

7. Variation

Background

A course covering modern physics

Familiarity with QSHO, H-atom

Concepts of primary interest:

The Variation Principle

Sample calculations:

Hydrogen atom ground state

The Helium Atom – 1st order perturbation and variation

The Hydrogen Molecular Ion - H_2^+

Tools of the trade:

This handout is keyed to Griffiths *Introduction to Quantum Mechanics*, 2nd Ed. It is not designed to be used independently.

The Variation Principle: The ground state of a quantum system has a very special property; it is the state with the lowest possible energy. The hamiltonian is an operator for the energy, and it has a complete set of eigenfunctions ψ_n each with its energy eigenvalue E_n . The completeness property ensures that any allowed wavefunction ϕ can be represented as a linear combination of those eigenstates. $\phi = \sum_k a_k \psi_k$ with

$\sum_k |a_k|^2 = 1$. It follows that the energy expectation value for the state ϕ is $\langle E \rangle = \sum_k |a_k|^2 E_k$.

We will label the ground state as $n = 1$, and all other states by indices greater than 1.

$$\langle E \rangle - E_1 = |a_1|^2 (0) + \sum_{k>1} |a_k|^2 (E_k - E_1) = \sum_{k>1} |a_k|^2 (E_k - E_1) \quad [\text{Var.1}]$$

Our goal is to find the ground state, the lowest energy state. Any change that reduces $|a_k|$ for $k > 1$ lowers $\langle E \rangle$ and adjusts ϕ to be *closer* to the desired ground state form. (To make life simpler, we assume that the ground state is non-degenerate.)

Sample Calculation: The Hydrogen Atom Ground State

Start by choosing $\phi(r)$ to be a function with any number of adjustable parameters. Any adjustment of the parameter that lowers the energy expectation value moves ϕ closer to the real ground state. Guided by hindsight, the trial wavefunction chosen is $\phi(r) = A e^{-\lambda r}$ where λ is the lone adjustable parameter. The parameter A is set by normalization, and A is expected to be a function of the adjustable parameters.

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \xrightarrow{\text{no } \theta, \phi} -\frac{\hbar^2}{2m} \frac{1}{r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) - \frac{e^2}{4\pi\epsilon_0 r}$$

The simpler (independent of angles) form of the hamiltonian is applicable because the trial wave function has only radial dependence.

Step 1: Choose an allowable wavefunction. It must be normalized.

$$\int \phi^* \phi d\tau \rightarrow |A|^2 \int_0^\infty e^{-2\lambda r} 4\pi r^2 dr = \frac{4\pi}{8\lambda^3} |A|^2 \int_0^\infty e^{-u} u^2 du = \frac{4\pi}{8\lambda^3} |A|^2 (2!) = \frac{\pi}{\lambda^3} |A|^2$$

As the wavefunction *can be chosen* to be real, a possible $A = \lambda^{3/2} / \sqrt{\pi}$.

Step 2: Evaluate the energy for arbitrary values of the parameter(s).

$$\langle E \rangle = \int \phi^* \hat{H} \phi d\tau \rightarrow \frac{\lambda^3}{\pi} \int_0^\infty e^{-\lambda r} \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) - \frac{e^2}{4\pi\epsilon_0 r} \right] e^{-\lambda r} 4\pi r^2 dr$$

$$\text{Where: } \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) e^{-\lambda r} = -\left(\frac{\partial}{\partial r} \lambda r^2 e^{-\lambda r} \right) = \lambda^2 r^2 e^{-\lambda r} - 2\lambda r e^{-\lambda r}$$

$$\langle E \rangle = \int \phi^* \hat{H} \phi d\tau \rightarrow \frac{\lambda^3}{\pi} \int_0^\infty e^{-\lambda r} \left[-\frac{\hbar^2}{2m} (\lambda^2 e^{-\lambda r} - 2\lambda r^{-1}) e^{-\lambda r} - \frac{e^2}{4\pi\epsilon_0 r} \right] e^{-\lambda r} 4\pi r^2 dr$$

$$\langle E \rangle = \frac{\lambda^5}{\pi} \int_0^\infty e^{-2\lambda r} \left[-\frac{\hbar^2}{2m} (1 - 2\lambda^{-1} r^{-1}) \right] 4\pi r^2 dr + \frac{\lambda^3}{\pi} \int_0^\infty e^{-2\lambda r} \left[-\frac{e^2}{4\pi\epsilon_0} \right] 4\pi r dr$$

$$\langle E \rangle = -4\pi \frac{\hbar^2}{2m} \frac{\lambda^5}{\pi} \frac{1}{8\lambda^3} \int_0^\infty e^{-u} \left[(1 - 4u^{-1}) \right] u^2 dr - \frac{e^2}{\epsilon_0} \frac{\lambda^3}{\pi} \frac{1}{4\lambda^2} \int_0^\infty e^{-u} u du$$

$$\langle E \rangle = -\frac{\hbar^2 \lambda^2}{4m} \int_0^\infty e^{-u} \left[(u^2 - 4u) \right] du - \frac{e^2 \lambda}{4\pi\epsilon_0} \int_0^\infty e^{-u} u du = \frac{\hbar^2 \lambda^2}{4m} (2) - \frac{e^2 \lambda}{4\pi\epsilon_0} \quad [\text{Var.2}]$$

$$\langle E \rangle = \frac{\hbar^2}{m} \left(\frac{1}{2} \lambda^2 - \frac{me^2 \lambda}{4\pi\epsilon_0 \hbar^2} \right) = \frac{\hbar^2}{m} \left(\frac{1}{2} \lambda^2 - \frac{\lambda}{a_0} \right) \quad \text{where } \frac{4\pi\epsilon_0 \hbar^2}{me^2} = a_0$$

Step 3: Vary the parameter(s) to minimize the energy.

$$\frac{d\langle E \rangle}{d\lambda} = \frac{\hbar^2 \lambda}{m} - \frac{e^2}{4\pi\epsilon_0} = 0 \Rightarrow \lambda = \frac{m e^2}{4\pi\epsilon_0 \hbar^2} = (a_0)^{-1} \quad [\text{Var.3}]$$

The magic value for λ is the inverse of the Bohr radius. Our trial function becomes

$\phi_1(r) = \frac{1}{\pi^{1/2} a_0^{3/2}} e^{-r/a_0}$ which is the true ground state wavefunction. (We found the ‘exact’ answer because the initial trial wavefunction family contained the target function.) One of the problems for this section is to repeat the process above using a Gaussian trial wave function.

Extension to first excited states: One can attempt to find the first excited state by constructing states that are *orthogonal* to the ground state and that are normalized. Varying the parameters of such functions you might find an approximation to the first excited state. Trial functions: $\phi_2(r) = B (1 - br) e^{-\beta r}$. Normalize the ϕ_2 to find $B(\beta, b)$. Find $b(\beta)$ to ensure that $\langle \phi_2 | \phi_1 \rangle = 0$. Using $b(\beta)$, vary β to minimize the energy of ϕ_2 .

What is you use a different representation for essentially the same parameter?

Suppose that one chose $\psi(x) = A e^{-bx^2}$ while another chose $\phi(x) = A e^{-x^2/a^2}$. The results would be unchanged. The minimization conditions $\frac{d}{db} \langle E \rangle = 0$ and $\frac{d}{da} \langle E \rangle = 0$ would lead to the same wavefunction and the same minimum energy.

The Helium Atom: Helium is an atom with *one electron too many*.

As a first step, we will model helium using the single electron hydrogenic wave functions, then include first order perturbation theory and finally add parameter variation to generate an approximate wavefunction and ground state energy.

The one electron (He^+) problem has the hamiltonian $-\frac{\hbar^2}{2m} \nabla^2 - \frac{Z e^2}{4\pi\epsilon_0 r}$ where $Z = 2$. The previous solution of the hydrogen atom problem is adequate to provide the answers. The doubled nuclear charge acts on the electron to half the linear dimension parameter

and halving the electron-nuclear separation while doubling the nuclear charge quadruples the potential energy. Using the particle in the box model, ($E_n = \frac{\hbar^2 n^2}{2ma^2}$) suggests that halving the length scale quadruples the kinetic energy as well. If you want something more formal, the virial theorem result is that $\langle K \rangle = -1/2 \langle V \rangle$ for a $1/r$ potential. The two energies must scale in the same manner (\approx [linear extent]⁻²).

