H_{11} - F & H_{12} - F\Delta \\ H_{12} - F\Delta & H_{22} - F \end{vmatrix} = 0 \qquad (14$$

This is called the secular equation. It will give a polynomial equation to solve for F.

The constant Δ is called an overlap integral because it measures how much the two wavefunctions x_1 and x_2 overlap



et us solve this equation for our particular case where $_{11} = H_{22}$. This is very common and simplifies the problem.

Ve now have

$$0 = \begin{vmatrix} H_{11} - F & H_{12} - F\Delta \\ H_{12} - F\Delta & H_{11} - F \end{vmatrix} = (H_{11} - F)^2 - (H_{12} - F\Delta)^2$$

o

$$F - H_{11} = F\Delta - H_{12}$$

$$F - H_{11} = -F\Delta + H_{12}$$

ws

$$\boxed{\begin{aligned} F_- &= \frac{H_{11} - H_{12}}{1 - \Delta} \\ F_+ &= \frac{H_{11} + H_{12}}{1 + \Delta} \end{aligned}} \qquad (15)$$

Now that we have found the eigenvalues, we plug them ach into Eq (13) to find c_1 and c_2

$$F_- \quad \begin{bmatrix} H_{11} - \frac{(H_{11} - H_{12})}{1 - \Delta} & H_{12} - \frac{(H_{11} - H_{12})\Delta}{1 - \Delta} \\ \cdots & \cdots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

(We don't need the 2 lines. One is enough).

thus

$$c_1\left[\frac{H_{11} - \Delta H_{11} - H_{11} + H_{12}}{1-\Delta}\right] + c_2\left[\frac{H_{12} - \Delta H_{12} - H_{11}\Delta + H_{12}\Delta}{1-\Delta}\right] =$$

$$c_1\left[\frac{H_{12} - \Delta H_{11}}{1-\Delta}\right] = -c_2\left[\frac{H_{12} - H_{11}\Delta}{1-\Delta}\right]$$

$$\therefore \quad c_1 = -c_2$$

Thus, the trial wave function $\psi = c_1 \chi_1 + c_2 \chi_2$ associated with F_- is

$$\psi_- = c_1(\chi_1 - \chi_2)$$

The normalization (2) then gives

$$1 = \langle \psi_- | \psi_- \rangle = c_1^2\left[1 + 1 - 2\Delta\right] = c_1^2(2 - 2\Delta)$$

thus the normalized wavefunction will be

$$\boxed{\begin{aligned} \psi_- &= \frac{\chi_1 - \chi_2}{\sqrt{2(1-\Delta)}} \\ \psi_+ &= \frac{\chi_1 + \chi_2}{\sqrt{2(1+\Delta)}} \end{aligned}} \qquad (16)$$

similarly

ere is what we found so far. We started with a variational
pproach using a linear combination of orbitals. We then
ound that the values of c_1 and c_2 which minimize F
e the solutions of Eq (12). Solving it we found two
ossibilities: either a symmetric wavefunction ψ_+
with an eigenvalue F_+ or a anti-symmetric wavefunction
with eigenvalue F_-.

But which is the true minimum? To know that we must compute the integrals H_{11}, H_{12} and Δ.

Calculation of integrals

Overlap Integral Δ (Eq (7))

$$\Delta = \langle \chi_1 | \chi_2 \rangle = \int \psi_0(r_1)\, \psi_0(r_2)\, d^3 r$$

$$= \frac{1}{\pi} \int e^{-r} e^{-\sqrt{r^2 + R^2 - 2 r R \cos\theta}}\, d^3 r$$

$$= \frac{2\pi}{\pi} \int_0^\infty dr\, r^2 e^{-r} \int_0^\pi e^{-\sqrt{r^2 + R^2 - 2 r R \cos\theta}} \sin\theta\, d\theta$$

