

Many-body systems - Interactions2-Body Problem, again

We begin our discussion of interacting many-particle systems by returning to the two-body problem, hydrogen. Write out the two-body Hamiltonian in the conventional manner:

$$\left\{ -\frac{\hbar^2}{2m_p} \nabla_p^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{|\vec{r}_p - \vec{r}_e|} \right\} \psi_\alpha(\vec{r}_p, \vec{r}_e) = E_\alpha \psi_\alpha(\vec{r}_p, \vec{r}_e)$$

where the p and e subscripts refer to proton and electron. Now, the potential term is a function only of the relative coordinates, so the motion of the c.m. should be conserved. Hence, we are tempted to write

$$\vec{R} = \frac{m_p \vec{r}_p + m_e \vec{r}_e}{m_p + m_e} \quad \vec{r} = \vec{r}_p - \vec{r}_e$$

so that the S.E. becomes

$$\left\{ -\frac{\hbar^2}{2(m_p + m_e)} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{r} \right\} \psi_\alpha = E_\alpha \psi_\alpha$$

where μ is the reduced mass. The wavefunction ψ_α can now be written as a product $\psi = \xi \phi$ with ϕ satisfying the usual S.E. and $\xi(R)$ satisfying

$$-\frac{\hbar^2}{2(m_p + m_e)} \nabla_R^2 \xi(R) = E^{cm} \xi(R)$$

$$\Rightarrow \xi(R) = e^{i\vec{k} \cdot \vec{R}} \quad ; \quad \hbar k = \sqrt{2(m_p + m_e) E^{cm}}$$

3-Body system - Helium atom (2-electrons)

The separation of the c.m. motion in the two body problem can be implemented in the 3-body one as well, assuming no external forces. However, this separation will not reduce the 3-body problem to a 1-body one as it did for hydrogen. We work through a series of approximations:

1st approx: No e^-e^- interaction:

We rewrite the total Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_{\text{He}}} \nabla_{\text{He}}^2 - \frac{\hbar^2}{2m_e} \nabla^{(1)2} - \frac{\hbar^2}{2m_e} \nabla^{(2)2} - \frac{2e^2}{r^{(1)}} - \frac{2e^2}{r^{(2)}} + \frac{e^2}{|\vec{r}^{(1)} - \vec{r}^{(2)}|}$$

Assume that this is small: i.e. centre coords. on He nucleus

by a) dropping the motion of the helium nucleus
b) neglecting the e^-e^- repulsion.
Then the problem just reduces to two 1-body problems and the energy becomes.

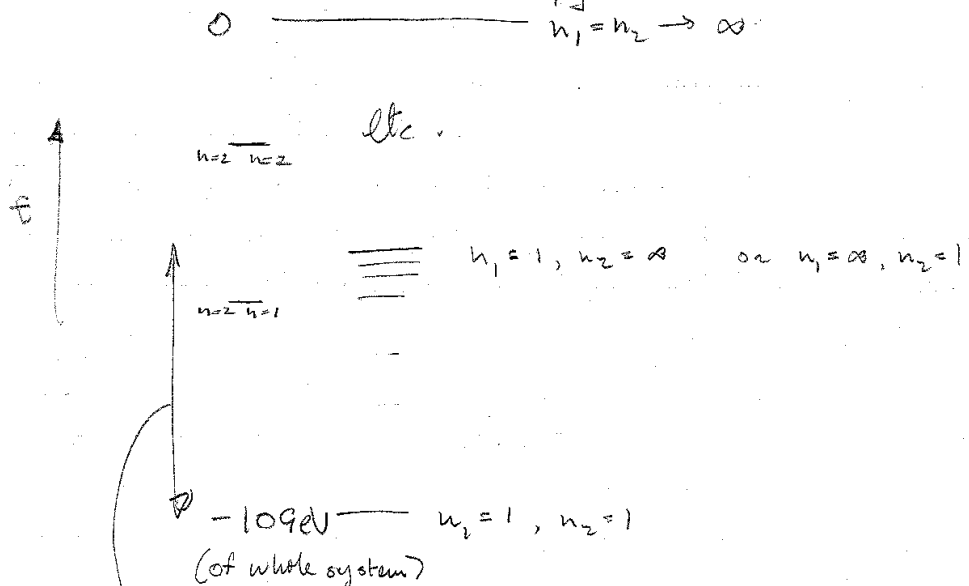
$$E_{n_1, n_2} = -\frac{2^2 (13.6 \text{ eV})}{n_1^2} - \frac{2^2 (13.6 \text{ eV})}{n_2^2}$$

$$= -54.4 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \quad n_1, n_2 = 1, 2, \dots$$