The single electron energies are $-54.4 eV/n^2$, and the wavefunctions have half the spatial extent of the hydrogenic functions. The two electrons fill the $n = 1$ level so the ground state energy is $-108.8 eV$. The only problem is that the experimental result is nearer to $-79.0 eV$. The model needs to be improved.

The most obvious omission is the electron-electron repulsion. The total hamiltonian

should be: $\hat{H} = \hat{H}_0 + \hat{H}' = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$. The first order perturbation correction is the expectation value of the perturbation in the unperturbed state.

$$\hat{H}' = +\frac{e^2}{4\pi\epsilon_0 r_{12}}; E_1^{(1)} = \langle \Psi_{gs} | \hat{H}' | \Psi_{gs} \rangle; \Psi_{gs}(\vec{r}_1, \vec{r}_2, t) = \psi_{1s}(\vec{r}_1, t) \psi_{1s}(\vec{r}_2, t) \quad [\text{Var.4}]$$

The evaluation is not as challenging as it first appears. While studying electrostatic boundary value problems, we derived the relation:

$$\frac{1}{|\vec{r}_2 - \vec{r}_1|} = \sum_{\ell=0}^{\infty} \frac{(r_{<})^{\ell}}{r_{>}^{(\ell+1)}} P_{\ell}(\hat{r}_2 \cdot \hat{r}_1) \quad \text{where } r_{>} \text{ is the larger of } r_1 \text{ and } r_2.$$

Choosing the coordinate 2 polar axis to lie along $\vec{r}_1, \hat{r}_1 \cdot \hat{r}_2$ becomes $\cos \theta_2$.

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \frac{(r_{<})^{\ell}}{r_{>}^{(\ell+1)}} P_{\ell}(\cos \theta_2) \quad [\text{Var.5}]$$

The wavefunction Ψ has no angular dependence so the orthogonality of the Legendre polynomials kills all but the $\ell = 0$ contribution. Our *effective* relation for spherically symmetric states becomes.

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \frac{(r_{<})^{\ell}}{r_{>}^{(\ell+1)}} P_{\ell}(\cos \theta_2) \rightarrow \frac{1}{r_1} \text{ for } r_2 < r_1 \text{ and } \frac{1}{r_2} \text{ for } r_2 > r_1. \quad [\text{Var.6}]$$

(In the case, that the wavefunctions have angular dependence, the orthogonality relations often can be used to reduce the effective expression for $(r_{12})^{-1}$ to a few terms.)

Exercise: Show that $\int_0^{2\pi} \frac{\sin \theta d\theta}{|\vec{r}_2 - \vec{r}_1|} = \int_0^{2\pi} \frac{\sin \theta d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}} = \frac{2}{r_{>}}$ where $\cos \theta = \hat{r}_1 \cdot \hat{r}_2$ and $r_{>}$ is the larger of r_1 and r_2 . As $\int_0^{2\pi} \sin \theta d\theta = 2$, equation [Var.6] gives the correct effective value for $|\vec{r}_2 - \vec{r}_1|^{-1}$. Recommended change of variable: $u = r_1^2 + r_2^2 - 2r_1r_2 \cos \theta$.

The wavefunction $\psi_{1S} = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}$ so the time independent form of $\Psi = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$.

$$E_1^{(1)} = \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int_0^{\infty} \int_0^{\infty} e^{-Z(r_1+r_2)/a_0} \left(\frac{e^2}{4\pi\epsilon_0 r_{12}}\right)_{\text{Effective}} e^{-Z(r_1+r_2)/a_0} 4\pi r_1^2 4\pi r_2^2 dr_1 dr_2 \quad [\text{Var.7}]$$

$$E_1^{(1)} = +\left(\frac{Z^3}{\pi a_0^3}\right)^2 \frac{e^2}{4\pi\epsilon_0} \int_0^{\infty} e^{-2Zr_1/a_0} \left\{ \int_0^{r_1} e^{-2Zr_2/a_0} \left(\frac{1}{r_1}\right) 4\pi r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-2Zr_2/a_0} \left(\frac{1}{r_2}\right) 4\pi r_2^2 dr_2 \right\} 4\pi r_1^2 dr_1$$

It's a tedious evaluation of several simple integrals using integration by parts.

$$E_1^{(1)} = +4\pi \left(\frac{Z^3}{\pi a_0^3}\right)^2 \frac{e^2}{\epsilon_0} \int_0^{\infty} e^{-2Zr_1/a_0} \left\{ \left(\frac{1}{r_1}\right) \int_0^{r_1} e^{-2Zr_2/a_0} r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-2Zr_2/a_0} r_2 dr_2 \right\} r_1^2 dr_1$$

Reducing the inner integrals:

$$\left(\frac{1}{r_1}\right) \int_0^{r_1} e^{-2Zr_2/a_0} r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-2Zr_2/a_0} r_2 dr_2 = \left(\frac{a_0}{2Zr_1}\right) \left(\frac{a_0}{2Z}\right)^2 \int_0^{2Zr_1/a_0} e^{-u} u^2 du + \left(\frac{a_0}{2Z}\right)^2 \int_0^{2Zr_1/a_0} e^{-u} u du$$

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Integrate[Exp[-u] u^2 , {u, 0, c}] = 2 - (2+c (2+c)) e^-c
Integrate[Exp[-u] u , {u, c, Infinity}] = (1+c) e^-c
FullSimplify[c^(-1) (2 - (2+c (2+c)) e^-c) + (1+c) e^-c]
= (e^-c (-2-c+2 e^c))/c

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$$E_1^{(1)} = +4\pi \left(\frac{Z^3}{\pi a_0^3} \right)^2 \frac{e^2}{\epsilon_0} \int_0^\infty e^{-2Zr_1/a_0} \left(\frac{a_0}{2Z} \right)^2 \left\{ e^{-2Zr_1/a_0} \left(-2 \left(\frac{a_0}{2Zr_1} \right) - 1 + 2 \left(\frac{a_0}{2Zr_1} \right) e^{+2Zr_1/a_0} \right) \right\} r_1^2 dr_1$$

$$\begin{aligned} E_1^{(1)} &= +4\pi \left(\frac{Z^3}{\pi a_0^3} \right)^2 \frac{e^2}{\epsilon_0} \left(\frac{a_0}{2Z} \right)^2 \int_0^\infty e^{-2Zr_1/a_0} \left\{ e^{-2Zr_1/a_0} \left(-2 \left(\frac{a_0}{2Zr_1} \right) - 1 + 2 \left(\frac{a_0}{2Zr_1} \right) e^{+2Zr_1/a_0} \right) \right\} r_1^2 dr_1 \\ &= +4\pi \left(\frac{Z^3}{\pi a_0^3} \right)^2 \frac{e^2}{\epsilon_0} \left(\frac{a_0}{2Z} \right)^2 \left\{ \int_0^\infty e^{-4Zr_1/a_0} \left(-2 \left(\frac{a_0}{2Zr_1} \right) - 1 \right) r_1^2 dr_1 + \int_0^\infty e^{-2Zr_1/a_0} 2 \left(\frac{a_0}{2Zr_1} \right) r_1^2 dr_1 \right\} \end{aligned}$$

Time Out: Sanity check. Is there any chance that the expression above is correct? First, everything inside the braces is a pure number. Both terms have the same dimensions. (✓)

Tracking the dimensions only: $+4\pi \left(\frac{Z^3}{\pi a_0^3} \right)^2 \frac{e^2}{\epsilon_0} \left(\frac{a_0}{2Z} \right)^2 r_1^2 dr_1 \approx \frac{e^2 r_1^2 dr_1}{4\pi \epsilon_0 a_0^4} \approx \frac{e^2}{4\pi \epsilon_0 \text{length}} \rightarrow \text{Energy}.$ (✓)

There is a chance that the expression is not pure nonsense. Return to the calculation.

