Chapter 15
Variational Approach

The variational approach is a powerful technique for obtaining ground state (and, to a lesser extent, excited state) energies. The idea behind the method is simple—guess a trial wave function. That is, choose a trial function

$$\psi_t(\mathbf{r}) \equiv \psi_t(\mathbf{r}, \alpha_1, \alpha_2, \ldots \alpha_N), \tag{15.1}$$

with as many free parameters $(\alpha_1, \alpha_2, \ldots \alpha_N)$ as you wish and use it to calculate the ground state energy. The trial function should be consistent with the boundary conditions of the problem. In that case, $\psi_t(\mathbf{r})$ can be expanded in terms of the *exact* eigenfunctions of a Hamiltonian $\hat{H}$ as

$$\psi_t(\mathbf{r}) = \sum_n c_n \psi_n(\mathbf{r}). \tag{15.2}$$

Now form

$$\begin{aligned} E &= \frac{\int \psi_t^*(\mathbf{r}) \hat{H} \psi_t(\mathbf{r}) d\mathbf{r}}{\int \psi_t^*(\mathbf{r}) \psi_t(\mathbf{r}) d\mathbf{r}} \\ &= \frac{\sum_{n,n'} \int \psi_{n'}^*(\mathbf{r}) \hat{H} \psi_n(\mathbf{r}) c_{n'}^* c_n d\mathbf{r}}{\sum_{n,n'} \int \psi_{n'}^*(\mathbf{r}) \psi_n(\mathbf{r}) c_{n'}^* c_n d\mathbf{r}} \\ &= \frac{\sum_n E_n \left|c_n\right|^2}{\sum_n \left|c_n\right|^2} \geq E_0, \end{aligned} \tag{15.3}$$

where E_0 is the ground state energy [i.e., the sum starts from $n = 0$)]. The denominator can be set equal to unity if the trial wave function is normalized. By varying the parameters $\alpha_1, \alpha_2, \ldots \alpha_N$ such that E is a minimum, you can get an *upper* bound on the ground state energy of the system since $E_0 \leq E$. If you know something about the wave functions and can choose a wave function that is

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orthogonal to the ground state wave function, then you can also use this method to estimate the energy of the first excited state. For example, if the ground state is an $\ell = 0$ state, you can choose a trial wave function for the first excited state that corresponds to a $\ell = 1$ state, implying that $c_0 = 0$. Most of the time the variational method is used to obtain ground state energies.

The advantage of the variational approach over perturbation theory is that the exact Hamiltonian is used. That is, sometimes the Hamiltonian cannot be written as $\hat{H} = \hat{H}_0 + \hat{H}'$ in any obvious fashion. The disadvantage of the method is that it depends on how good your guess is. There is no simple way to estimate its accuracy. Generally speaking you keep adding parameters to your trial wave function and see if the energy converges.

Another advantage of the variational approach is that if you are a fairly good guesser, you are rewarded with an excellent approximation to the energy. Imagine you guess

$$\psi_t(\mathbf{r}) = \psi_n(\mathbf{r}) + \delta\psi_n(\mathbf{r}), \tag{15.4}$$

where $\psi_n(\mathbf{r})$ is the exact wave function. Then

$$\begin{aligned}
E &= \frac{\int \psi_t^*(\mathbf{r})\hat{H}\psi_t(\mathbf{r})d\mathbf{r}}{\int \psi_t^*(\mathbf{r})\psi_t(\mathbf{r})d\mathbf{r}} \\
&= \frac{\int \left[\psi_n(\mathbf{r}) + \delta\psi_n(\mathbf{r})\right]^* \hat{H} \left[\psi_n(\mathbf{r}) + \delta\psi_n(\mathbf{r})\right] d\mathbf{r}}{\int \left[\psi_n(\mathbf{r}) + \delta\psi(\mathbf{r})\right]^* \left[\psi_n(\mathbf{r}) + \delta\psi_n(\mathbf{r})\right] d\mathbf{r}} \\
&= \frac{E_n + E_n \int \left\{\psi_n^*(\mathbf{r})\delta\psi_n(\mathbf{r}) + \left[\delta\psi_n(\mathbf{r})\right]^* \psi_n(\mathbf{r})\right\} d\mathbf{r}}{1 + \int \left\{\psi_n^*(\mathbf{r})\delta\psi_n(\mathbf{r}) + \left[\delta\psi_n(\mathbf{r})\right]^* \psi_n(\mathbf{r})\right\} d\mathbf{r}} + O\left(\left[\delta\psi_n(\mathbf{r})\right]^2\right) \\
&= E_n + O\left(\left[\delta\psi_n(\mathbf{r})\right]^2\right);
\end{aligned} \tag{15.5}$$