Let

$$x = \sqrt{r^2 + R^2 - 2 r R \cos\theta} \qquad (17)$$

It is convenient to use the trick

$$d(x^2) = 2x\, dx = 2 r R \sin\theta\, d\theta$$

so

$$\sin\theta\, d\theta = \frac{x}{rR}\, dx \qquad (18)$$

Then

$$\int_0^\pi e^{-r_2} \sin\theta\, d\theta = \frac{1}{rR} \int e^{-x} x\, dx = -\frac{1}{rR} (1 + x) e^{-x}$$

$$= -\frac{1}{rR} \left[(1 + r + R)\, e^{-(r+R)} - (1 + |r - R|)\, e^{-|r-R|} \right]$$

ubstituting back on the r integral we obtain, after a unch of simplifications

$$\boxed{\Delta = e^{-R}\left(1 + R + R^2/3\right)} \qquad (19)$$

Note that $\Delta \to 0$ when $R \to \infty$, which shows why we call Δ an <u>overlap</u> integral.

Direct integral $H_{11} = \langle \chi_1 | H | \chi_1 \rangle$

Note that χ_1 is the ground state wave function of a hydrogen atom centered around r_1. Thus

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{q^2}{r_1} \right] \chi_1 = E_1 \chi_1 \qquad (20)$$

Thus

$$H_{11} = \langle \chi_1 | H | \chi_1 \rangle = \langle \chi_1 | \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{q^2}{r_1} - \frac{q^2}{r_2} + \frac{q^2}{R} \right] | \chi_1 \rangle$$

$$= E_1 + \frac{q^2}{R} - q^2 \langle \chi_1 | \frac{1}{r_2} | \chi_1 \rangle$$

because R is fixed. Now:

$$\langle \chi_1 | \frac{1}{r_2} | \chi_1 \rangle = \frac{1}{\pi} \int \frac{e^{-2r}}{r_2} d^3 r$$

$$= \frac{2\pi}{\pi} \int_0^\infty dr \, r^2 e^{-2r} \int_0^\pi \frac{\sin\theta \, d\theta}{\sqrt{r^2 + R^2 - 2rR\cos\theta}}$$

$$= 2 \int_0^\infty dr \, r^2 e^{-2r} \left[\frac{1}{rR} \int \frac{x \, dx}{x} \right]$$

$$= 2 \int_0^\infty dr \, r^2 e^{-2r} \frac{1}{rR} \left[(r+R) - |r-R| \right]$$

computing the integral we find

$$\langle \chi_1 | \frac{1}{r_2} | \chi_1 \rangle = \frac{1}{R} - e^{-2R}\left(1+\frac{1}{R}\right) \qquad (21)$$

hus

$$H_{11} = E_1 + \underbrace{\frac{q^2}{R} - \frac{q^2}{R}}_{0} + q^2 e^{-2R}\left(1+\frac{1}{R}\right)$$

Note also that
$$E_1 = -\frac{q^2}{2a_0}$$

But we are using $a_0 = 1$ so

$$q^2 = -2E_1$$

whence
$$\boxed{H_{11} = E_1\left\{1 - 2e^{-2R}\left(1+\frac{1}{R}\right)\right\}} \qquad (22)$$

Note that when $R \to \infty$ we get $H_{11} = E_1$, which is the energy of the electron in a hydrogen atom. It makes sense

Exchange integral : $H_{12} = \langle \chi_1 | H | \chi_2 \rangle = \langle \chi_2 | H | \chi_1 \rangle$

This integral describes the effect of having overlap in the interaction energy. It represents the probability that the electron will hop from one proton to the other.

Using (20) we get

$$H_{12} = \langle \chi_2 | H | \chi_1 \rangle = \left[E_1 + \frac{q^2}{R} \right] \underbrace{\langle \chi_2 | \chi_1 \rangle}_{\Delta} - q^2 \langle \chi_2 | \frac{1}{r_2} | \chi_1 \rangle$$

we have

$$\langle \chi_2 | \frac{1}{r_2} | \chi_1 \rangle = \frac{1}{\pi} \int \frac{e^{-r_2} e^{-r}}{r_2} d^3 r$$

$$= \frac{2\pi}{\pi} \int dr\, r^2 e^{-r} \int_0^{\pi} \frac{e^{-r_2}}{r_2} \sin\theta \, d\theta$$

$$= 2 \int dr\, r^2 e^{-r} \left[\frac{1}{rR} \int \frac{e^{-x}}{x} x \, dx \right]$$

$$= -2 \int dr\, r^2 e^{-r} \left[\frac{e^{-(r+R)} - e^{-|r-R|}}{rR} \right]$$

The result is

$$\boxed{\langle \chi_2 | \frac{1}{r_2} | \chi_1 \rangle = e^{-R}(1+R)} \qquad (23)$$