$$\begin{aligned} E_1^{(1)} &= +4\pi \left(\frac{Z^3}{\pi a_0^3} \right)^2 \frac{e^2}{\epsilon_0} \left(\frac{a_0}{2Z} \right)^2 \\ &\quad \times \left\{ \int_0^\infty e^{-4Zr_1/a_0} \left(-4 \left(\frac{a_0}{4Zr_1} \right) - 1 \right) \left(\frac{a_0}{4Z} \right)^3 \left(\frac{4Zr_1}{a_0} \right)^2 \left(\frac{4Z}{a_0} \right) dr_1 + \int_0^\infty e^{-2Zr_1/a_0} 2 \left(\frac{a_0}{2Z} \right)^3 \left(\frac{2Z}{a_0} \right) r_1 \left(\frac{2Z}{a_0} \right) dr_1 \right\} \\ &= +4\pi \left(\frac{Z^3}{\pi a_0^3} \right)^2 \frac{e^2}{\epsilon_0} \left(\frac{a_0}{2Z} \right)^2 \left(\frac{a_0}{4Z} \right)^3 \left\{ \int_0^\infty e^{-u} (-4u - u^2) du + 2 \left(\frac{4}{2} \right)^3 \int_0^\infty e^{-u} u du \right\} = \frac{Ze^2}{64\pi\epsilon_0 a_0} \{-4\Gamma(2) - \Gamma(3) + 16\Gamma(2)\} \\ E_1^{(1)} &= \frac{Ze^2}{64\pi\epsilon_0 a_0} \{-4(1!) - (2!) + 16(1!)\} = \frac{5}{8} Z \frac{e^2}{4\pi\epsilon_0 a_0} = \frac{5}{8} (2)(27.2 eV) = +34 eV \end{aligned}$$

The energy estimate including the correction from first order perturbation for the electron-electron repulsion is $-108.8 eV + 34.0 eV = -74.8 eV$. As the experimental value is about $-79 eV$, the first order correction has overshoot the mark. This situation is rather common. In first order, expectation value of the perturbation is computed in the unperturbed state. In the next order, the ground state wavefunction adjusts to lower the overall energy including that associated with the perturbation.

A variation approach is to be applied instead of further perturbation. The two electron wavefunction is $\Psi = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr_1/a_0} \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr_2/a_0} = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$. The cloud grows in extent to lower the electron-electron repulsion. That is, the effective nuclear charge Z is less than 2. We will treat Z as a variable parameter in Ψ , but we will take care to keep the nuclear charge fixed at $2e$, its physical value, in the potential term.

$$V_1 = -\frac{Z e^2}{4\pi\epsilon_0 r_1} + \frac{(Z-2)e^2}{4\pi\epsilon_0 r_1}$$

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{(Z-2)e^2}{4\pi\epsilon_0 r_1} + \frac{(Z-2)e^2}{4\pi\epsilon_0 r_2} \quad [\text{Var.8}]$$

By this point, nobody wants to launch into another calculation, so let us just assemble

our previous results for $\psi = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}$, the solution for $\hat{H}_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Z e^2}{4\pi\epsilon_0 r}$.

$$\begin{aligned} \left\langle -\frac{\hbar^2}{2m} \nabla^2 \right\rangle &= +Z^2 (13.6eV); \quad \left\langle -\frac{Z e^2}{4\pi\epsilon_0 r} \right\rangle = -Z^2 (27.2eV); \quad \left\langle \frac{e^2}{4\pi\epsilon_0 r_{12}} \right\rangle = \frac{5}{8} Z (27.2eV) \\ \left\langle -\frac{Z e^2}{4\pi\epsilon_0 r} \right\rangle &= -Z^2 (27.2eV) \Rightarrow \left\langle \frac{e^2}{4\pi\epsilon_0 r} \right\rangle = Z (27.2eV), \quad \left\langle \frac{(Z-2)e^2}{4\pi\epsilon_0 r} \right\rangle = (Z-2)Z (27.2eV) \\ E = \langle \hat{H} \rangle &= 2 \left\langle -\frac{\hbar^2}{2m} \nabla^2 \right\rangle + 2 \left\langle -\frac{Z e^2}{4\pi\epsilon_0 r} \right\rangle + \left\langle \frac{e^2}{4\pi\epsilon_0 r_{12}} \right\rangle + 2 \left\langle \frac{(Z-2)e^2}{4\pi\epsilon_0 r} \right\rangle \quad [\text{Var.9}] \\ E = \langle \hat{H} \rangle &= (13.6eV) \left\{ 2Z^2 - 4Z^2 + \frac{5}{8} Z (2) + 2(Z-2)Z (2) \right\} \end{aligned}$$

Applying the first derivative test, $Z = 27/16$ minimizes the value of E yielding $-77.5 eV$ which is only $1.5 eV$ high. We will be content with this approximation. Our zero-order estimate was $-108.8 eV$ or about $30 eV$ low. Our current estimate is about $1.5 eV$ high or about $1/3$ the error prior to incorporating variation. Improvements to this estimate are usually delayed until graduate school when the Hartree-Fock¹ method might be employed.

The Hylleraas Trial Function for the Helium Ground State:

The perturbation term is a function of the electron-electron separation r_{12} . It follows that this parameter could be important in the trial functions. In the presence of this

¹ The Hartree-Fock method is also called the **self-consistent field method (SCF)**. One computes the potential for the nucleus plus the charge density of the other electron as a function of r . One then solves the radial equation numerically and inserts the corrected wavefunction into the electron density used to compute the potential. The process is iterated until it converges.
http://en.wikipedia.org/wiki/Self_consistent_field_method

term, the wave function is no longer expected to separate into a function of \vec{r}_1 times one of \vec{r}_2 .

Hylleraas proposed $\phi(\vec{r}_1, \vec{r}_2) = A e^{-\beta r_1/a_0} e^{-\beta r_2/a_0} (1 + b r_{12})$. The function is first normalized to find $A(\beta, b)$. The energy is then evaluated as a function of β and b . That energy is then minimized with respect to variations of the parameters β and b . The minimized values are found to be $\beta = 1.849$ and $b = 0.364/a_0$. The ground state energy estimate for those values is -78.7 eV .

The Hydrogen Molecular Ion

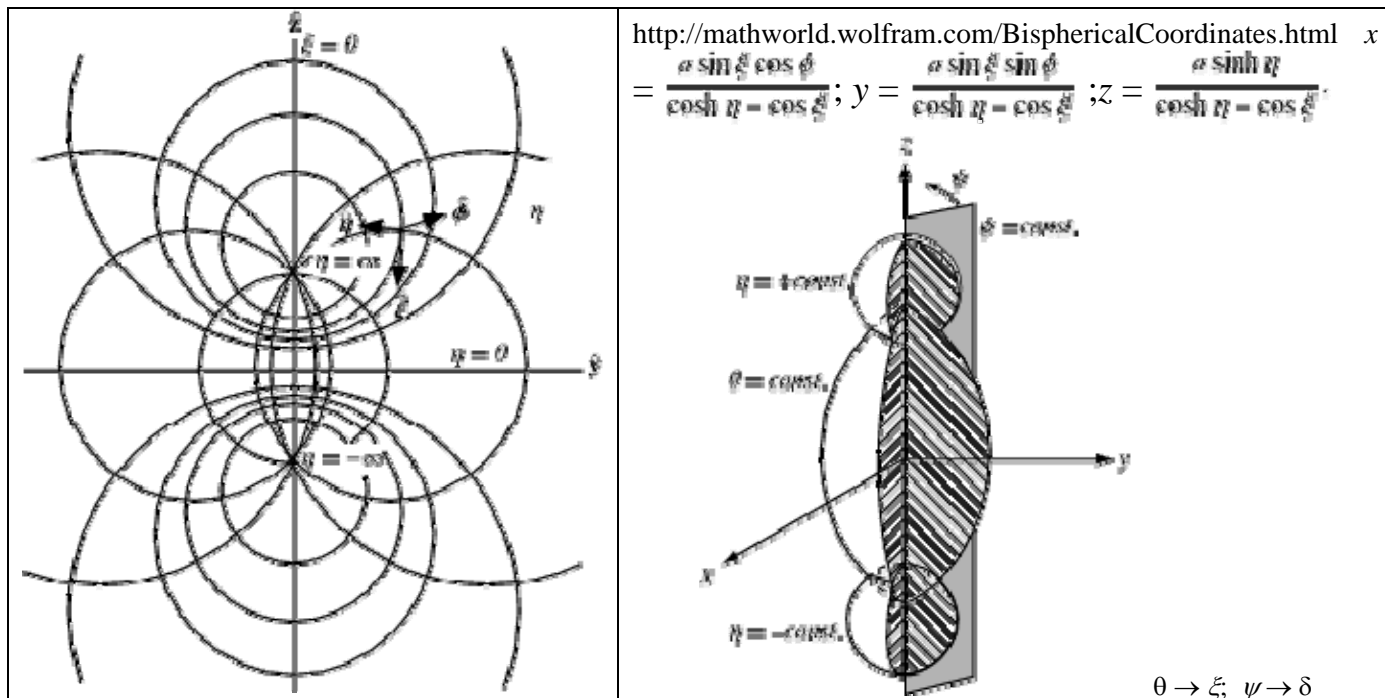
This problem is widely treated, and it can be solved exactly by adopting one of the generalized locally orthonormal coordinate systems, bispherical coordinates.