The wavefunction, of course is the usual Slater determinant

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{n_1}(1) & \psi_{n_1}(2) \\ \psi_{n_2}(1) & \psi_{n_2}(2) \end{vmatrix}$$

Next, we look at the energy levels:



This is the ionization energy to move 1 electron out to infinity. Clearly, it is calculated here to have a value of 54.4 eV . Experimentally, it is $\sim 24 \text{ eV}$.

So the system is overbound as calculated. Of course it is, we neglected $e-e$ repulsion!

2nd Approximation - 1st order perturbation theory

As a next attempt, we use the zeroth order wavefunctions from the previous calculation to calculate V_{11} , where the perturbing potential is $\frac{e^2}{|r^{(2)} - r^{(1)}|}$.

The zeroth order wavefunction is $\psi_{100}(r^{(2)})\psi_{100}(r^{(1)})$. The antisymmetrization has gone into the spin $\uparrow \downarrow$ n, l, m_l

$$\psi_{\text{Tot}} = \psi_{100}(r^{(1)}) \psi_{100}(r^{(2)}) \left(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2 \right)$$

$$\Rightarrow \Delta V_{11} = \int dr^{(1)} dr^{(2)} \psi_{100}^*(r^{(1)}) \psi_{100}^*(r^{(2)}) \frac{e^2}{|r^{(2)} - r^{(1)}|}$$

$$\psi_{100}(r^{(1)}) \psi_{100}(r^{(2)})$$

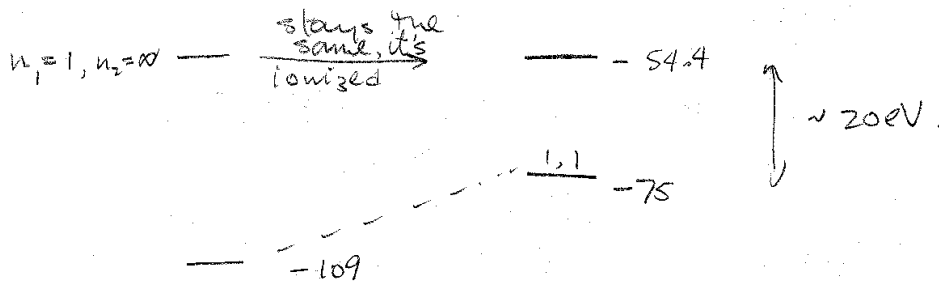
Evaluating with

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{a} \right)^{3/2} e^{-zr/a}$$

$$\begin{aligned} z &= \text{charge} \\ a &= \text{Bohr radius} \\ &= \frac{\hbar^2}{me^2} \end{aligned}$$

one finds (Weiden): $\Delta V_{11} = 34 \text{ eV}$.

Now, the ground state energy is shifted up by 34 eV to -75 eV.



This is in much better agreement with experiment ($\sim 24 \text{ eV}$). However, the fact that the shift was so large implies that using only 1st order perturbation theory is a little shaky. So try a further test.

3rd Approx - Variational Approach

Our problem is that we can write down

$$\hat{H} \psi_\alpha = E_\alpha \psi_\alpha$$

but we can't solve it. Suppose we made a guess for $\psi_{g.s.}$, which we call ψ_{trial} . What

would $\hat{H} \psi_{trial}$ yield? Well, it might not yield an eigenvalue equ. at all. How about

$$E_{trial} = \int \psi_{trial}^* \hat{H} \psi_{trial} d^3r \dots$$

This energy, E_{trial} , should be larger than E_α . If it were smaller, then ψ_{trial} would be a lower energy state than ψ_α , a contradiction. So what we could do is try a number of ψ 's [chosen wisely] and see how close to the ground state we can come. This method is called the variational approach and is generally useful for ground states.

