

Variational Methods

The variational technique represents a completely different way of getting approximate energies and wave functions for quantum mechanical systems. It is most frequently used to compute the ground state, but can be extended to compute the low lying excited states. The technique involves guessing a reasonable, parametric form for a *trial* ground state wave function. An example of such a parametric form for a symmetric well ground state centered about the origin might be a Gaussian distribution (simple harmonic oscillator ground state) of the form:

$$\tilde{\psi}(x) = \left(\sqrt{\frac{a}{\pi}} \right)^{1/2} e^{-ax^2/2} \quad (1)$$

The adjustable parameter for this wave function is a which is related to the inverse of the width of the wave function. We will argue later, that choosing a trial wave function such as the harmonic oscillator ground state which is the exact solution for another potential is frequently a wise choice since it eliminates considerable drudge work. The harmonic oscillator ground state is often a good choice for one dimensional square wells, and the $\psi_{100}(\vec{r})$ hydrogen ground state is often a good choice for radially symmetric, 3-d problems.

The variational procedure involves adjusting all free parameters (in this case a) to minimize \tilde{E} where:

$$\tilde{E} = \langle \tilde{\psi} | H | \tilde{\psi} \rangle \quad (2)$$

As you can see \tilde{E} is sort of an expectation value of the actual Hamiltonian using the trial wave function. The minimum \tilde{E} is generally an excellent estimate of the true ground state energy, and parameter choice which minimizes \tilde{E} produces a trial wave function which sometimes reasonably approximates the true ground state wave function.

Why does it work?

Because of the completeness of bound state wave functions we can expand any function, including our trial wave function, as a linear combination of the true bound state wave functions which we'll write as $\psi_n(x)$, $n \in 1, 2, 3, \dots$. We thus know that our trial wave function can be written as:

$$\tilde{\psi} = \sum_n b_n \psi_n \quad (3)$$

where b_n are the relative amplitudes for the trial wave function. Since the ψ_n are bound state wave functions, they must be eigenstates of the Hamiltonian with eigenvalues given the the bound state energies or $H \psi_n = E_n \psi_n$. Let us evaluate \tilde{E} in terms of the b_n expansion coefficients.

$$\begin{aligned} \langle \tilde{E} \rangle &= \langle \tilde{\psi} | \check{H} | \tilde{\psi} \rangle = \langle \sum_m b_m \psi_m | \check{H} | \sum_n b_n \psi_n \rangle \\ &= \sum_m \sum_n b_m^* b_n E_n \langle \psi_m | \psi_n \rangle = \sum_n |b_n|^2 E_n \end{aligned} \quad (4)$$

where the last equality follows from the orthonormality of the bound state wave functions: $\langle \psi_m | \psi_n \rangle = 0$ unless $m = n$ in which case $\langle \psi_m | \psi_m \rangle = 1$.[†] Let us assume that there is a choice of parameter a which allows the the trial wave function to closely approach the actual wave function. As $\tilde{\psi} \rightarrow \psi_1$ it must be true that $b_n \rightarrow 0$ for all $n \neq 1$. In this limit Eq.(4) tells us that $\tilde{E} \rightarrow E_1$.

But how do we know that the trial wave function $\tilde{\psi}$ which provides the best estimate of E_1 is the one with the lowest value for \tilde{E} ? If we can show that $\tilde{E} \geq E_1$ for all trial wave wave functions, it becomes clear that the lowest possible \tilde{E} must represent the best guess for E_1 .

[†] Eq. (4) is also obvious from the measurement axiom since $|b_n|^2$ gives the probability of measuring E_n .

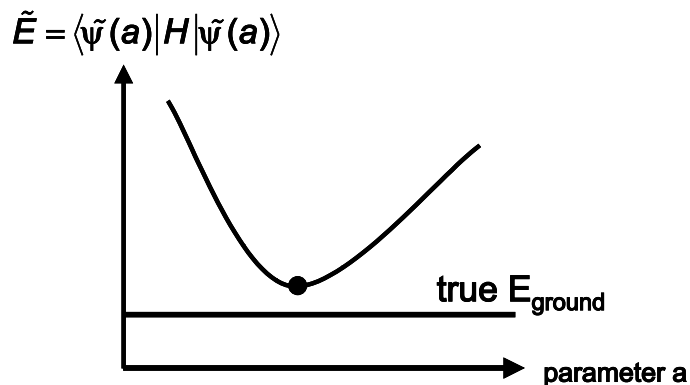
The proof of this inequality is quite simple. We note that for all n , $E_n \geq E_1$ since E_1 is the ground state or lowest energy state.

$$\tilde{E} = \sum_n |b_n|^2 E_n \geq \sum_n |b_n|^2 E_1 \geq \left(\sum_n |b_n|^2 \right) E_1 \geq E_1 \quad (5)$$

where the last inequality follows from condition that the trial wave function is normalized:

$$\left(\sum_n |b_n|^2 \right) = 1$$

Since the true energy is always lower than the \tilde{E} , the minimum \tilde{E} for all trial wave functions is clearly the best estimate.

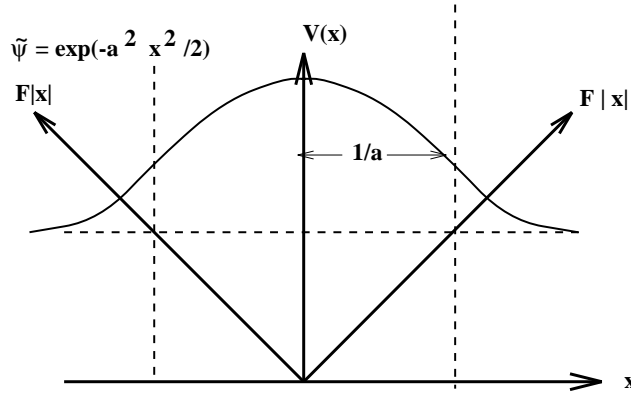


To the extent that the trial wave function is close to the wave function $\tilde{E} \rightarrow E_1$. All we can actually prove is that $\tilde{E} \geq E_1$ but experience shows that reasonable trial wave functions typically result in extremely close estimates to the ground state energy. Often even extremely crude trial wave functions give good ground state energy estimates.

Variational Technique Example

As an example of the variational technique, consider solving for the ground state of the double ramp well illustrated below using a the harmonic ground

state: $\psi_0 = \left(\sqrt{\frac{a}{\pi}}\right)^{1/2} \exp\left(-\frac{ax^2}{2}\right)$ where a is the adjustable parameter which is inversely related to the width of the wave function.