See: http://en.wikipedia.org/wiki/Hydrogen_molecular_ion;

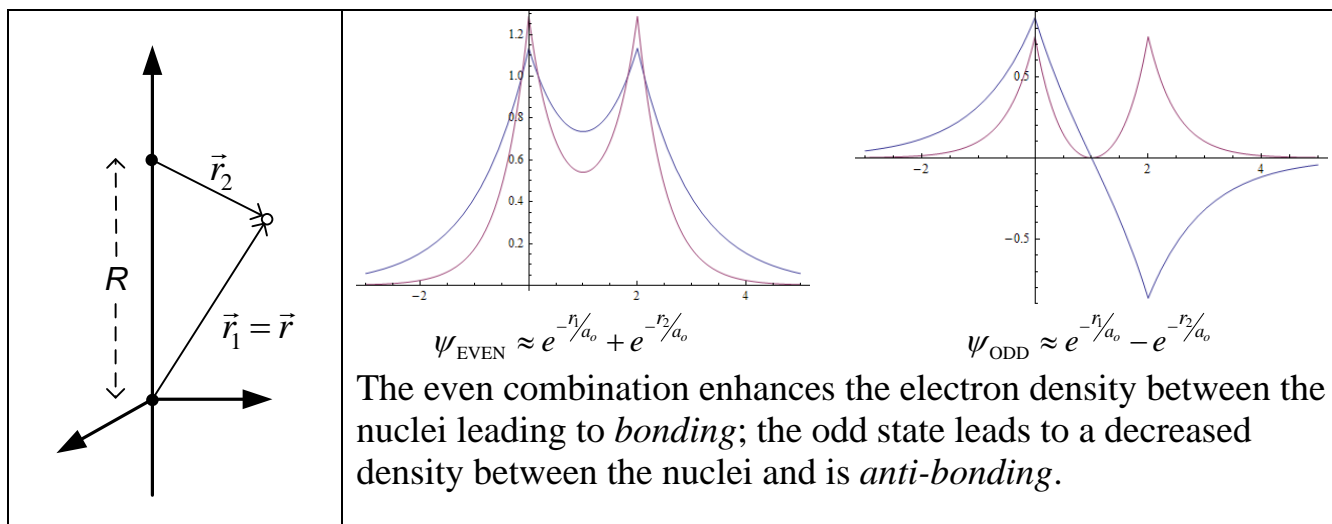
The hydrogen molecular ion, dihydrogen cation, or H_2^+ , is the simplest molecular ion. It is composed of two positively-charged protons and one negatively-charged electron, and can be formed from ionization of a neutral hydrogen molecule. It is of great historical and theoretical interest as, having only one electron, the Schrödinger equation for the system can be solved in a relatively straightforward way due to the lack of electron–electron repulsion (electron correlation). The analytical solutions for the energy eigenvalues [1] are a generalization of the Lambert W function (see Lambert W function and references therein for more details on this function). Consequently, it is included as an example in most quantum chemistry textbooks.

The first successful quantum mechanical treatment of H_2^+ was published by the Danish physicist Øyvind Burrau in 1927,[2] just one year after the publication of wave mechanics by Erwin Schrödinger. Earlier attempts using the old quantum theory had been published in 1922 by Karel Niessen[3] and Wolfgang Pauli,[4] and in 1925 by Harold Urey.[5] In 1928, Linus Pauling published a review putting together the work of Burrau with the work of Walter Heitler and Fritz London on the hydrogen molecule.[6] Bonding in H_2^+ can be described as a covalent one-electron bond, which has a formal bond order of one half.[7]

http://en.wikipedia.org/wiki/Bispherical_coordinates,
<http://www.dartmouth.edu/~chem81/thps/h2plus.html>



Our model of the hydrogen molecular ion is two fixed (proton) Coulomb force centers separated by R , and an electron moving in the potential field due to the two protons. Actually, the inter-nuclear separation oscillates, and the *dumbbell* of the nuclei (with the electron) rotates about the center of mass. Our fixed-nuclei model is a first cut.



The goal is to search for a bound state of the hydrogen molecule; that is: a state with energy lower than that of an isolated hydrogen atom plus a proton. Any trial state that

we choose will provide an upper bound for this energy so any negative energy result could indicate a bound state. The wavefunction will be represented as either the even or odd combination of 1S hydrogenic wavefunctions centered of each of the protons.

$$\psi_{\text{EVEN}} = A_+ [e^{-r_1/a_0} + e^{-r_2/a_0}] \quad \psi_{\text{ODD}} = A_- [e^{-r_1/a_0} - e^{-r_2/a_0}]$$

The *yet-to-be-normalized* wavefunctions are plotted in blue and the probability densities in a contrasting color. Clearly, a state like the even one is required to enhance the probability of the electron being between the nuclei. In such a position, the Coulomb attraction of the electron for the nuclei might overwhelm the Coulomb repulsion of the nuclei. The coordinates are chosen with the origin at the location of the first proton such that $\vec{r}_1 = \vec{r}$. The second proton lies a distance R away on the polar (positive z) axis. With this choice, $r_2 = [R^2 + r^2 - 2rR \cos\theta]^{1/2}$. Here, R is in fact the parameter to be varied to find the minimum energy. The electron hamiltonian is:

$$\hat{H}_{el} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2}$$

The energy of the full system includes $\frac{e^2}{4\pi\epsilon_0 R}$, the Coulomb energy of the proton pair.

$$\hat{H}_{full} = \hat{H}_{el} + \hat{H}_{p-p} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 R}$$

Note that the protons are treated as classical fixed charges so there is no proton kinetic energy. (The mass of the proton is very large compared to that of the electron so the proton kinetic energy term is small in any case.) The $p-p$ Coulomb interaction energy is just added to the electron energy.

Normalize the trial functions:¹

¹ The geometry and change of variable required to solve this problem were treated in the E&M Integration section of the Math Methods notes. Review that handout for additional details and insights.

$$\int \psi_{\text{EVEN}}^* \psi_{\text{EVEN}} d\tau = |A_+|^2 \int \left\{ e^{-2r_1/a_0} + e^{-2r_2/a_0} + 2e^{-(r_1+r_2)/a_0} \right\} r_1^2 dr_1 \sin \theta d\theta d\phi = 2|A_+|^2 \{I_1 + I_2\}$$

$$\int \psi_{\text{ODD}}^* \psi_{\text{ODD}} d\tau = |A_-|^2 \int \left\{ e^{-2r_1/a_0} + e^{-2r_2/a_0} - 2e^{-(r_1+r_2)/a_0} \right\} r_1^2 dr_1 \sin \theta d\theta d\phi = 2|A_-|^2 \{I_1 - I_2\}$$

$$A_{\pm} = \frac{1}{\sqrt{2(I_1 \pm I_2)}}; \text{ the normalization constant can be assumed real}$$

$$I_1 = \int e^{-2r_1/a_0} r_1^2 dr_1 \sin \theta d\theta d\phi = 4\pi \left(\frac{a_0}{2}\right)^3 \int_0^{\infty} e^{-u} u^2 du = \pi a_0^3$$

$$I_2 = \int e^{-(r_1+r_2)/a_0} r_1^2 dr_1 \sin \theta d\theta d\phi$$

The integrals of the first two terms are equal. The I_1 integral is just the standard normalization integral for the hydrogenic 1S state.