Thus

$$H_{12} = \left[E_1 + \frac{q^2}{R} \right] \Delta - q^2 e^{-R}(1+R)$$

$$= E_1 \left\{ \Delta - \frac{2\Delta}{R} + 2 e^{-R}(1+R) \right\}$$

$$\boxed{H_{12} = E_1 e^{-R}\left(1 - \frac{2}{R} + \frac{7}{3}R + \frac{R^2}{3}\right)} \qquad (24)$$

Just like Δ, the exchange integral goes to zero when $R \to \infty$

Analysis of F_+ and F_-

In summary we have

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

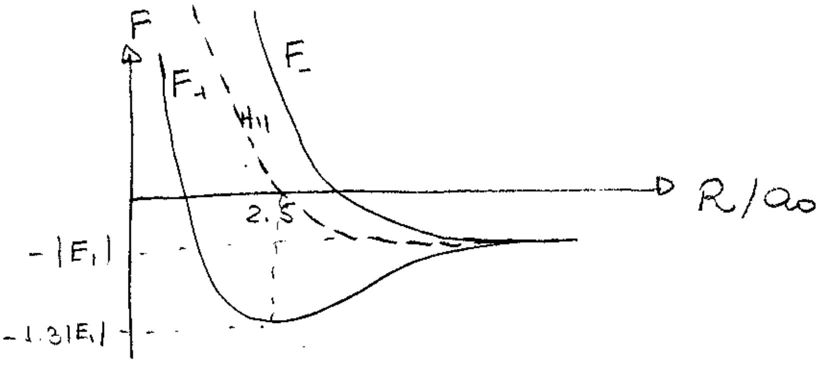
$$H_{11} = E_1\left[1 - 2e^{-2R}\left(1 + \frac{1}{R}\right)\right]$$

$$H_{12} = E_1\, e^{-R}\left[1 - \frac{2}{R} + \frac{7}{3}R + \frac{R^2}{3}\right]$$

After same simplifications we get

$$\boxed{\begin{aligned} F_+ &= \frac{H_{11} + H_{12}}{1 + \Delta} = |E_1| \, \frac{2e^{-R}\left(1 + \frac{1}{R}\right) - e^{R} + \frac{2}{R} - 1 - \frac{7R}{3} - \frac{R^2}{3}}{e^{R} + 1 + R\left(1 + \frac{R}{3}\right)} && (25 \\ F_- &= \frac{H_{11} - H_{12}}{1 - \Delta} = |E_1| \, \frac{2e^{-R}\left(1 + \frac{1}{R}\right) - e^{R} - \frac{2}{R} + 1 + \frac{7R}{3} + \frac{R^2}{3}}{e^{R} - 1 - R\left(1 + \frac{R}{3}\right)} && (26) \end{aligned}}$$

I took care to recall that $E_1 = -13.6$ eV < 0. Note also that R is given in units of a_0.



We see that the symmetric configuration has a region of R where the energy is lower than E_1. Thus, in this configuration there may be a bond!

And this is all due to H_{12}, the exchange integral!

e anti-symmetric configuration does not lead to bonding. the minimum of F_+ may be computed numerically and ads

$$\boxed{R_0 = 2.5\, a_0 \simeq 1.37\ \text{Å}} \qquad (27)$$

this is the "size" of the H_2^+ molecule. the experimental value is 1.06 Å, so we are not bad.

the overlap integral Δ, at $R = R_0$, has the value

$$\Delta(R_0) \simeq 0.46$$

this shows that the overlap is significant. In fact, it is due to the overlap that there is binding

The binding energy is defined as the difference between the minimum of F_+ and the energy of infinite separation E_1. For this problem we have

$$\boxed{E_{\text{binding}} = 1.77\ \text{eV}} \qquad (28)$$

the experimental value is 2.78 eV. So we are not doing great, but we are not bad either.