Our job is to evaluate $\langle H \rangle = \langle T \rangle + \langle V \rangle$. To evaluate $\langle V \rangle$ we will need integrals of the form $J_n = \int_0^{+\infty} dy y^n e^{-ay^2}$. These differ from our previous integrals that appear in the Bound States chapter since they involve odd powers of x and are integrated from $0 \rightarrow \infty$ rather than from $-\infty \rightarrow \infty$. We can get any "odd" integrals we need by starting with

$$J_1 = \frac{1}{2}a^{-1} \quad \text{and the recursion relation } J_{n+2} = -\frac{\partial J_n}{\partial a}$$

We begin with

$$\langle V \rangle = \langle F|x| \rangle = 2 \left(\sqrt{\frac{a}{\pi}}\right) \int_0^{\infty} dx F x \exp(-ax^2) = 2 \left(\sqrt{\frac{a}{\pi}}\right) F J_1 = \frac{F}{\sqrt{\pi}} a^{-1/2}$$

We next compute the $\langle T \rangle$. This can in principle be done by brute force

$$\langle T \rangle = \frac{\hbar^2}{2m} \left\langle \psi_0 \left| \frac{\partial^2}{\partial x^2} \right| \psi_0 \right\rangle$$

It is apparent, that $\langle T \rangle$ only involves derivatives and integrals of the trial wave function and thus can only depend on the shape parameter a and the mass of

the particle m and will thus be independent of the potential well. We can thus exploit the fact that ψ_0 is the ground state of a harmonic oscillator which allows us to compute the kinetic energy very easily by the virial theorem for a harmonic oscillator wave function: $\langle T \rangle = E_o/2 = \hbar\omega/4$. But what ω corresponds to our trial wave function a parameter? Fortunately this is easy since $a = m\omega/\hbar$ for the harmonic oscillator wave function. Hence

$$\langle T \rangle = \frac{\hbar\omega}{4} = \left(\frac{\hbar}{4}\right) \left(\frac{\hbar a}{m}\right) = \frac{\hbar^2 a}{4m}$$

We can now write the \tilde{E} for the trial wave function

$$\tilde{E} = \langle H \rangle = \frac{\hbar^2 a}{4m} + \frac{F}{\sqrt{\pi}} a^{-1/2}$$

The formation of a minimum \tilde{E} is very easy to understand. As a is increased, the $\tilde{\psi}_0$ becomes narrower and more peaked. Hence its double derivative or kinetic energy increases. At the same time, the narrowing of $\tilde{\psi}_0$ means that $\tilde{\psi}_0$ probes closer to the bottom of the well where the potential is lower. There is clearly a happy balance between lowering the kinetic energy at the expense of raising the potential.

Minimizing with respect to a we have:

$$\frac{\partial \tilde{E}}{\partial a} = \frac{\partial}{\partial a} \left\{ \frac{\hbar^2 a}{4m} + \frac{F}{\sqrt{\pi}} a^{-1/2} \right\} = 0 \rightarrow \frac{\hbar^2}{4m} = \frac{F}{2\sqrt{\pi}} a_*^{-3/2} \rightarrow a_* = \left(\frac{2mF}{\hbar^2 \sqrt{\pi}} \right)^{2/3}$$

Inserting a_* into our expression for \tilde{E} and performing some algebra we have:

$$\tilde{E} = \left(\frac{27}{16\pi} \right)^{1/3} \left(\frac{\hbar F}{\sqrt{m}} \right)^{2/3}$$

It would certainly be great to check our variational estimate for ground state energy against the true ground state energy. Unfortunately I don't know the exact

answer. We can get some confidence in the answer by comparing the inflection point of our $\tilde{\psi}_0$ solution to the classical turning point for the two ramp system. If we had the true solution, the inflection point would equal the turning point. Recall at the classical turning point $E = V$ and $\partial^2\psi/\partial x^2 = 0$. The inflection point of our trial wave function occurs at:

$$\begin{aligned} \frac{\partial^2}{\partial x^2} e^{-ax^2/2} &= (-a + a^2x^2) e^{-a^2x^2/2} = 0 \\ \rightarrow x_{\text{inflect}} &= \frac{1}{\sqrt{a}} = \left(\frac{\sqrt{\pi}\hbar^2}{2mF} \right)^{1/3} = 0.961 \left(\frac{\hbar^2}{mF} \right)^{1/3} \end{aligned} \quad (6)$$

Lets next compute the x coordinate of the classical turning point:

$$\begin{aligned} \tilde{E} &= \left(\frac{27}{16\pi} \right)^{1/3} \left(\frac{\hbar F}{\sqrt{m}} \right)^{2/3} = V = F x_{\text{turn}} \\ \text{or } x_{\text{turn}} &= \left(\frac{27}{16\pi} \right)^{1/3} \left(\frac{\hbar^2}{mF} \right)^{1/3} = 0.813 \left(\frac{\hbar^2}{mF} \right)^{1/3} \end{aligned}$$

Both the classical turning point and inflection point are in reasonable agreement. It would be very surprising if they were in perfect agreement since a Gaussian wave function is the correct ground state for an $V(x) = K x^2/2$ potential which goes to infinity much faster than the linear potential $V(x) = F|x|$ being considered here.

Just a quick review of the variational strategy. The best bet is to pick a trial wave function that that is the normalized, ground state of a physical system that solves a potential similar to that of the novel problem at hand. The virial theorem will then allow one to quickly write down the kinetic energy part of the Hamiltonian and avoid all of the work of taking the double derivative of $\tilde{\psi}$ and then integrating. One is left with doing a single integral over the new potential in order to set up \tilde{E} and the minimization can frequently be done analytically.

One could get better estimates of the true ground state by allowing for more adjustable parameters. For example in this problem, one could add in another ground state oscillator contribution, with another adjustable shape parameter and a third parameter that gives the relative contribution of each ground state oscillator wave function.

Perturbation versus Variation

Recall that the first order perturbation estimate of the energy when a “small” perturbation ΔV is added to a Hamiltonian with a known solution \check{H}_o is $E_n \approx E_n^0 + \langle n|\Delta V|n\rangle$ where $|n\rangle$ is the unperturbed state that satisfies $\check{H}_o|n\rangle = E_n^0|n\rangle$. We can cast this solution in a form that resembles the variational method:

$$\tilde{E}_n = \langle n|\check{H}|n\rangle = \langle n|\check{H}_o + \Delta V|n\rangle \quad (7)$$

Now since $\check{H}_o|n\rangle = E_n^0|n\rangle$ we have $\langle n|\check{H}_o|n\rangle = E_n^0$ we can write Eq. (7) in the form:

$$\tilde{E}_n = \langle \tilde{\psi}|\check{H}|\tilde{\psi}\rangle = \langle n|\check{H}|n\rangle = E_n^0 + \langle n|\Delta V|n\rangle \text{ where } \tilde{\psi} \equiv |n\rangle \quad (8)$$

The interpretation of Eq. (8) is that first order perturbation theory is equivalent to a variational estimate where the trial wave function is the solution to the unperturbed Hamiltonian. The usual case is we are trying to find the ground state using the variational technique and as discussed above, we always overestimate the true ground state energy. Eq. (8) then tells us that since first order perturbation theory is equivalent to a variational estimate, the first order perturbation theory calculation is always an *overestimate* of the true ground state energy. If we allow a shape parameter in $\tilde{\psi}$ instead of fixing it to $|n\rangle$ we should nearly always get closer to the true answer than the first order perturbative estimate.