$$I_2 = \int e^{-r/a_0} e^{-\sqrt{(R/a_0)^2 + (r/a_0)^2 - 2\cos\theta(Rr/a_0^2)}} r^2 dr \sin \theta d\theta d\phi$$

First, define some dimensionless variables: $s = (r/a_0)$ and $S = (R/a_0)$.

$$I_2 = a_0^3 \int e^{-s} e^{-\sqrt{S^2+s^2-2sS\cos\theta}} s^2 ds \sin \theta d\theta d\phi$$

$$I_2 = 2\pi a_0^3 \int_0^{\infty} e^{-s} s^2 \left(\int_0^{\pi} e^{-\sqrt{S^2+s^2-2sS\cos\theta}} \sin \theta d\theta \right) ds$$

The ϕ integration is trivial. Following our practice, the argument of a function in the integrand is chosen as the new variable as we attack the θ integral.

$$u = \sqrt{S^2+s^2-2sS\cos\theta}; \quad du = \frac{sS\sin\theta d\theta}{\sqrt{S^2+s^2-2sS\cos\theta}}; \quad u du = sS \sin \theta d\theta$$

$$I_2 = 2\pi a_0^3 \int_0^{\infty} e^{-s} s^2 \left(\int_{|S-s|}^{S+s} e^{-u} \frac{u du}{sS} \right) ds = \frac{2\pi a_0^3}{S} \int_0^{\infty} e^{-s} s \left(\int_{|S-s|}^{S+s} e^{-u} u du \right) ds$$

The limits on integration are changed when the integration variable is changed. The absolute value is needed as the square root represents a *distance*.

$$\begin{aligned} \int_{|S-s|}^{S+s} e^{-u} u du &= \left(-e^{-u} u \right) \Big|_{|S-s|}^{S+s} + \int_{|S-s|}^{S+s} e^{-u} du = -\left(e^{-u} u + e^{-u} \right) \Big|_{|S-s|}^{S+s} \\ &= -\left(e^{-u} u - e^{-u} \right) \Big|_{|S-s|}^{S+s} = e^{-|S-s|} (|S-s|+1) - e^{-(S+s)} (S+s+1) \end{aligned}$$

Inserting this result into the expression for I_2 , and breaking the s range into $s < S$ and $s > S$,

$$I_2 = \frac{2\pi a_0^3}{S} \left\{ -\int_0^\infty e^{-(S+2s)} ([S+1]s + s^2) ds + \int_0^S e^{-S} ([S+1]s - s^2) ds + \int_s^\infty e^{S-2s} ([1-S]s + s^2) ds \right\}$$

$$I_2 = \frac{2\pi a_0^3}{S} \left\{ -e^{-S} \left(\frac{S+2}{4} \right) + e^{-S} \left(\frac{S^3+S^2}{2} - \frac{S^3}{3} \right) + e^{-S} \left(\frac{2+3S}{4} \right) \right\} = \frac{2\pi a_0^3}{S} e^{-S} \frac{2S^3+6S^2+6S}{12}$$

$$I_2 = \pi a_0^3 e^{-S} \left(1 + S + \frac{1}{3} S^2 \right)$$

$$|A_\pm|^2 = \left(\frac{1}{\pi a_0^3} \right) \left[2 \pm 2e^{-S} \left(1 + S + \frac{1}{3} S^2 \right) \right]^{-1} \quad [\text{Var.10}]$$

$$A_\pm = \left(\frac{1}{\pi a_0^3} \right) \left[2 \pm 2e^{-R/a_0} \left(1 + R/a_0 + \frac{1}{3} (R/a_0)^2 \right) \right]^{-1/2}$$

Apply a sanity check. The normalized form of a 1S state is $\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$. In the limit that S is large, the cross terms should vanish so $\int \left(e^{-r_1/a_0} \pm e^{-r_2/a_0} \right)^2 d\tau$ yields πa_0^3 from the region around the first proton and πa_0^3 from the region around the second proton. Hence in the large S limit, $|A_\pm|^2 \rightarrow \frac{1}{2\pi a_0^3}$. The large S limit works. The result *might* be valid.

Now that the states are normalized, we compute the electron energy. Dirac notation is adopted as a short hand. $\Rightarrow \int \phi(\vec{r})^* \hat{H} \psi(\vec{r}) d\tau \rightarrow \langle \phi | \hat{H} | \psi \rangle$

$$\begin{aligned} \langle \psi_\pm | \hat{H}_{el} | \psi_\pm \rangle &= |A_\pm|^2 \left\langle e^{-r_1/a_0} \pm e^{-r_2/a_0} \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} \right| e^{-r_1/a_0} \pm e^{-r_2/a_0} \right\rangle \\ &= |A_\pm|^2 \left\langle \left(e^{-r_1/a_0} \pm e^{-r_2/a_0} \right) \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} \right| e^{-r_1/a_0} \pm e^{-r_2/a_0} \right\rangle \\ &= |A_\pm|^2 \left\langle \left(e^{-r_1/a_0} \pm e^{-r_2/a_0} \right) \left| E_{1s} e^{-r_1/a_0} \pm E_{1s} e^{-r_2/a_0} \right. \right\rangle \\ &\quad + |A_\pm|^2 \left\langle \left(e^{-r_1/a_0} \pm e^{-r_2/a_0} \right) \left| \left(-\frac{e^2}{4\pi\epsilon_0 r_2} \right) e^{-r_1/a_0} \pm \left(-\frac{e^2}{4\pi\epsilon_0 r_1} \right) e^{-r_2/a_0} \right. \right\rangle \end{aligned}$$

The simplification followed as e^{-r/a_0} is an eigenfunction of $-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$ with the 1S energy.

$$\langle \psi_{\pm} | \hat{H}_{el} | \psi_{\pm} \rangle = E_{1S} \left\{ |A_{\pm}|^2 \left\langle e^{-r_1/a_0} \pm e^{-r_2/a_0} \left| e^{-r_1/a_0} \pm e^{-r_2/a_0} \right\rangle \right\} + \right. \\ \left. - \frac{e^2}{4\pi\epsilon_0} |A_{\pm}|^2 \left\{ \left\langle e^{-r_1/a_0} \left| \frac{1}{r_1} e^{-r_2/a_0} \right\rangle + \left\langle e^{-r_2/a_0} \left| \frac{1}{r_2} e^{-r_1/a_0} \right\rangle \pm \left\langle e^{-r_1/a_0} \left| \frac{1}{r_2} e^{-r_1/a_0} \right\rangle \pm \left\langle e^{-r_2/a_0} \left| \frac{1}{r_1} e^{-r_2/a_0} \right\rangle \right\} \right\}$$

The integral in the first set of braces is one as it is the normalization condition. $E_{1S} = -\frac{e^2}{8\pi\epsilon_0 a_0} = -13.6 \text{ eV}$. As the two proton positions are equivalent, the first pair of integrals in the second brace set is equal as is the second pair.

$$\langle \psi_{\pm} | \hat{H}_{el} | \psi_{\pm} \rangle = E_{1S} + 2 E_{1S} |A_{\pm}|^2 \left\{ 2 \left\langle e^{-r_1/a_0} \left| \frac{a_0}{r_1} e^{-r_2/a_0} \right\rangle \pm 2 \left\langle e^{-r_1/a_0} \left| \frac{a_0}{r_2} e^{-r_1/a_0} \right\rangle \right\} = E_{1S} + 4 E_{1S} |A_{\pm}|^2 \{I_3 \pm I_4\}$$