Given the form of $\psi_{100} \psi_{100}$, let's try

$$\psi_{trial}(r^{(1)}, r^{(2)}) = \frac{\gamma^3}{\pi a^3} \exp\left(-\frac{\gamma}{a}(r^{(1)} + r^{(2)})\right) \quad \left(\gamma \text{ looks like an effective charge}\right)$$

$(a = \text{Bohr radius} = \hbar^2/m_e^2)$

where γ is treated as a variational parameter against which the energy is to be minimized. Then

$$E(\gamma) = \int d\vec{r}^{(1)} d\vec{r}^{(2)} \psi_{trial}^*(\vec{r}^{(1)}, \vec{r}^{(2)}) \left\{ -\frac{\hbar^2}{2m} \nabla^{(1)2} - \frac{\hbar^2}{2m} \nabla^{(2)2} - \frac{ze^2}{r^{(1)}} - \frac{ze^2}{r^{(2)}} + \frac{e^2}{|\vec{r}^{(1)} - \vec{r}^{(2)}|} \right\} \psi_{trial}(\vec{r}^{(1)}, \vec{r}^{(2)})$$

$$= \langle T_1 \rangle + \langle T_2 \rangle + \langle V_1 \rangle + \langle V_2 \rangle + \langle V_{12} \rangle$$

where $\langle \rangle$ is with respect to ψ_{trial} . These integrals give

$$\langle T_1 \rangle = \langle T_2 \rangle = -\gamma^2 E_0 \quad [E_0 = -13.6 \text{ eV}]$$

$$\langle V_1 \rangle = \langle V_2 \rangle = 4\gamma E_0$$

$$\langle V_{12} \rangle = -\frac{5}{4} \gamma E_0$$

Now, we minimize the energy with respect to γ :

$$\begin{aligned} 0 &= \frac{d}{d\gamma} E(\gamma) = \frac{d}{d\gamma} \left[-2\gamma^2 + 8\gamma - \frac{5}{4}\gamma \right] E_0 \\ &= -4\gamma + 8 - \frac{5}{4} = 0 \Rightarrow \gamma = \frac{32-5}{4 \times 4} = \frac{27}{16} \end{aligned}$$

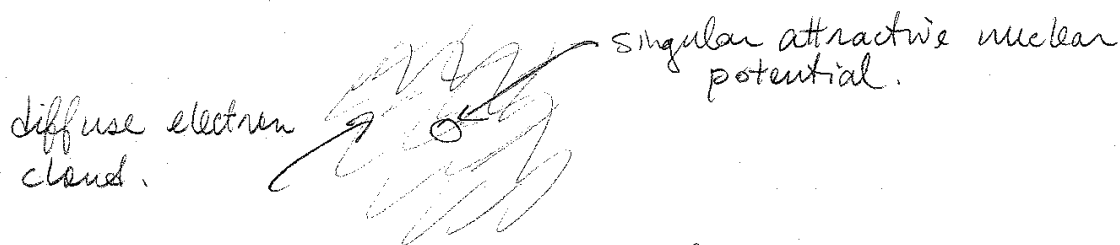
The corresponding energy is then

$$\begin{aligned} E\left(\gamma = \frac{27}{16}\right) &= \left[-2\left(\frac{27}{16}\right)^2 + \left(8 - \frac{5}{4}\right)\left(\frac{27}{16}\right) \right] (-13.6) \\ &= -76.6 \text{ eV} \end{aligned}$$

This result is even better than the perturbative approach. The real ground state energy is -78.6 eV . Of course, if we had not made such a good choice for ψ_{trial} , this method would not have been very useful!

Z - Electron Atoms

As we move to poly-electronic atoms from the simple helium atom - a 3-body system - the calculations rapidly become more complex. However, there are approximation techniques that can be used. Essentially, these techniques rely upon the fact that the deBroglie wavelength of the electron is comparable to the dimension of the system.



This allows the possibility that fluctuations in the electron density may not be so large - one may be able to use Gauss' law to construct an effective potential for the "screened" nuclear charge. There are two numerical methods that are frequently used

Thomas - Fermi Model: Based more on classical considerations; uses the Fermi energy as determined by the local density to produce an effective potential. Will not be considered further here.

$$E_F = \frac{\hbar^2}{2m} [3\pi^2 \rho]^{2/3}$$

Hartree - Fock (or Hartree - Fock - Slater) Method.
Defines a potential using wavefunctions then calculates until results are self-consistent.