that is, the error is of order $[\delta\psi_n(\mathbf{r})]^2$.

Of course there may be no way you can guess the wave function. However, if the Hamiltonian can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}', \tag{15.6}$$

where $\hat{H}'$ is a small perturbation to $\hat{H}_0$, you can use the wave function obtained from perturbation theory that is correct to second order in $\hat{H}'$ as a trial function to calculate the energy correct to order $\hat{H}'^4$.

I will give two examples of calculations using the variational approach. First, suppose that

$$\hat{H} = \frac{\hbar\omega}{2}\left(-\frac{d^2}{d\xi^2} + \xi^2\right), \tag{15.7}$$

where

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x \tag{15.8}$$

is a dimensionless variable. I guess

$$\psi_t = e^{-\alpha\xi^2} \tag{15.9}$$

since I know the ground state must have even parity. Then I can use

$$\frac{\int_{-\infty}^{\infty} e^{-\alpha\xi^2}\xi^2 e^{-\alpha\xi^2} d\xi}{\int_{-\infty}^{\infty} e^{-2\alpha\xi^2} d\xi} = \frac{1}{4\alpha} \tag{15.10}$$

and calculate

$$\begin{aligned}
E &= \frac{\int_{-\infty}^{\infty} \psi_t^*(x)\hat{H}\psi_t(x)dx}{\int_{-\infty}^{\infty} \psi_t^*(x)\psi_t(x)dx} \\
&= \frac{\frac{\hbar\omega}{2}\int_{-\infty}^{\infty} e^{-\alpha\xi^2}\left(-\frac{d^2}{d\xi^2} + \xi^2\right) e^{-\alpha\xi^2} d\xi}{\int_{-\infty}^{\infty} e^{-2\alpha\xi^2} d\xi} \\
&= \frac{\frac{\hbar\omega}{2}\int_{-\infty}^{\infty} e^{-\alpha\xi^2}\left(2\alpha - 4\alpha^2\xi^2 + \xi^2\right) e^{-\alpha\xi^2} d\xi}{\int_{-\infty}^{\infty} e^{-2\alpha\xi^2} d\xi} \\
&= \hbar\omega\left(\frac{\alpha}{2} + \frac{1}{8\alpha}\right) \geq E_0.
\end{aligned} \tag{15.11}$$

I minimize this expression with respect to α,

$$\frac{dE}{d\alpha} = \hbar\omega\left(\frac{1}{2} - \frac{1}{8\alpha^2}\right) = 0; \tag{15.12a}$$

$$\alpha = 1/2. \tag{15.12b}$$

For this value of α,

$$\psi_t = e^{-\xi^2/2} \tag{15.13a}$$

$$E = \hbar\omega/2 \geq E_0. \tag{15.13b}$$

I ended up with the exact wave function and the exact ground state energy since I made a perfect guess! On the other hand, the results associated with some other guesses are

$$\psi_t = e^{-\beta\xi^4}; \quad \beta = 1/6; \quad E = 0.585\hbar\omega; \tag{15.14a}$$

$$\psi_t = \operatorname{sech}(\beta\xi); \quad \beta = \sqrt{\frac{\pi}{2}} = 1.2533; \quad E = 0.524\hbar\omega; \tag{15.14b}$$

$$\psi_t = \frac{1}{\beta^2 + \xi^2}; \quad \beta = \frac{1}{2^{1/4}} = 0.841; \quad E = 0.707\hbar\omega, \tag{15.14c}$$

where the value of β in each case is chosen to minimize the energy. Thus, how well I do depends on my guess. There is no easy way to estimate the error.