Using $\psi_{100}(r)$ as the $\tilde{\psi}(r)$ in 3-d problems

Often trial wave function based on the hydrogen ground state wave function is a convenient choice in 3 dimensional problems with spherically symmetric

potentials.

$$\tilde{\psi}_{100}(r) = \frac{1}{\sqrt{\pi} a^3} \exp\left(-\frac{r}{a}\right) \quad (9)$$

In Eq. (9) we think of a as our adjustable parameter rather than setting $a = a_0$ for hydrogen or $a = a_0/Z$ for single electron ion. The main convenience of this form besides its simplicity is the ability to calculate the kinetic energy term $\langle \tilde{T} \rangle$. If we were to set $a = a_0$, to get the actual hydrogen solutions, we would have the following relationships between a_0 and the ground state energy E_1 :

$$a = \frac{\hbar}{\alpha mc} \quad , \quad E_1 = -\frac{1}{2}mc^2\alpha^2 \quad \text{where} \quad \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137} \quad (10)$$

We know that $\langle \tilde{T} \rangle$ can really only depend on a , m and \hbar since:

$$\langle T \rangle = \frac{\hbar^2}{2m} \left\langle \tilde{\psi} \left| \nabla^2 \right| \tilde{\psi} \right\rangle$$

and a is the only variable in $\tilde{\psi}_{100}$. Since $\langle E \rangle = -\langle T \rangle$ as we show shortly from the virial theorem, it follows that it must be possible to eliminate α and write \tilde{E} as a function of a , m and \hbar :

$$\alpha = \frac{\hbar}{amc} \quad , \quad \tilde{E} = -\frac{1}{2}mc^2\alpha^2 = -\frac{1}{2}mc^2 \left(\frac{\hbar}{amc} \right)^2 = -\frac{\hbar^2}{2ma^2} \quad (11)$$

Our trial wave function is a solution to the Coulomb potential and hence we can use the virial theorem to relate $\langle T \rangle$ to the total energy \tilde{E} . According to the radial version of the virial theorem $\langle T \rangle = \langle r \frac{dV}{dr} \rangle / 2$. For the case of a $1/r$ potential $\langle T \rangle = \langle r \frac{dV}{dr} \rangle / 2 = -\langle V \rangle / 2$. Hence $\langle T \rangle = -2 \langle T \rangle = \tilde{E}$ or $\langle T \rangle = -\tilde{E}$. Hence:

$$\langle T \rangle = -\tilde{E} = \frac{\hbar^2}{2ma^2} = \frac{\hbar^2}{2ma_0^2} \left(\frac{a_0}{a} \right)^2 = -E_1 \left(\frac{a_0}{a} \right)^2 \quad (12)$$

The last equality, which is particularly useful in atomic problems, follows from the observation that if $a = a_0$ then $\tilde{E} = E_1 = -13.6 \text{ eV}$. Another useful result

that we will need shortly also follows from the virial theorem.

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a} \quad (13)$$

This is based on the observation that:

$$\tilde{E} = -\frac{e^2}{4\pi\epsilon_o(2a)} \quad (14)$$

which you can obtain by manipulating the results in Eq. (10). You then use the virial theorem result $\langle V \rangle = -2\langle T \rangle$ and the potential expression for a hydrogen atom [$V = e^2/(4\pi\epsilon_o r)$] to obtain:

$$-\frac{e^2}{4\pi\epsilon_o(2a)} = \langle T \rangle + \langle V \rangle = -\frac{\langle V \rangle}{2} + \langle V \rangle = \frac{\langle V \rangle}{2} = \frac{1}{2} \left\langle \frac{e^2}{4\pi\epsilon_o r} \right\rangle \rightarrow \left\langle \frac{1}{r} \right\rangle = \frac{1}{a}$$

Again this will be true of any solution of the hydrogen ground state and will thus be true for our trial wave function. We are now very well set up to tackle helium.

The Helium Ground State

The problem of estimating the helium ground state energy is becoming a classic illustrative problem in the variational technique in quantum mechanics courses since one gets a value close to the experimental answer, and the problem can be done analytically - albeit using some clever tricks.

For the chemically challenged, helium has two electrons orbiting about a $Z = 2$ nucleus. The ground state energy is the total energy of these two electrons which is less than zero. We can measure this energy by measuring the minimum energy required to remove both electrons to leave a helium nucleus and two electrons at rest at infinity. Experimentally it takes 24.6 eV to remove one electron from a neutral He atom leaving singly ionized He^+ . Since He^+ is a single electron atom with $n = 1$ we can reliably compute its energy from the Bohr formula. The

ionization energy for the He^+ ion is then $Z^2 13.6 = 4 \times 13.6 = 54.4 \text{ eV}$. Hence it takes $54.4 + 24.6 = 79 \text{ eV}$ to remove both electrons. This means the experimental value for the He ground state is -79 eV .

The helium Hamiltonian is given by:

$$\check{H} = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \quad (15)$$

The factors of 2 come from the nuclear charge. You can easily spot the kinetic energy terms. The fact that there are 3 particles in the final state means that there is no obvious reduced mass so we work in the limit of an infinite mass nucleus. The last term represents the Coulomb repulsion energy between the two electrons.

In the absence of the $1/|\vec{r}_1 - \vec{r}_2|$ term, the two electron Hamiltonian is just $\check{H} = \check{H}_1 + \check{H}_2$, the ground wave function would be just the direct product:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{100}(r_1) \psi_{100}(r_2) \frac{\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2}{\sqrt{2}}$$

and the energy would just be $E = E_{(1)} + E_{(2)}$ where $E_{(1),(2)}$ are the energies of a single electron helium ion in the ground state or -54.4 eV for a total of -108.8 eV .[†] Since the true ground state energy of helium is -79 eV the electron-electron repulsion must be important.

Our approach will be to construct a trial, two electron wave function of the form: $\tilde{\Psi}(\vec{r}_1, \vec{r}_2) = \tilde{\psi}_{100}(r_1) \tilde{\psi}_{100}(r_2)$ where we use the floating a form given by Eq. (9). If we set $a = a_0/Z = a_0/2$ and use this to evaluate $\langle \tilde{\Psi} | \check{H}(r_1, r_2) | \tilde{\Psi} \rangle$ we will be effectively doing a first order perturbation calculation as described in the previous section.

[†] Since the two electrons are identical Fermions, we put the electrons in an antisymmetric spin state with $S = 0$.

If we vary a , to get the minimal \tilde{E} , we are pretty much guaranteed to get a more accurate answer since the \tilde{E} will be lower with an adjustable compared to a fixed a parameter and thus closer to the true value.

If we use $a = a_0/2$, we would estimate the ground state energy as:

$$E_g = 8E_1 + \frac{e^2}{4\pi\epsilon_0} \langle \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) \rangle = 8E_1 + \langle \Delta V \rangle \quad (16)$$

Although it is surprising how well this approach will work, we clearly seem to be in a regime where perturbation theory is unreliable given we know the correct result is -79 eV and the zero order answer is -108.8 eV.