The calculation we just discussed was done by Pauling in 1928. this is only 2 years after Schrödingers paper!

Other variational calculations for the H_2^+ molecule

Finkelstein and Horowitz, in 1928, extended the calculation to include an effective nuclear charge Z'. They found a minimum at $Z' = 1.228$. The equilibrium sepparation was $R_0 = 1.06$ Å, in complete agreement with experiment. But the binding energy was 2.25 eV, still smaller than the 2.78 eV expected from experiment.

Dickinson in 1933 introduced additional terms to account for the polarization of the molecule, which our treatment so far was unable to account since our trial wavefunction was spherically symmetric. Dickinson's choice was

$$\psi = \psi_{100}(\vec{r}_1, Z') + \psi_{100}(\vec{r}_2, Z') + \sigma\left[\psi_{210}(\vec{r}_1, Z'') + \psi_{210}(\vec{r}_2, Z'')\right]$$

where

$$\psi_{210} \sim r e^{-r/2} \cos\Theta$$

Thus, the function $\psi_{100} + \sigma\psi_{210}$ is not symmetrical with respect to r

The parameter σ then represents the degree of polarization.

Dickinson found the minimum values

$$z' = 1.247 \qquad z'' = 2.868 \qquad \sigma = 0.145$$

e equilibrium distance he obtained was then

$$R_0 = 1.06 \text{ Å}$$

the binding energy was

$$E_{binding} = 2.73 \text{ eV}$$

which is now remarkably close to 2.78eV

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It is also worth noting that the H_2^+ molecule may be solved exactly using elliptic coordinates. the calculation is very complicated, but it gives R_0 and E_b in *complete* agreement with experiment. this was a great triumph of quantum mechanics. It is also the inspiration of researchers which work with *ab* *initio* methods

Generalization of the LCAO method

It is straightforward to generalize these calculations to a linear combination of more than two orbitals. If we use as trial wave function

$$\psi = c_1 \chi_1 + c_2 \chi_2 + \dots + c_m \chi_m \tag{29}$$

then we must compute

$$H_{ij} = \langle \chi_i | H | \chi_j \rangle \tag{30}$$

$$\Delta_{ij} = \langle \chi_i | \chi_j \rangle \tag{31}$$

where, if the orbitals are appropriately normalized, then $\Delta_{ii} = 1$.

The minimum value of F is then obtained from the secular determinant

$$\begin{vmatrix} H_{11} - F\Delta_{11} & \dots & H_{1m} - F\Delta_{1m} \\ \vdots & & \\ H_{m1} - F\Delta_{m1} & \dots & H_{mm} - F\Delta_{mm} \end{vmatrix} = 0 \tag{32}$$

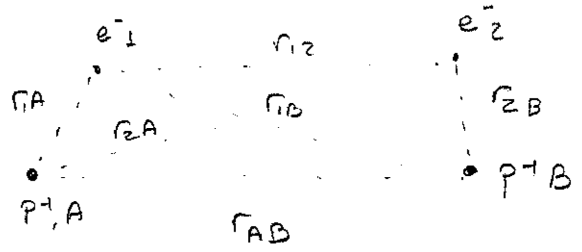
After finding the eigenvalues $F_1, F_2, \dots$ we solve for the c_i as

$$\begin{bmatrix} H_{11} - F\Delta_{11} & \dots & H_{1m} - F\Delta_{1m} \\ \vdots & & \\ H_{m1} - F\Delta_{m1} & \dots & H_{mm} - F\Delta_{mm} \end{bmatrix} \begin{bmatrix} c_1 \\ \cdot \\ c_m \end{bmatrix} = 0 \tag{33}$$

The H_2 molecule

The H_2 molecule has the same Hamiltonian of the Van der waals interaction

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{q^2}{r_{1A}} - \frac{q^2}{r_{2B}} - \frac{q^2}{r_{1B}} - \frac{q^2}{r_{2A}} + \frac{q^2}{r_{12}} + \frac{q^2}{r_{AB}} \qquad (34$$



when $R \to \infty$ we have two possible configurations for the ground state

$$\chi_1 = \psi_0(r_{1A})\,\psi_0(r_{2B})$$
$$\chi_2 = \psi_0(r_{1B})\,\psi_0(r_{2A}) \qquad (35)$$