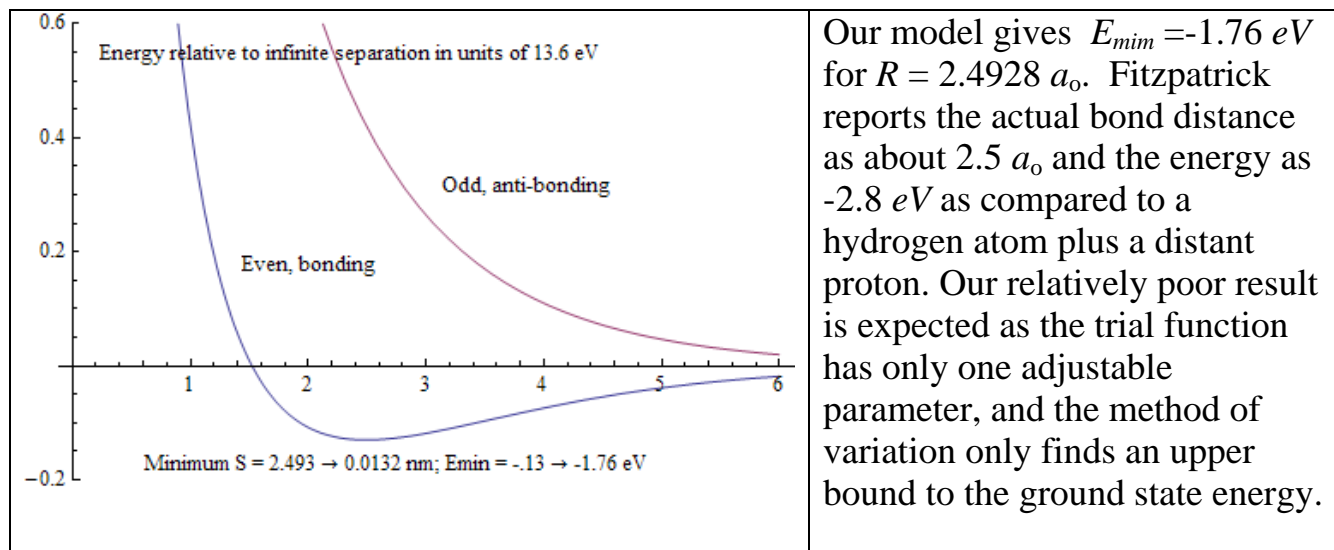
$$I_3 = a_0 \int e^{-(r_1+r_2)/a_0} r_1 dr_1 \sin \theta d\theta d\phi \quad I_4 = a_0 \int e^{-2r_1/a_0} \frac{r_1^2}{r_2} dr_1 \sin \theta d\theta d\phi$$

While tedious, the integrals I_3 and I_4 can be evaluated using the same methods as we employed to compute the normalization integrals. Their evaluation is left for homework. Following Richard Fitzpatrick, the p - p interaction energy is added and the terms combined to yield $E(S)$ where $S = R/a_0$, the inter-nuclear separation in units of the Bohr radius. .

$$E(S) = (-13.6 \text{ eV}) \left\{ 1 - \frac{2}{S} \left(\frac{(1+S)e^{-2S} \pm (1-\frac{2}{3}S^2)e^{-S}}{1 \pm (1+S + \frac{1}{3}S^2)e^{-S}} \right) \right\}$$

$$E_{\text{binding}}(S) = (13.6 \text{ eV}) \left\{ \frac{2}{S} \left(\frac{(1+S)e^{-2S} \pm (1-\frac{2}{3}S^2)e^{-S}}{1 \pm (1+S + \frac{1}{3}S^2)e^{-S}} \right) \right\} = 13.6 \text{ eV} - E(S)$$

As the energy of a hydrogen atom separated by a large distance from a proton would be -13.6 eV , a energy 13.6 eV is added to the total energy before plotting. The energy is plotted in units of 13.6 eV and the separation in units of a_0 .



Appendix

Computing kinetic energy - a Hermitian approach:

The Hermitian conjugate of an operator \hat{Q} is represented by the symbol \hat{Q}^\dagger and it is defined such that:

$$\int [\hat{Q}^\dagger \Phi(q_i, t)]^* \Psi(q_i, t) d\tau = \int \Phi^*(q_i, t) [\hat{Q} \Psi(q_i, t)] d\tau$$

for any two functions $\Phi(q_i, t)$ and $\Psi(q_i, t)$ that are permissible wavefunctions for the problem.

For a 1D problem, the kinetic energy can be computed as:

$$\begin{aligned} -\frac{1}{2m} \int \Psi^*(x, t) [\hat{p} \hat{p} \Psi(x, t)] dx &= -\frac{1}{2m} \int [\hat{p}^\dagger \Psi(x, t)]^* [\hat{p} \Psi(x, t)] dx = \\ &= -\frac{1}{2m} \int [\hat{p} \Psi(x, t)]^* [\hat{p} \Psi(x, t)] dx = \frac{\hbar^2}{2m} \int \left[\frac{\partial \Psi(x, t)}{\partial x} \right]^* \left[\frac{\partial \Psi(x, t)}{\partial x} \right] dx \\ \langle T \rangle &= + \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left[\frac{\partial \Psi(x, t)}{\partial x} \right]^* \left[\frac{\partial \Psi(x, t)}{\partial x} \right] dx \quad [\text{Var.11}] \end{aligned}$$

The Hermitian property of the momentum operator was used above. The form of the equation [Var.11] shows that $\langle T \rangle$ is positive.

Integrals for some variation technique problems: [Var.12]

$$\int_{-\infty}^{\infty} (\operatorname{sech}[wx])^2 dx = 2/w$$

$$\int_{-\infty}^{\infty} (\tanh[wx] \operatorname{sech}[wx])^2 dx = 2/(3w)$$

$$\int_{-\infty}^{\infty} (x \operatorname{sech}[wx])^2 dx = \pi^2/(6w^3)$$

$$\int_{-\infty}^{\infty} (x^2 \operatorname{sech}[wx])^2 dx = 7\pi^4/(120w^5)$$

$$\int_{-\infty}^{\infty} (\operatorname{sech}[wx] - wx \tanh[wx] \operatorname{sech}[wx])^2 dx = 1/(18w)$$

In[1]= Integrate[Sech[x]^2, x]

Out[1]= Tanh [x]

In[3]= Integrate[Sech[x] D[D[Sech[x], x], x], x]

Out[3]= $-\frac{\operatorname{Tanh}[x]}{3} - \frac{2}{3} \operatorname{Sech}[x]^2 \operatorname{Tanh}[x]$

In[5]= Integrate[x^2 Sech[x]^2, {x, -Infinity, Infinity}]

Out[5]= $\frac{\pi^2}{6}$

In[6]= Integrate[Csch[x]^2, x]

Out[6]= -Coth [x]

In[7]= Integrate[Csch[x] D[D[Csch[x], x], x], x]

Out[7]= $\frac{\operatorname{Coth}[x]}{3} - \frac{2}{3} \operatorname{Coth}[x] \operatorname{Csch}[x]^2$

In[8]= Integrate[x^2 Csch[x]^2, {x, -Infinity, Infinity}]

Out[8]= $\frac{\pi^2}{3}$

Problems

1.) Derive a result analogous to [Var.11] that is valid for the kinetic energy of a particle in three dimensions.

2.) Show that $\langle T \rangle = \langle K \rangle = -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} [\Psi(x,t)]^* \frac{\partial^2}{\partial x^2} \Psi(x,t) dx$ yields [Var.11] after a simple integration by parts. Show that the 3D result follows from:

$$\vec{\nabla} \cdot [\Phi^* \vec{\nabla} \Psi] - \Phi^* \nabla^2 \Psi = (\vec{\nabla} \Phi^*) \cdot (\vec{\nabla} \Psi)$$

and one of the standard integral theorems of vector calculus.

$$\langle T \rangle = +\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} (\vec{\nabla} \Psi)^* \cdot (\vec{\nabla} \Psi) dx$$

3.) Choose $A \operatorname{sech}[w x]$ as a trial function for the variation approach to determining the ground state energy of a quantum harmonic oscillator. The parameter w is a positive real value. Consider using [Var.11]; use the tabulated integrals [Var.12].

4.) Show that $B x \operatorname{sech}[u x]$ is orthogonal to $A \operatorname{sech}[w x]$. Treat u as a positive real adjustable parameter that is independent of w in order to estimate the energy of the first excited state of the oscillator. Why do we believe that the state $B x \operatorname{sech}[u x]$ is orthogonal to the true ground state of the oscillator as well as to the trial function for the previous problem?