Essentially the bulk of the drudge work is in the calculation of $\langle \tilde{\Psi} | \Delta V | \tilde{\Psi} \rangle$. We will pursue this calculation and then show how we can use the $\langle \tilde{\Psi} | \Delta V | \tilde{\Psi} \rangle$ in a true variational calculation where we put some adjustable parameters in Ψ .

Computing the ΔV integral

I would have guessed that this 6 dimensional integral is intractable like most integrals but it can actually be done using an elegant technique. The $\langle \Delta V \rangle$ integral is just $\langle \Delta V \rangle = [e^2/(4\pi\epsilon_0)] \langle |\vec{r}_1 - \vec{r}_2|^{-1} \rangle$. We can be fairly confident that $\langle |\vec{r}_1 - \vec{r}_2|^{-1} \rangle = \xi/a$ where ξ is a dimensionless number since a is the only length scale involved with our trial wave function. We will work out the integral in full detail, just to prove it can be done, but the integral is considerably beyond the skills of most undergraduates, graduates, or Professor's who aren't working in this branch of computational atomic physics. Our conclusion will be $\xi = 5/8$ but getting there is half the fun.

To compute $\langle |\vec{r}_1 - \vec{r}_2|^{-1} \rangle$ we write $|\vec{r}_1 - \vec{r}_2|^2$ in the spherical variables we will use for the integration.

$$|\vec{r}_1 - \vec{r}_2|^2 = (\vec{r}_1 - \vec{r}_2) \cdot (\vec{r}_1 - \vec{r}_2) = r_1^2 - 2\vec{r}_1 \cdot \vec{r}_2 + r_2^2 = r_1^2 - 2r_1 r_2 \cos \theta_{12} + r_2^2$$

where θ_{12} is the angle between \vec{r}_1 and \vec{r}_2 . We next insert the $\tilde{\psi}_{100}$ wave functions

$$\tilde{\psi}_{100} = \frac{1}{\sqrt{\pi} a^3} e^{-r/a}$$

$$\langle \Delta V \rangle = \frac{e^2}{4\pi\epsilon_o} \left(\frac{1}{a^6 \pi^2} \right) \int d^3r_1 d^3r_2 \frac{e^{-2r_1/a} e^{-2r_2/a}}{\sqrt{r_1^2 - 2r_1 r_2 \cos \theta_{12} + r_2^2}} = \frac{e^2}{4\pi\epsilon_o} \left(\frac{1}{a^6 \pi^2} \right) \mathcal{I}$$

We note that the ψ_{100} expression appears four times in the integral (twice in the bra and twice in the cket) hence some of the surprising numerical factors. We begin by partitioning the integral as an integral over r_1 and \vec{r}_2 .

$$\mathcal{I} = \int d^3r_1 e^{-2r_1/a} \mathcal{I}_2(\vec{r}_1) \quad , \quad \mathcal{I}_2(\vec{r}_1) = \int d^3r_2 \frac{e^{-2r_2/a}}{\sqrt{r_1^2 - 2r_1 r_2 \cos \theta_{12} + r_2^2}} \quad (17)$$

We note that the inner \mathcal{I}_2 integral will have a dependence on \vec{r}_1 and no dependence on \vec{r}_2 since that is being integrated over. Part of this dependence will come from the r_1 (1st electron radial coordinates) under the $\sqrt{\quad}$, the other piece looks like it will come from $\cos \theta_{12}$ piece. Now we introduce a famous trick. We have a double integral. The first integral involves varying \vec{r}_1 over all of its space. However in performing the inner integral, one is essentially varying \vec{r}_2 over all space *but* keeping \vec{r}_1 fixed. Now the trick is since \vec{r}_1 is fixed, why not use it to define \hat{z} direction during the evaluation of the \mathcal{I}_2 integral? If we do this, we can equate $\cos \theta_{12}$ with the $\cos \theta$ that describes \vec{r}_2 since if \vec{r}_1 is in the same direction as \hat{z} , θ_{12} will be the usual angle of \vec{r}_2 with respect to the z axis. We then have:

$$\mathcal{I}_2(\vec{r}_1) = \int_0^\infty r^2 dr e^{-2r/a} \int_{-1}^1 \frac{d \cos \theta}{\sqrt{r_1^2 - 2r_1 r \cos \theta + r^2}} \int_0^{2\pi} d\phi \quad (18)$$

The ϕ integral is just 2π . The θ integral is very easy. Just substitute $v = r_1^2 + r^2 - 2rr_1 \cos \theta$. Then $d \cos \theta = dv/(-2rr_1)$ and the limits become $v_1 = r_1^2 + r^2 - 2rr_1 = (r_1 - r)^2$ and $v_2 = r_1^2 + r^2 + 2rr_1 = (r_1 + r)^2$

$$\begin{aligned}\mathcal{I}_\theta &= \int_{-1}^1 \frac{d \cos \theta}{\sqrt{r_1^2 - 2r_1 r \cos \theta + r^2}} \rightarrow \frac{-1}{2rr_1} \int_{v_1}^{v_2} v^{-1/2} dv \\ &= \frac{-1}{rr_1} (\sqrt{v_1} - \sqrt{v_2}) = \frac{(r_1 + r) - |r_1 - r|}{rr_1} = \begin{cases} 2/r_1 & \text{if } r < r_1 \\ 2/r & \text{if } r > r_1 \end{cases}\end{aligned}$$

The last equality is sort of interesting and follows from $|r_1 - r|$ is either $r_1 - r$ or $r - r_1$ depending on the magnitude of r versus r_1 . The conditional is easy to insert by breaking up Eqn. (18) into 2 pieces:

$$\mathcal{I}_2(\vec{r}_1) = 4\pi \left(\int_0^{r_1} r^2 dr \frac{e^{-2r/a}}{r_1} + \int_{r_1}^{\infty} r^2 dr \frac{e^{-2r/a}}{r} \right) = \frac{\pi a_o^3}{r_1} \left[1 - \left(1 + \frac{r_1}{a} \right) e^{-2r_1/a} \right]$$

The exponential integrals can be found in any integral table. We can now insert $\mathcal{I}_2(r_1)$ into Eqn. (17).

$$\mathcal{I} = \int d^3 r_1 e^{-2r_1/a} \mathcal{I}_2(r_1) = 4\pi^2 a^3 \int_0^{\infty} r_1^2 dr_1 e^{-2r_1/a} \frac{1}{r_1} \left[1 - \left(1 + \frac{r_1}{a} \right) e^{-2r_1/a} \right]$$

Since \mathcal{I} integrand has no angular dependence, the angular pieces integrate to 4π . The remaining r_1 integral is very easy using $\int_0^{\infty} dy y^n \exp(-by) = n!/b^{n+1}$ to get:

$$\mathcal{I} = 4\pi^2 a^3 \frac{5a^2}{32} = \text{or } \langle \Delta V \rangle = \frac{e^2}{4\pi\epsilon_o} \left(\frac{1}{a^6 \pi^2} \right) \times 4\pi^2 a^3 \frac{5a^2}{32} = \frac{5}{8a} \left(\frac{e^2}{4\pi\epsilon_o} \right)$$

$$\langle \Delta V \rangle = -\frac{5}{4} \left(-\frac{e^2}{4\pi\epsilon_o (2a)} \right) = -\frac{5}{4} \left(-\frac{e^2}{4\pi\epsilon_o (2a_0)} \right) \left(\frac{a_0}{a} \right)$$

$$\text{Thus } \langle \Delta V \rangle = -\frac{5}{4} E_1 \left(\frac{a_0}{a} \right) \quad (19)$$

If we insert $a = a_0/2$ we get $\langle \Delta V \rangle = -5E_1/2 = +34 eV$. We estimate from the forgoing that the helium ground state energy is $E_g < -108.8 + 34 = -74.8 eV$.