Let's look at the Hartree-Fock method in more detail.
We start with the many electron Hamiltonian (again, neglecting the nuclear motion):

$$\hat{H} = \sum_{n=1}^N \left(-\frac{\hbar^2}{2m} \nabla^{(n)2} - \frac{Ze^2}{r^{(n)}} \right) + \frac{1}{2} \sum_l \sum_n \frac{e^2}{|r^{(l)} - r^{(n)}|}$$

and add and subtract a sum of single electron "effective potentials":

$$\hat{H} = \sum_{n=1}^N \left(-\frac{\hbar^2}{2m} \nabla^{(n)2} - \frac{Ze^2}{r^{(n)}} + \underline{V_{\text{eff}}^{(n)}}(r^{(n)}) \right)$$

These are supposed to represent the "screening" due to other electrons.

$$+ \left\{ \frac{1}{2} \sum_l \sum_n \frac{e^2}{|r^{(l)} - r^{(n)}|} - \sum_n \underline{V_{\text{eff}}^{(n)}}(r^{(n)}) \right\}$$

Now, if one can get a reasonably accurate V_{eff} , then the second term can be treated as a perturbation to the first. Hence, to lowest order we solve just

$$\hat{H} = \sum_{n=1}^N \left(-\frac{\hbar^2}{2m} \nabla^{(n)2} - \frac{Ze^2}{r^{(n)}} + \underline{V_{\text{eff}}^{(n)}}(r^{(n)}) \right)$$

Now, make the further approximation that this does not depend on n .

We then have a sequence of N decoupled, identical equations. Then, numerically integrate

$$\hat{H} \psi_i = \epsilon_i \psi_i$$

But what is V_{eff} ? As yet, we haven't gained very much. However, what we could do is proceed in an iterative fashion:

1. Solve for single electron u.f. with no V_{eff} , or with Thomas-Fermi V_{eff} .
- ↓
2. Calculate electron density from (assumes no correlations)
 e.g. $\rho(r) = e \sum_{i=1} |\psi_i|^2$ $i = \text{set of lowest occupied states.}$
- ↓
3. Calculate V_{eff} from $\rho(r)$ [through Gauss' law, or some other procedure].
- ↓
4. Calculate ψ_i 's corresponding to this V_{eff} .

The calculation is repeated until a self-consistent solution emerges. The critical step is 3, the calculation of the effective potential.

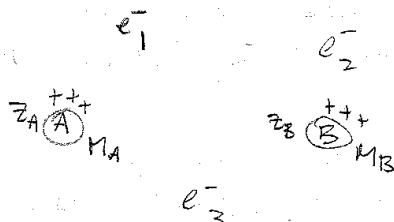
Hartree potential:
$$V_{\text{eff}} = e^2 \int \frac{dr' \rho(r')}{|r - r'|}$$
no e-e correlations from antisym.

Fock: included correlations, but result numerically unstable. looks like Fermi gas.

Slater: substituted for $V_{\text{eff}} = e^2 \int \frac{dr' \rho(r')}{|r - r'|} - \frac{3}{4} e^2 \left(\frac{3}{\pi} \rho(r) \right)^{1/3}$

Diatomic Systems

Diatomic systems are more complicated than polyelectronic atoms because of the presence of nuclear motion:



Now, our Hamiltonian looks like

$$\hat{H} = \left\{ -\frac{\hbar^2}{2M_A} \nabla^{(A)2} - \frac{\hbar^2}{2M_B} \nabla^{(B)2} \right\} + \left\{ \sum_{j=1}^{Z_A+Z_B} -\frac{\hbar^2}{2m_e} \nabla^{(j)2} \right\} + V_{\text{Tot}}(r^{(j)}, R^{(A)}, R^{(B)})$$

The total potential energy looks like:

$$V_{\text{Tot}} = \underbrace{\frac{Z_A Z_B e^2}{|R^{(A)} - R^{(B)}|}}_{\text{nuclear repulsion}} + \underbrace{\frac{1}{2} \sum_i \sum_j \frac{e^2}{|r^{(i)} - r^{(j)}|}}_{e^-e^- \text{ repulsion}} - e^2 \sum_i \left(\frac{Z_A}{|r^{(i)} - R^{(A)}|} + \frac{Z_B}{|r^{(i)} - R^{(B)}|} \right)$$