5. You have a complete set ψ_n of energy eigenfunctions with energy eigenvalues E_n :

$$\begin{aligned} \mathbf{H} |\psi_n\rangle &= E_n |\psi_n\rangle, & \langle \psi_n | \psi_m \rangle &= \delta_{mn}, & |\Psi\rangle &= \sum c_k |\psi_k\rangle, \\ \langle \Psi | \Psi \rangle &= \sum_k |c_k|^2 = 1 \text{ and } \langle \Psi | \mathbf{H} | \Psi \rangle = \langle E \rangle = \sum_k |c_k|^2 E_k. \end{aligned}$$

Assume that all the states are non-degenerate. You can approach the ground state by varying the parameters in your solution to minimize the expectation value of the energy. You can find the first excited state by seeking the lowest energy that is orthogonal to the ground state. You must keep the wavefunction normalized at all times. Some suggest that this method does a better job of predicting the ground state energy than it does of predicting the ground state wavefunction. Can you think of any reason why this might be true?

Consider the state $\Psi = a \psi_1 + b \psi_2$ for which the expectation value of the energy is $|a|^2 E_1 + |b|^2 E_2$. Suppose $b = 0.1$. What is the value of a if it is assumed to be real positive?

6.) For the hydrogen atom, the hamiltonian is: $-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$.

Assume that that $\psi(r) = A e^{-r^2/a^2}$ where a is the parameter to be varied. Normalize the wavefunction. Compute the expectation value of the hamiltonian in this state. Find the value of a that minimizes this energy. Compute the numerical value of a . Compare the a and the minimized energy with the Bohr radius and the ground state energy of the hydrogen atom.

Recall:
$$\nabla^2 = \left(\frac{1}{r^2}\right) \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r}\right) + \left(\frac{1}{r^2 \sin \theta}\right) \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta}\right) + \left(\frac{1}{r^2 \sin^2 \theta}\right) \frac{\partial^2}{\partial \phi^2}$$

First cut answers: $\langle T \rangle = \frac{3\hbar^2}{2ma^2}$; $\langle V \rangle = -\frac{2^{3/2}}{\pi^{1/2}} \frac{e^2}{4\pi\epsilon_0 a}$; $a_{\min} = \frac{3\pi^{1/2}}{2^{3/2}} \frac{4\pi\epsilon_0 \hbar^2}{me^2} = \frac{3\pi^{1/2}}{2^{3/2}} a_0$

$$E_{\min} = \frac{e^2}{4\pi\epsilon_0 a_0} \left(\frac{4}{3\pi}\right) - \frac{e^2}{4\pi\epsilon_0 a_0} \left(\frac{8}{3\pi}\right) = 27.2 eV \left(-\frac{4}{3\pi}\right) = -11.5 eV$$

If you start with a poor model, you usually get poor results!

7.) For a QHO, the hamiltonian is: $-\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} + \frac{1}{2} k x^2$. See equation: [Var.12]

a.) Assume that that $\psi(x) = A e^{-ax^2}$ where a is a constant. Normalize the wavefunction. Compute the expectation value of the hamiltonian in this state. Find the value of a that minimizes this energy. What is that energy? Compare it with $\frac{1}{2} \hbar \omega_c$.

b.) Assume that that $\psi(x) = A \operatorname{sech}[cx]$ where c is a constant. Normalize the wavefunction. Compute the expectation value of the hamiltonian in this state. Find the value of c that minimizes this energy. What is that energy? Compare it with $\frac{1}{2} \hbar \omega_c$.

c.) Repeat with $B \operatorname{csch}[cx]$. This state is orthogonal to $A \operatorname{sech}[cx]$. How can you conclude that the states are orthogonal without computing an integral?

In[1]:= Integrate[Sech[x]^2, x]

Out[1]= Tanh [x]

In[3]:= Integrate[Sech[x] D[D[Sech[x], x], x], x]

Out[3]= $-\frac{\text{Tanh}[x]}{3} - \frac{2}{3} \text{Sech}[x]^2 \text{Tanh}[x]$

In[5]:= Integrate[x^2 Sech[x]^2, {x, -Infinity, Infinity}]

Out[5]= $\frac{\pi^2}{6}$

In[6]:= Integrate[Csch[x]^2, x]

Out[6]= -Coth [x]

In[7]:= Integrate[Csch[x] D[D[Csch[x], x], x], x]

Out[7]= $\frac{\text{Coth}[x]}{3} - \frac{2}{3} \text{Coth}[x] \text{Csch}[x]^2$

In[8]:= Integrate[x^2 Csch[x]^2, {x, -Infinity, Infinity}]

Out[8]= $\frac{\pi^2}{3}$

8.) For a QHO, the hamiltonian is: $-\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} + \frac{1}{2} k x^2$. See equation: [Var.12]

a.) Assume that that $\psi_\alpha(x) = A e^{-ax^2}$ where a is a parameter. Normalize the wavefunction. Compute the expectation value of the hamiltonian in this state. Find the value of a that minimizes this energy. What is that energy? Compare it with $\frac{1}{2} \hbar \omega_c$.

b.) Assume that that $\psi_\beta(x) = B x e^{-bx^2}$ where b is a parameter. Normalize the wavefunction. Compute the expectation value of the hamiltonian in this state. Find the value of b that minimizes this energy. What is that energy? Compare it with $\frac{3}{2} \hbar \omega_c$.

c.) Show that $\langle \psi_\beta | \psi_\alpha \rangle = 0$.

d.) Assume that that $\psi_\gamma(x) = C (1 + b x + c x^2) e^{-\gamma x^2}$ where b , c and γ are parameters.

Conduct a variation to find the third level of the oscillator.

i.) Find the constraints that $\langle \psi_\beta | \psi_\gamma \rangle = 0$ and $\langle \psi_\alpha | \psi_\psi \rangle = 0$ impose. Why are these conditions needed if one wants to use variation to find the third level of the oscillator?

ii.) Normalize the constrained form of the trial wavefunction.

iii.) How many free parameters remain after the constraints are applied? Vary the constrained set of parameters to minimize the energy.

e.) It is possible that the variations of part *a* did not produce the exact ground state. In this case, do the second and third variation attempts necessarily generate energy level estimates that are greater than or equal to the true values?

f.) Based on the general character of energy eigenfunctions and the form of the potential energy, the claim is that the procedure in part *b* yields an energy that is greater than or equal to the true energy of the second level. Explain why this must be true.

9.) One can attempt to find the first excited state by constructing states that are *orthogonal* to the ground state and that are normalized. Varying the parameters of such functions you might find an approximation to the first excited state. Estimate the $n = 2$ energy level for the hydrogen atom problem. Assume the trial wavefunction family: $\phi_2(r) = B(1 - br)e^{-\beta r}$. Normalize the ϕ_2 to find $B(\beta, b)$. Find $b(\beta)$ to ensure that $\langle \phi_2 | \phi_1 \rangle = 0$. Using this b , vary β to minimize the energy of ϕ_2 .

10.) Evaluate the integrals I_3 and I_4 that appear in the computation of the energy of the hydrogen molecular ion.

11.) It is a good practice to transform integrals to dimensionless forms before they are evaluated. For the hydrogen molecular ion problem, the normalization integrals are rendered dimensionless by defining the lengths in units of the Bohr radius. The process is straightforward because the normalization procedure yields a pure number, one. The integrals needed to evaluate the expectation value of the energy require that a collection of constants with the dimensions of energy be extracted. We might choose

$E_{1S} = -\frac{e^2}{8\pi\epsilon_0 a_0} = -13.6 \text{ eV}$. Chemists use *atomic units* in which lengths are measured in

units of the Bohr radius, but energies are measured in units of the Hartree $= \frac{e^2}{4\pi\epsilon_0 a_0} =$

27.2 eV. Find the dimensionless forms of I_3 and I_4 that are appropriate when the energy is measured in units of E_{1s} .

12.) The approximate S for maximum bonding in the model is about 2.5. Use the value and compute the probability to find the electron in the region of space $\frac{1}{2}\pi < \theta < \pi$ in both ψ_{EVEN} (ψ_+) and ψ_{ODD} . Use the results to find the probabilities that the electron is *between* the protons in each of the two states. The electron is to be considered as between the protons if might be measured to be in the region $0 < z < S = 2.5 a_0$. Include a figure as part of your solution.

13.) **Mega-Problem:** Make an estimate of the ground state energy of the H^- , the 1 minus hydrogen atom ion (one proton with two electrons). Make your estimate by applying in sequence all the methods applied to the calculation of the ground state energy of helium. Compute the expectation value of r for one of the electrons in your *final* approximate ground state.