We are thus much closer to the true answer of -79 eV which is remarkable given either the size of the perturbation or the fact that we used a very naive wave function which ignores the electron-electron repulsion.

Improving our Bound

We can do better by allowing a to vary. I find it more instructive to write $a = a_0/Z$ and allow $Z = Z_{\text{effective}}$ to be the adjustable parameter. This is a nice approach since we can think of the Coulomb repulsion of the other electron, as creating a “shielded” nuclear charge for a given electron. As such we might expect an effective nuclear charge of $Z < 2$ and which will place the electrons further away that we were assuming before with our $Z = 2$ Bohr wave functions.

Our goal is to compute \tilde{E} from Eqn(15) which gives the true helium Hamiltonian:

$$\tilde{E} = \langle \Psi | \tilde{T}_1 + \tilde{T}_2 | \Psi \rangle - \frac{e^2}{4\pi\epsilon_0} \left(2 \left\langle \Psi \left| \frac{1}{r_1} + \frac{1}{r_2} \right| \Psi \right\rangle - \left\langle \Psi \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi \right\rangle \right) \quad (20)$$

$$\text{where } \tilde{T}_{1,2} = -\frac{\hbar^2}{2m} \nabla_{1,2}^2$$

You will recognize the last term as $\langle \Delta V \rangle$ which we computed in the previous section in Eq. (19):

$$\langle \Delta V \rangle = -\frac{5}{4} \left(\frac{a_0}{a} \right) E_1 = -\frac{5Z}{4} E_1 \quad (21)$$

We next compute one of the kinetic energy terms:

$$\langle \Psi(\vec{r}_1, \vec{r}_2) | \tilde{T}_1 | \Psi(\vec{r}_1, \vec{r}_2) \rangle = \langle \psi_{100}(\vec{r}_1) | \tilde{T}_1 | \psi_{100}(\vec{r}_1) \rangle \langle \psi_{100}(\vec{r}_2) | \psi_{100}(\vec{r}_2) \rangle = \langle \psi_{100}(\vec{r}) | \tilde{T} | \psi_{100}(\vec{r}) \rangle$$

$$\langle T_1 \rangle = \frac{\hbar^2}{2ma^2} = Z^2 \frac{\hbar^2}{2ma_0^2} = -Z^2 E_1$$

$$\langle T_1 + T_2 \rangle = 2\langle T_1 \rangle = -2 Z^2 E_1 \quad (22)$$

where we have used Eq. (11) to equate E_1 with $-\hbar^2/(2ma_0^2)$ and the fact that the two electrons are indistinguishable to conclude $\langle T_1 \rangle = \langle T_2 \rangle$.

The same reasoning tells us $\langle 1/r_1 \rangle = \langle 1/r_2 \rangle$. Using Eq. (13) we have $\langle 1/r_1 \rangle = \langle 1/r_2 \rangle = 1/a = Z/a_0$. Hence the second term of Eq. (20) representing the attraction of the two electrons to the nucleus is:

$$-\frac{e^2}{4\pi\epsilon_0} \left(2 \left\langle \Psi \left| \frac{1}{r_1} + \frac{1}{r_2} \right| \Psi \right\rangle \right) = -4Z \frac{e^2}{4\pi\epsilon_0 a_0} = 8ZE_1 \quad (23)$$

Assembling Eq. (21) - Eq. (23), we have:

$$\tilde{E} = -2Z^2 E_1 + 8ZE_1 - \frac{5Z}{4} E_1 = \left(-2Z^2 + \frac{27}{4} Z \right) E_1$$

We thus obtain a classic concave up parabola (remember E_1 is negative) with a minimum at $d\tilde{E}/dZ = (-4Z + 27/4)E_1 = 0$ or $Z = 27/16 = 1.69$ or $\tilde{E}_{\min} = (3^6/2^7)E_1 = -77.5 \text{ eV}$ which is getting pretty close to the experimental value of -79 eV . Our first order calculation where we set $Z = 2$ placed us 4.2 eV above the true value. By allowing Z to be an adjustable parameter in a variational calculation, we are now only 1.5 eV above the experimental value. We have thus shrunk the gap between calculation and observation by a factor of 2.8 with very little additional work.

The Z value is quite sensible as well. Without the additional electron, a given electron would see $Z = 2$. If the additional electron provided perfect shielding we would have $Z = 1$. A value of $Z = 1.69$ seems quite reasonable.

Although this problem is solveable analytically, it would not be that difficult to perform even the 6 dimensional $\langle \Delta V \rangle$ integral on a computer by summation. Essentially we know that $\langle |\vec{r}_1 - \vec{r}_1|^{-1} \rangle$ which is the essence of the $\langle \Delta V \rangle$ calculation must be of the form $\langle |\vec{r}_1 - \vec{r}_1|^{-1} \rangle = \xi/a$ where ξ is a numerical constant since a is the only thing in our $\tilde{\Psi}$ that carries dimensions of length. All of the clever analytic integration did was to establish that $\xi = 5/8$. It is likely to be simpler and faster to write such a program to do the calculation numerically from the get go. But there is a sense of accomplishment in doing the seemingly

impossible analytic calculation. I do hope you find you are able to follow the basic QM that we used in this example.


The H_2^+ Molecule

In this section we summarize a variational calculation on the binding energy H_2^+ where an electron “orbits” about two protons to form the simplest molecule. This was one of the earliest attempts to understand the nature of a covalent bond performed within a few years after the development of the Schrödinger Equation. I will leave out many of the mathematical details which are discussed in **Griffiths** and other quantum mechanics books such as **Quantum Mechanics by Goswami** and **Quantum Physics by Gasiorowicz**. We are describing a “covalent” bond. There are also ionic bonds in chemistry.