Now, if we work out the typical velocity scales of the problem, we find that the electronic motion is much faster than the nuclear motion, given an equivalent energy:

$$v = \sqrt{\frac{2E}{m}} \quad \therefore \frac{v_N}{v_e} \sim \sqrt{\frac{m_e}{2Z m_N}} \sim \frac{1}{60} \frac{1}{\sqrt{Z}}$$

equal # of protons & neutrons

- Born & Oppenheimer suggested (B-O Approx) that one simply decouple the nuclear motion from the electronic. That is, for the electronic motion regard $R = R^{(A)} - R^{(B)}$ as fixed in the potential. Then solve

$$\left\{ - \sum_j \frac{\hbar^2}{2m_e} \nabla_j^2 + V_{\text{TOT}}(r^{(j)}, R) \right\} \psi_R(r^{(j)}) = E_0(R) \psi_R(r^{(j)})$$

includes $\frac{e^2}{R}$

fixed. This is now the electronic wavefunction, with R treated like an externally fixed parameter.

The nuclear part of the wavefunction then separates out

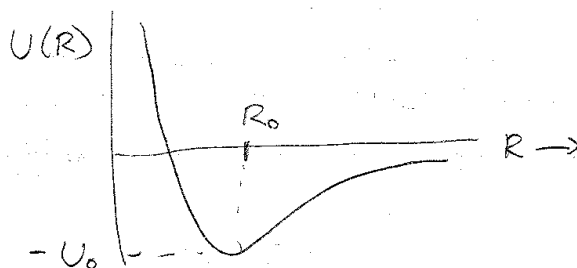
$$\psi_{\text{TOT}} = Q(R) \psi_R(r^{(j)}).$$

We will return to the electronic part later. Once we have solved for the ground state energy $E_0(R)$ electronically, we could vary R and find a family of $E_0(R)$'s. This E_0 term then looks like an internuclear potential in:

$$H_{\text{nuc}} = - \frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + E_0(R)$$

The general form of $E_0(R)$ looks like [Morse potential]

$$E_0(R) \equiv U(R) = -U_0 \left(1 - e^{-\frac{(R-R_0)}{a}} \right)^2 - U_0 \quad (U_0 > 0)$$



Now, we can take this two body problem and cast out the c.m. motion of the two nuclei, leaving

$$\left(-\frac{\hbar^2}{2\mu_{AB}} \nabla^2 + U(R) \right) \xi_v(R) = E_v \xi_v(R)$$

relate wavefunction, no c.m. motion.

$$\mu_{AB} = \frac{M_A M_B}{M_A + M_B}$$

Since $U(R)$ is a central potential, then ξ_v can be separated into $u_{v,k}(R) Y_{k,m_k}(\theta, \phi)$ as was done

in our earlier discussion of the 1-body problem. Hence

$$-\frac{\hbar^2}{2\mu_{AB}} \frac{d^2 u_{v,k}}{dR^2} + \left(U(R) + \frac{\hbar^2}{2\mu_{AB}} \frac{k(k+1)}{R^2} \right) u_{v,k} = E_{v,k} u_{v,k}$$

Now, suppose we expand $U(R)$ around $U(R_0) \equiv U_0$ (assuming the system is near the ground state).

$$U(R) = U_0 + \frac{1}{2} U_0'' (\Delta R)^2 + \dots \quad \Delta R = R - R_0$$

no linear term,
or U_0 wouldn't be a minimum.

The U_0'' term looks like a restoring force and leads to vibrations.

$$\begin{aligned} U''|_{R_0} &= \left(U_0 \cdot 2 \left(1 - e^{-\frac{\Delta R}{a}} \right) (-1) \left(-\frac{1}{a} \right) e^{-\frac{\Delta R}{a}} \right)' \Big|_{\Delta R=0} \\ &= \left(-\frac{2U_0}{a} e^{-\frac{\Delta R}{a}} \left(1 - e^{-\frac{\Delta R}{a}} \right) \right)' \Big|_{\Delta R=0} \\ &= \underbrace{\frac{2U_0}{a} \left(-\frac{1}{a} \right) e^{-\frac{\Delta R}{a}} \left(1 - e^{-\frac{\Delta R}{a}} \right)}_{0} + \frac{2U_0}{a} e^{-\frac{\Delta R}{a}} (-1) \left(-\frac{1}{a} \right) e^{-\frac{\Delta R}{a}} \\ &= 0 + \frac{2U_0}{a^2} \end{aligned}$$