Wild guesses: $E_{\text{GS}} < -0.478 \text{ eV}$ and $\langle r \rangle = 16 a_0$. confidence: Low

Additions:

14.) Estimate the energy of the 1s 2s first excited state of helium. Use a $Z = 2$ hydrogenic wavefunction for the 1s electron and a variable parameter for the effective nuclear charge in the case of the 2s electron. Include the kinetic, electron-nuclear Coulomb and electron-electron Coulomb terms in the energy. The variation 2S state is assumed to be orthogonal to the 1s state (with $Z = 2$).

$$\psi_{1s} = A e^{-2r/a_0} \text{ and } \psi_{2s} = B[1 - \beta (r/a_0)] e^{-\gamma r/a_0}$$

a.) Find the normalized versions of ψ_{1s} and ψ_{2s} .

b.) Show that $\beta = (2 + \gamma)/3$ is required in order that $\langle \psi_{1s} | \psi_{2s} \rangle = 0$. That is, the value of β is set once γ is known. The only free parameter in the wavefunction is β .

c.) Vary γ to find the lowest overall energy state for this family of wavefunctions. What is the energy? Compare it to the 3S and 1S states.

Major Point and Warning: This exchange behavior impacts energies if the particles interact via a separation dependent potential. **BUT** it is wrong to believe that the only energy contribution arises through the direct potential interaction channel. The wavefunctions may be required to *bend more or less* in the case of odd under spatial exchange which could add a kinetic energy contribution to the net energy shift. Use the full hamiltonian when you evaluate energies.

15.) Estimate the energy splitting between the 3S and 1S metastable states of helium. Use a $Z = 2$ hydrogenic wavefunction for the 1s electron and $Z = 1$ for the 2s electron. Evaluate the exchange term for the singlet and triplet cases. **DO NOT** assume that the only contribution is from the $e-e$ Coulomb interaction. Use the full hamiltonian.

$$\begin{aligned} & \int u^2 (2 - 2u/3) \text{Exp}[-u] \\ & \left(\int v^2 (2 - 2v/3) \text{Exp}[-v], \{v,0,u\} \right) / u \\ & + \int v (2 - 2v/3) \text{Exp}[-v], \{v,u,\text{Infinity}\} \right) \int u,0,\text{Infinity} \} = 1/3 \\ & \text{Implies } \Delta V_{\text{int}} = 1.2 \text{ eV for } Z = 2 \text{ } ^2S \text{ state} \end{aligned}$$

$$\begin{aligned} & \int u^2 (1 - 5u/6) \text{Exp}[-u] \\ & \left(\int v^2 (1 - 5v/6) \text{Exp}[-v], \{v,0,u\} \right) / u \\ & + \int v (1 - 5v/6) \text{Exp}[-v], \{v,u,\text{Infinity}\} \right) \int u,0,\text{Infinity} \} = 85/48. \\ & \text{Implies } \Delta V_{\text{int}} = 0.9 \text{ eV for } Z = 1 \text{ } ^2S \text{ state} \end{aligned}$$

16.) Estimate the energy splitting between the 3S and 1S metastable states of helium. Use a $Z = 2$ hydrogenic wavefunction for the 1s electron and the wavefunction found in 14 for the 2s electron. Evaluate the exchange term for the singlet and triplet cases. Repeat using the effective charge found in the previous problem. **DO NOT** assume that the only contribution is from the $e-e$ Coulomb interaction. Use the full hamiltonian.

17.) Use the Hylleraas trial function to estimate the ground state energy of a neutral helium atom. Hylleraas proposed $\phi(\vec{r}_1, \vec{r}_2) = A e^{-\beta r_1/a_0} e^{-\beta r_2/a_0} (1 + b r_{12})$. The function is first normalized to find $A(\beta, b)$. The energy is then evaluated as a function of β and b . That energy is then minimized with respect to variations of the parameters β and b . The best values found are: $\beta = 1.849$ and $b = 0.364/a_0$. The ground state energy for those values is -78.7 eV .

18.) The H^- ion (called the hydride ion) is a bound state on two electrons around a proton. It has recently been adopted in popular culture as a health supplement with powers rivaling those of magnetic bracelets. Hydride ions exist in liquids and in interstitials in materials. Examine the case of the isolated hydride ion using a trial function of the form proposed by Hylleraas for the ground state of helium. If you find a negative energy, then the hydride ion can exist, and it would have a ground state energy less than that predicted by the ‘Hylleraas’ model.

The binding energy of a hydride ion is estimated to be $> 0.7 \text{ eV}$. The ion *may* have a weakly bound excited state. (G. F. W. Drake, *Phys. Rev. Lett.* **24**, 126 (1970).)

19.) Show that small changes in the parameterization do not change the results.

Suppose that one chose $\psi(x) = A e^{-bx^2}$ while another chose $\phi(x) = A e^{-x^2/a^2}$. Basically, the exponential length scale is being set in either case. In particular $b = b(a) = a^{-2}$.

Show that if $\frac{d}{db}\langle E \rangle = 0$ then $\frac{d}{da}\langle E \rangle = 0$ and hence the same final results will be found.

References:

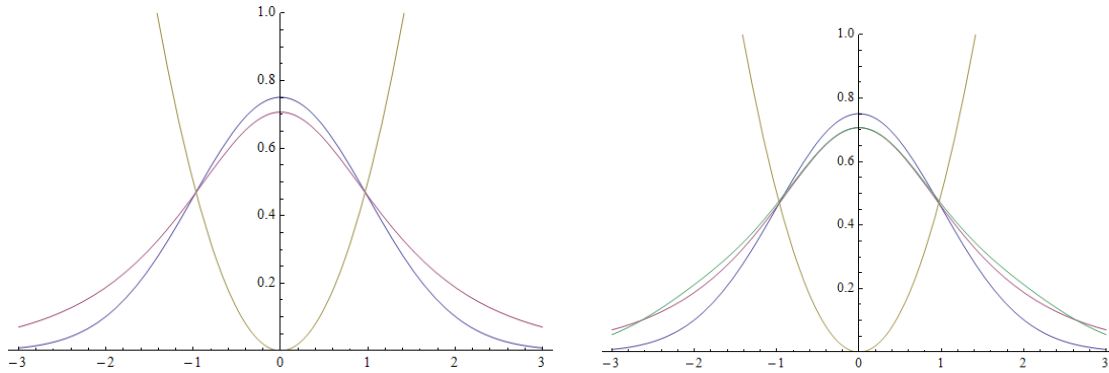
1. David J. Griffiths, *Introduction to Quantum Mechanics*, 2nd Edition, Pearson Prentice Hall (2005).
2. Richard Fitzpatrick, *Quantum Mechanics Note Set*, University of Texas.
2. Ira N. Levine, *Quantum Chemistry*, 5th Edition, Pearson Prentice Hall (2000).

Problem Comments:

This comment is preliminary. The plots should be reworked to insure that the correct model values were used. Add normalizations at all levels.

CG7.7 Variation using $\text{sech}[cx]$ as the trial function for a quantum harmonic oscillator.

`Plot[{Sqrt[Sqrt[1/Pi]]Exp[-x^2/2], Sech[x]/Sqrt[2], x^2/2},{x,-3,3},PlotRange -> {0,1}]`



`a = 0.155; b = 0.085; Plot[{Sqrt[Sqrt[1/Pi]]Exp[-x^2/2], Sech[x]/Sqrt[2], x^2/2, Sqrt[Sqrt[1/Pi]]Exp[-x^2/2]+(0.155) ((4 x^2 - 2)Sqrt[Sqrt[1/Pi]/8]Exp[-x^2/2]) +(0.085) ((12-48 x^2+16 x^4)Sqrt[Sqrt[1/Pi]/384]Exp[-x^2/2]/Sqrt[1 + a^2+b^2])}, {x,-3,3}, PlotRange -> {0,1}]`

The minimized energy for the sech trial function is $0.5236 \hbar\omega$. On the left, the sech and the exact ground state are plotted. The energy is correct to within 5%, but the wave variation derived function is not a great approximation to the true ground state wavefunction.

In the second plot, $\psi_0 + 0.155 \psi_2 + 0.085 \psi_4$ is normalized and plotted. That normalized state has an energy of $0.522 \hbar\omega$.