This calculation is concerned with whether or not the H_2^+ molecule will even exist. How does the “orbiting” electron’s attraction to either proton, overcome the Coulomb repulsion between the two protons to form a bound state *i.e.* a state with negative energy? Actually the existence of a negative energy state is really not enough by itself since the molecular configuration must be energetically favored over a final state consisting of a hydrogen atom plus a free proton. This means the system must have a total energy of less than E_1 or -13.6 eV. It is really not all that obvious *a priori* that the H_2^+ ion should exist. For example in the upper part of the below figure we placed the electron half way between the two protons which are separated by $2a_0$. Adding the potential energies we find a net potential energy of $3E_1 = -40.8$ eV which is considerably smaller than $E_1 = -13.6$ eV suggesting that this configuration lies considerably lower in energy than a hydrogen atom with an additional proton infinitely far away and at rest. Of course we need to worry about the fact that the electron has a kinetic energy which will raise its energy, perhaps by $\langle T \rangle = -E_1$. It is still plausible that if the electron were often between the two protons as shown, the hydrogen molecule might bind even when kinetic energy is considered.

Of course, the electron cannot be precisely located between the two protons

but is described by a probability function that extends over all space.



$$E = -\frac{e^2}{4\pi\epsilon_0 a_0} - \frac{e^2}{4\pi\epsilon_0 a_0} + \frac{e^2}{4\pi\epsilon_0 (2a_0)} = 3E_1$$



$$E = +\frac{e^2}{4\pi\epsilon_0 a_0} - \frac{e^2}{4\pi\epsilon_0 a_0} - \frac{e^2}{4\pi\epsilon_0 (2a_0)} = E_1$$

For example the electron could easily be in the position shown in the lower half of the above figure. In this position the sum of the potential energies is just E_1 which is the same energy as single hydrogen atom with a distant proton at rest. When kinetic energy is taken into account the electron would bind into a hydrogen atom rather than forming a molecule with the two protons in this case. To really know if the H_2^+ molecule exists we need a legitimate quantum mechanical calculation which we will base on a variational approach.

Here is the essence of our variational approach. We will place the two protons a distance R apart and assume they are “nailed” down at these positions. This will give a positive proton-proton repulsion contribution of

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0 R} = \frac{-2a_0}{R} \frac{-e^2}{4\pi\epsilon_0 2a_0} = -\frac{2a_0}{R} E_1$$

to the total binding energy.[†] The electron will then have a Hamiltonian given

[†] It also seems by nailing down the protons we are ignoring their own quantum physics such as the fact that need to move about to conform to the uncertainty principle. My guess (as a non-expert) is this sort of kinetic energy $\langle p^2/2M \rangle$ may be may be ignorable owing to the large proton mass.

by

$$\check{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_o}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (24)$$

where r_1 and r_2 are shorthands for $r_1 = |\vec{r} - \vec{R}_1|$ and $r_2 = |\vec{r} - \vec{R}_2|$, \vec{r} is the coordinate of the electron where \vec{R}_1 , and \vec{R}_2 are the positions of the two protons and $R = |\vec{R}_2 - \vec{R}_1|$. Our approach will be to use a trial wave function (Ψ), compute $\tilde{E} = \langle \Psi | \check{H} | \Psi \rangle + V_{pp}$ and vary R looking for the minimum of \tilde{E} . If we agree with the fixed R assumption, the true energy will lie below \tilde{E} hence if $\tilde{E} < -13.6 \text{ eV}$ the molecule will form.

We will use a linear combination of the atomic orbits (known LCAO) as our trial wave function based on the hydrogen ground state. Specifically we will use:

$$\Psi(\vec{r}) = \mathcal{N} \left(\psi_{100}(|\vec{r} - \vec{R}_1|) + \psi_{100}(|\vec{r} - \vec{R}_2|) \right) = \mathcal{N} (\psi(r_1) + \psi(r_2))$$

This Ψ is again motivated for mathematical convenience and physical intuition. We are saying the electron has an equal probability of being in a ground state hydrogen centered about either proton in the molecule. These wave functions satisfy the Schrödinger equation of a very similar Hamiltonian which cuts down on the mathematical drudgery. The factor \mathcal{N} reflects the fact that we have a non-trivial normalization. Now it is apparent from symmetry that we want an equal probability for being attached to either proton but we could also achieve this with any arbitrary unimodular phase: $\Psi = \mathcal{N} (\psi(r_1) + \exp(i\delta)\psi(r_2))$.

Actually the only two possible choices are $\exp(i\delta) = \pm 1$ because the Hamiltonian has $r_1 \leftrightarrow r_2$ symmetry which we will define in terms of a symmetry operator: $\check{\chi}\psi(r_1, r_2) = \psi(r_2, r_1)$. This suggests that the wave function can be chosen to be a simultaneous eigenfunction of $\check{\chi}$ and \check{x} . Writing the eigenvalue of $\check{\chi}$ as λ we have: $\check{\chi}^2\psi(r_1, r_2) = \psi(r_1, r_2) = \lambda^2\psi(r_1, r_2)$ which implies $\lambda^2 = 1$ or $\lambda = \pm 1$. This

means

$$\tilde{\chi} (\psi(r_1) + \exp(i\delta)\psi(r_2)) = (\psi(r_2) + \exp(i\delta)\psi(r_1)) = \pm (\psi(r_1) + \exp(i\delta)\psi(r_2))$$

Solving this we see the only two phase choices are $\exp(i\delta) = \pm 1$. It turns out that our initial phase choice ($\delta = 0$) gives the best bound. You will explore the other choice ($\delta = \pi$) in the exercises.

Lets begin with the normalization

$$\mathcal{N}^2 \langle \psi(r_1) + \psi(r_2) | \psi(r_1) + \psi(r_2) \rangle = 1 = \mathcal{N}^2 (2 + 2 \langle \psi(r_1) | \psi(r_2) \rangle)$$

We use the fact that

$$\langle \psi(r_1) | \psi(r_1) \rangle = \langle \psi(r_2) | \psi(r_2) \rangle = 1, \quad \langle \psi(r_1) | \psi(r_2) \rangle = \langle \psi(r_2) | \psi(r_1) \rangle$$

The first relation follows for the atomic orbital normalization. The second follows from the fact that the wave functions are real. We often call $\langle \psi(r_1) | \psi(r_2) \rangle \equiv I$ the “overlap” integral. One form for this, where we put one proton at the origin and the other on the \hat{z} axis, would be:

$$I = \frac{1}{\pi a_o^3} \int d^3r \exp\left(-\frac{r}{a_o}\right) \times \exp\left(-\frac{|\vec{r} - R\hat{z}|}{a_o}\right)$$

Clearly the overlap integral I can only depend on R and a_o and in fact only depends on the ratio $\xi = R/a_o$. One can show (although its not trivial) that:

$$I = \exp(-\xi) \left(1 + \xi + \frac{\xi^2}{3}\right) \quad \text{and} \quad \mathcal{N} = \frac{1}{\sqrt{2(1+I)}} \quad (25)$$

We can now proceed to construct \tilde{E} using the Hamiltonian given by Eqn. (24). However, our wave function is constructed from hydrogen wave functions

which are eigenfunctions of pieces of the Hamiltonian. Hence for example:

$$\check{H}\psi(r_1) = \left\{ -\frac{\hbar^2}{2m}\nabla^2\psi(r_1) - \frac{e^2}{4\pi\epsilon_o}\frac{1}{r_1}\psi(r_1) \right\} - \frac{e^2}{4\pi\epsilon_o}\frac{1}{r_2}\psi(r_1)$$