— To first order, then, the vibrational energies look like:

$$E_v = (v + \frac{1}{2}) \omega \hbar \quad \omega = \sqrt{\frac{k}{\mu_{AB}}} = \left(\frac{2U_0}{a^2 \mu_{AB}} \right)^{1/2}$$

The rotational part can also be solved by expanding:

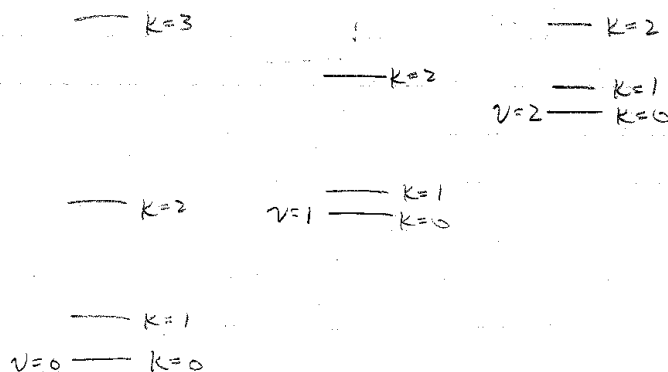
$$\frac{\hbar^2}{2\mu_{AB}} K(K+1) \frac{1}{(R_0 + \Delta R)^2} = \left(\frac{\hbar^2}{2\mu_{AB} R_0^2} \right) K(K+1) \left[1 - 2 \frac{\Delta R}{R_0} + 3 \left(\frac{\Delta R}{R_0} \right)^2 - \dots \right]$$

treat these as a perturbation

$$E_{v,K} = (v + \frac{1}{2}) \omega \hbar + \left(\frac{\hbar^2}{2\mu_{AB} R_0^2} \right) K(K+1)$$

moment of inertia of the molecule.

Hence, for the nuclear motion we have



Lastly, we return to the electronic part of the wavefunction. We rearrange the electronic part to read (this is for hydrogen molecule).

$$H = \underbrace{-\frac{\hbar^2}{2m} \nabla^{(1)2} - \frac{e^2}{|r^{(1)} - R^A|}}_{H_0^{(1,A)}} - \underbrace{\frac{\hbar^2}{2m} \nabla^{(2)2} - \frac{e^2}{|r^{(2)} - R^B|}}_{H_0^{(2,B)}} + \frac{e^2}{R} + \frac{e^2}{|r^{(1)} - r^{(2)}|} - \frac{e^2}{r^{(1)} - R^B} - \frac{e^2}{r^{(2)} - R^A}$$

The last part of the potential has terms which will tend to cancel. So it's tempting to take

$$\hat{H} = \hat{H}_0^{(1,A)} + \hat{H}_0^{(2,B)} + \lambda \hat{V}$$

perturbation.

$$\rightarrow \psi_0 = \psi_0^A(1) \psi_0^B(2)$$

hydrogen like.

However, the electrons are indistinguishable fermions. Hence

$$\psi_0^\pm = \psi_0^A(1) \psi_0^B(2) \pm \psi_0^B(1) \psi_0^A(2)$$

which sign to choose depends on the spin configuration. If $S=0$, then the spin w.f. is antisymmetric and the $+$ sign is chosen.

One can then use these wavefunctions as an unperturbed set to evaluate

$$\Delta E = \frac{\lambda \int (\psi_0^\pm)^* \hat{V} \psi_0^\pm d\vec{r}_1 d\vec{r}_2}{\int \psi_0^\pm^* \psi_0^\pm d\vec{r}_1 d\vec{r}_2}$$

For normalization. Remember the cross terms.

One finds
$$E^\pm = \frac{D \pm I}{1 \pm N}$$

Where $D = \lambda \int \hat{V} |\psi_0^A(1) \psi_0^B(2)|^2 d\vec{r}_1 d\vec{r}_2$

$I = \lambda \int \hat{V} \operatorname{Re}(\psi_0^A(1) \psi_0^B(2) \psi_0^A(2) \psi_0^B(1)) d\vec{r}_1 d\vec{r}_2$

$N = \operatorname{Re} \int \psi_0^{A*}(1) \psi_0^{B*}(2) \psi_0^A(2) \psi_0^B(1) d\vec{r}_1 d\vec{r}_2$