χ_1 means electron 1 @ proton A and electron 2 @ proton B; χ_2 is the opposite possibility.

for the LCAO method we now take as a trial wave function

$$\psi = c_1 \chi_1 + c_2 \chi_2 \qquad (36)$$

the overlap integral is

$$\langle \chi_1 | \chi_2 \rangle = \int \psi_0(r_{1A})\,\psi_0(r_{2B})\,\psi_0(r_{1B})\,\psi_0(r_{2A})\, d^3r_1\, d^3r_2$$
$$= \int \psi_0(r_{1A})\,\psi_0(r_{1B})\, d^3r_1 \int \psi_0(r_{2B})\,\psi_0(r_{2A})\, d^3r_2$$

ach of these integrals is precisely that function Δ that we

ed before in Eq (19). Thus

$$\langle \chi_1 | \chi_2 \rangle = \Delta^2 \qquad (37)$$

Due to symmetry we again have $H_{22} = H_{11}$ and $H_{21} = H_{12}$.

ws, the eigenvalues of the secular Eq are still given by (15),

ut with $\Delta \to \Delta^2$:

$$\begin{aligned} F_+ &= \frac{H_{11} + H_{12}}{1 + \Delta^2} \\ F_- &= \frac{H_{11} - H_{12}}{1 - \Delta^2} \end{aligned} \qquad (38)$$

But the formulas for H_{11} and H_{12} are now different.

Let

$$\begin{aligned} H &= H_0 + V \\ H_0 &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{q^2}{r_{1A}} - \frac{q^2}{r_{2B}} + \frac{q^2}{R} \\ V &= -\frac{q^2}{r_{1B}} - \frac{q^2}{r_{2A}} + \frac{q^2}{r_{12}} \end{aligned} \qquad (39)$$

Then, since $r_{AB} = R$ is fixed

$$H_0 \, \chi_{1,2} = \left(2E_1 + \frac{q^2}{R} \right) \chi_{1,2} \qquad (40)$$

Thus

$$H_{11} = \langle \chi_1 | H | \chi_1 \rangle = 2E_1 + \frac{q^2}{R} + \langle \chi_1 | V | \chi_1 \rangle \qquad (41)$$

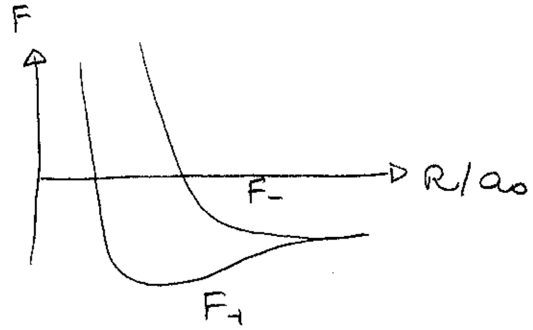
Now:

$$\langle \chi_1 | V | \chi_1 \rangle = q^2 \int \left[\frac{-1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} \right] \psi(r_{1A}) \psi(r_{2B}) d^3r_1 d^3r_2$$

By symmetry, the first two terms will give exactly the same result as Eq (21). The last integral is

$$\langle \chi_1 | \frac{1}{r_{12}} | \chi_2 \rangle = \frac{1}{R} - e^{-2D} \left(\frac{1}{R} + \frac{11}{8} + \frac{3R}{4} + \frac{R^2}{6} \right) \qquad (42)$$

Similarly we must compute H_{12}. The result will depend on an integral that cannot be computed analytically. For more details see the book by Pauling. The results are plotted below:



As before, the symmetric configuration leads to a stable bond, at

$$R_0 = 0.8 \text{ Å}$$

This compares well with the experimental value of 0.74 Å. The binding energy is

$$E_b = 3.14 \text{ eV}$$

and the experimental value is 4.72 eV. So, as before, the agreement is not great.

nce the bound state is symmetric, the spin part must be anti-symmetric; ie, it must be the singlet state. Since there is one singlet and 3 triplets, we e that when two H atoms interact, there is a 1/4 chance that they form a stable bond.