The piece of the Hamiltonian within the $\{\}$ is the Hamiltonian for a hydrogen atom displaced by \vec{R}_1 acting on a similarly displaced $\psi_{100}(\vec{r} - \vec{R}_1)$. It will thus return the usual energy $E_1\psi(r_1)$. Hence:

$$\check{H}\psi(r_1) = E_1\psi(r_1) - \frac{e^2}{4\pi\epsilon_o}\frac{1}{r_2}\psi(r_1) \text{ and similarly } \check{H}\psi(r_2) = E_1\psi(r_2) - \frac{e^2}{4\pi\epsilon_o}\frac{1}{r_1}\psi(r_2)$$

Thus $\check{H}\Psi = \mathcal{N}\check{H}[\psi(r_1) + \psi(r_2)]$ or:

$$\check{H}\Psi = E_1\Psi - \mathcal{N}\frac{e^2}{4\pi\epsilon_o}\left(\frac{1}{r_2}\psi(r_1) + \frac{1}{r_1}\psi(r_2)\right)$$

Hence:

$$\tilde{E} = \langle \Psi | \check{H} | \Psi \rangle = E_1 \langle \Psi | \Psi \rangle$$

$$-\mathcal{N}^2\frac{e^2}{4\pi\epsilon_o}\left(\left\langle \psi(r_1) + \psi(r_2) \left| \frac{1}{r_2} \right| \psi(r_1) \right\rangle + \left\langle \psi(r_1) + \psi(r_2) \left| \frac{1}{r_1} \right| \psi(r_2) \right\rangle\right)$$

Taking advantage of some $r_1 \leftrightarrow r_2$ symmetries:

$$\tilde{E} = E_1 - 2\mathcal{N}^2\frac{e^2}{4\pi\epsilon_o}\left(\left\langle \psi(r_1) \left| \frac{1}{r_2} \right| \psi(r_1) \right\rangle + \left\langle \psi(r_1) \left| \frac{1}{r_1} \right| \psi(r_2) \right\rangle\right)$$

$$\tilde{E} = E_1 - 4\mathcal{N}^2\frac{e^2}{4\pi\epsilon_o 2a_o}\left(\left\langle \psi(r_1) \left| \frac{a_o}{r_2} \right| \psi(r_1) \right\rangle + \left\langle \psi(r_1) \left| \frac{a_o}{r_1} \right| \psi(r_2) \right\rangle\right)$$

$$\tilde{E} = E_1 + 4E_1\mathcal{N}^2(D+X) \text{ where } D = \left\langle \psi(r_1) \left| \frac{a_o}{r_2} \right| \psi(r_1) \right\rangle \text{ and } X = \left\langle \psi(r_1) \left| \frac{a_o}{r_1} \right| \psi(r_2) \right\rangle$$

where D and X are dimensionless positive integrals which can be worked out

analytically but are non-trivial:

$$D = \frac{1}{\xi} - \left(1 + \frac{1}{\xi}\right) e^{-2\xi} \quad , \quad X = (1 + \xi)e^{-\xi} \quad \text{where } \xi = R/a_o \quad (26)$$

We note that the two integrals X , I that are based on $\langle \psi(r_1) |$ anything $|\psi(r_2) \rangle$ fall off as $\exp(-R/a_o)$ as $\xi \rightarrow \infty$ as one might expect since the Bohr ground state wave functions fall off exponentially as R/a_o . We can take $D(\xi)$ to the $R = |\vec{R}| \rightarrow \infty$ by realizing $\vec{r}_2 - \vec{r}_1 = \vec{R}$ thus $\vec{r}_2 = \vec{r}_1 + \vec{R} \rightarrow \vec{R}$ and

$$D = \left\langle \psi(r_1) \left| \frac{a_o}{r_2} \right| \psi(r_1) \right\rangle \rightarrow \left\langle \psi(r_1) \left| \frac{a_o}{R} \right| \psi(r_1) \right\rangle = \frac{a_o}{R} = \frac{1}{\xi}$$

which is borne out by Eq. (26).

Another check is to go to the opposite limit where $\xi \rightarrow 0$ or $R \rightarrow 0$. In this limit $r_2 \rightarrow r_1$. Hence

$$I(\xi) \rightarrow \langle \psi(r) | \psi(r) \rangle = 1 \quad ; \quad D(\xi) \rightarrow I(\xi) \rightarrow \left\langle \psi(r) \left| \frac{a_o}{r} \right| \psi(r) \right\rangle = a_o \left\langle \frac{1}{r} \right\rangle = 1$$

where we use the result from Eq. (13) that $\langle r^{-1} \rangle = a_0^{-1}$. Indeed the forms for all three functions Eq. (25) and Eq. (26) approach 1 as $\xi \rightarrow 0$, although one must take some care in taking $D(\xi)$ to this limit.

Including the V_{pp} term, and inserting our expression for \mathcal{N}^2 in terms of third non-trivial integral (I) we have our total energy \mathcal{E}

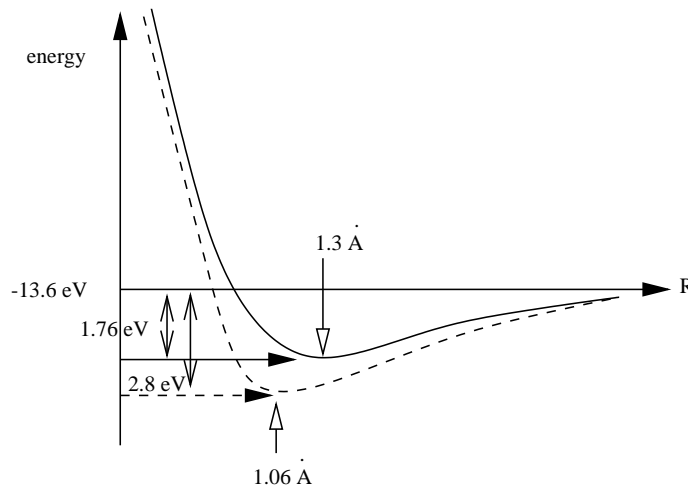
$$\mathcal{E} = \tilde{E} + V_{pp} = -\frac{2}{\xi}E_1 + E_1 + 2E_1 \frac{D + X}{1 + I}$$

Collecting the expressions for the D , X , I integrals we have:

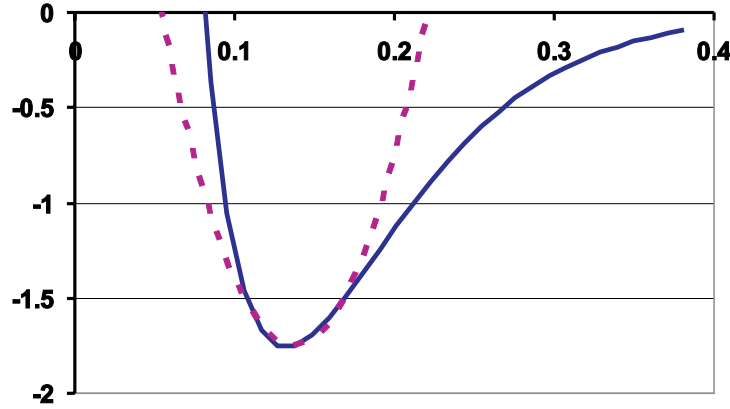
$$f(\xi) = \frac{\mathcal{E}}{-E_1} = -1 + \frac{2}{\xi} \left(\frac{(1 - (2/3)\xi^2) e^{-\xi} + (1 + \xi) e^{-2\xi}}{1 + (1 + \xi + (1/3)\xi^2) e^{-\xi}} \right)$$

As $\xi \rightarrow \infty$ all three integrals D , X , I vanish as does V_{pp} and $\mathcal{E} \rightarrow E_1$. This makes perfect sense since as $R \rightarrow \infty$ we are essentially left with a superposition

of a hydrogen atoms and a free proton. As $R \rightarrow 0$ the V_{pp} term dominates and $\mathcal{E} \rightarrow +\infty$. But between these two extremes we have $\mathcal{E} < E_1$ with a minimum near $\mathcal{E} = -13.6 - \underline{1.76} \text{ eV}$. The 1.76 eV would be our bound on the molecular binding energy for the H^+ ion. Because this is a variational calculation we know this ion is more tightly bound and in fact has a binding energy of 2.8 eV implying an actual energy lower than \mathcal{E} . Our estimate was not a great estimate of the binding energy, indicating our trial wave function wasn't that realistic. Our minimizing R is at 1.27 \AA whereas experimentally the number is closer to 1.06 \AA . We could do much better by putting some adjustability in our trial wave functions. But at least its plausible that molecules will form as stable entities. Given we are constructed from molecules its good we proved the simplest one exists! Here is a crude sketch of ours and a much more sophisticated molecular calculation that agrees with the experimental values.



In the exercises I ask you to consider binding of an alternative trial wave function $\Psi = \mathcal{N}(\psi_{100}(r_1) - \psi_{100}(r_2))$ where the normalization is different. I think you will find that this wave function will not bind. I think the reason is that with this relative phase, the trial wave function vanishes on the plane where $r_1 = r_2$ and therefore cannot take advantage of the large binding contribution near this plane. These are called “anti-bonding” orbitals and play an important role in understanding molecular dynamics in chemical processes.



Although we know our variational calculation is not terribly accurate it does resemble more accurate calculations of the binding energy versus the atomic separation R . At some risk, I have crudely represented the energy near the minimum by the dashed parabola shown above to find an effective spring constant of $k = 500 \text{ eV/nm}^2$ where the parabola is given by $\tilde{E} = kx^2/2 - E_{\min}$. We can roughly think of the two protons as interacting through the approximate 1 dimensional simple harmonic oscillator Hamiltonian of the form

$$\check{H} = \frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

where $x = x_1 - x_2$ is a relative coordinate and $\omega = \sqrt{k/\mu}$ where $\mu = M/2$ is the reduced mass for two protons. We thus expect a set of vibrational molecular levels separated by energies of $\Delta E = \hbar\omega$ or

$$\Delta E = \hbar c \sqrt{\frac{2k}{Mc^2}} = 197 \text{ eV nm} \sqrt{\frac{2 \times 500 \text{ eV/nm}^2}{940 \times 10^6 \text{ eV}}} = 0.203 \text{ eV}$$

where we used $940 \times 10^6 \text{ eV}$ as Mc^2 for a proton. Indeed one does typically get a series of roughly evenly spaced infrared absorption and emission lines at energies on the order of a few hundredths to a few tenths of an electron volt due

to molecular vibrations. Typically, as in this case, the level spacing will get smaller for the more highly excited states since the well is only approximately parabolic.

Another feature of molecular absorption or emission spectra are rotational excitations. We can think of the H_2 molecule as a rigid rotator with a moment of inertia given by μR^2 that can be in various L^2 states. The kinetic energy will then be of the form:

$$E_\ell = \frac{\ell(\ell+1)\hbar^2}{2\mu R^2} = \ell(1+\ell) \frac{(197 \text{ eV nm})^2}{2 \frac{1}{2}(940 \times 10^6 \text{ eV}) (0.13 \text{ nm})^2} = \ell(\ell+1) 2.4 \times 10^{-3} \text{ eV}$$

where we have used the minimum of our admittedly crude potential well calculation as a bond length of 0.13 nm. In fact measuring the energy level spacing due to rotational excitations of molecules is a frequently used method for measuring bond lengths – which of course play a crucial role in constructing chemical models of molecules.

Hence superimposed on the infrared absorption spectra due to vibrational modes will be a series of even closer spaced rotational spectra.

Important Points

1. We discussed the use of a variational technique to compute the approximate energy of a quantum mechanical ground state. The technique requires you to guess a “reasonable” trial wave function, $\tilde{\psi}(x)$, with at least one adjustable (shape) parameter. The wisest choice is to pick an actual ground state of a related system such as a harmonic oscillator ground state. We proved the inequality:

$$\tilde{E} = \langle \tilde{\psi} | H | \tilde{\psi} \rangle > E_{\text{ground}}$$

In computing \tilde{E} one must be careful to include both the kinetic and potential energy terms. If one chooses a ground state of a related system the

kinetic energy can be written down very easily using the virial theorem. The minimum value of \tilde{E} (as its parameters are varied) generally provides a good estimate for the true ground state energy of the system.

2. We applied the variational technique to the helium ground state. The complication to the quantum mechanics of helium is the electron-electron repulsion term. For this problem we used the product of two shielded hydrogen atom ground state orbit to act as a two particle trial wave function and got within 2% of the experimental result and a reasonable result for the shielded nuclear charge.
3. We computed the binding energy of the H_2^+ molecule where an electron orbits about two protons. We did the calculation by placing the two protons a distance R apart and then tried a trial wave function of the form $\Psi \propto \psi_{100}(r_1) + \psi_{100}(r_2)$ where r_1 is the distance of the electron to one proton and r_2 is the distance of the electron to the other. This is sometimes called a LCAO approach or linear combination of atomic orbitals. We found that it was indeed possible to get a variational estimate that had the total energy of the system (including the Coulomb repulsion between the two protons) less than -13.6 eV which means the molecule has a smaller energy than a hydrogen atom and free proton. We varied the R separation between the two protons but did not vary the LCAO wave function. The molecular binding energy was rather small and not terribly accurate but we concluded that molecules exist.
4. Finally we showed how the \tilde{E} versus R curve can be used to crudely estimate bond lengths and effective spring constants that can be used to estimate the vibrational and rotational energy levels of diatomic molecules. Typically the vibrational levels absorb infrared photons and the rotational levels absorb far infrared photons.