As a second example, I consider

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + mg\,|x| \tag{15.15}$$

and use a trial wave function

$$\psi_t = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}, \tag{15.16}$$

which is normalized. Then

$$\begin{aligned} E &= \int_{-\infty}^{\infty} \psi_t^*(x)\hat{H}\psi_t(x)dx \\ &= \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + mg\,|x|\right) e^{-\alpha x^2} dx \\ &= \frac{\hbar^2\alpha}{2m} + \frac{mg}{\sqrt{2\pi\alpha}} \geq E_0. \end{aligned} \tag{15.17}$$

Setting

$$\frac{dE}{d\alpha} = \left(\frac{\hbar^2}{2m} - \frac{mg}{2\alpha\sqrt{2\pi\alpha}}\right) = 0; \tag{15.18a}$$

$$\alpha = \left(\frac{m^2 g}{\sqrt{2\pi}\hbar^2}\right)^{2/3}, \tag{15.18b}$$

which leads to

$$E = \frac{3}{2\,(2\pi)^{1/3}}\left(mg^2\hbar^2\right)^{1/3} = 0.813\left(mg^2\hbar^2\right)^{1/3} \geq E_0, \tag{15.19}$$

whereas the exact eigenvalue (obtained from solving the Schrödinger equation in terms of Airy functions) is $E_0 = 0.809\left(mg^2\hbar^2\right)^{1/3}$. The calculated upper bound for the ground state energy is almost equal to the exact eigenenergy, since the Gaussian trial function is a good approximation to the exact ground state wave function.

15.1 Combining Perturbation Theory and the Variational Approach

The variational approach gives an upper bound for the ground state energy of a quantum system. It is sometimes possible to use conventional perturbation theory to get a *lower* bound for the ground state energy. In this way you can get both upper and lower bounds for the energy. Suppose you have a quantum system for which the Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}'. \tag{15.20}$$

It is assumed that you know the eigenenergies and eigenfunctions of $\hat{H}_0$ and that $\hat{H}'$ can be considered as a perturbation. I denote the ground state energy by $E_g^{(0)}$ and the change in the ground state energy resulting from the perturbation by ΔE_g. Moreover I assume that the first order correction resulting from the perturbation vanishes, $H'_{gg} = 0$. Then the change in the ground state energy, calculated using perturbation theory, is given approximately by

$$\begin{aligned} \Delta E_g &= \sum\nolimits'_{n\neq g} \frac{\left|H'_{gn}\right|^2}{E_g^{(0)} - E_n^{(0)}} \geq \frac{1}{E_g^{(0)} - E_1^{(0)}} \sum\nolimits'_{n\neq g} \left|H'_{gn}\right|^2 \\ &= \frac{1}{E_g^{(0)} - E_1^{(0)}} \left[\left(\hat{H}'\right)^2\right]_{gg}. \end{aligned} \tag{15.21}$$

where $E_1^{(0)}$ is the energy of the lowest energy state for which $H'_{g1} \neq 0$ (this choice leads to the most restrictive lower bound). The completeness relation, $\sum_n \left|H'_{gn}\right|^2 = 1$, along with the fact that $H'_{gg} = 0$, was used in the last step of the derivation. Recall that the prime on the summation symbol is a shorthand notation for a sum over bound states and an integral over continuum states. To illustrate the technique, I calculate both upper and lower bounds for the van der Waals interaction energy between two ground state hydrogen atoms.

The Hamiltonian in this case is given by Eq. (15.20) with

$$\hat{H}_0 = -\frac{\hbar^2\nabla_1^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2\nabla_2^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r_2} \tag{15.22}$$

and

$$H' = -e^2\frac{2z_1z_2 - x_1x_2 - y_1y_2}{4\pi\epsilon_0 R^3} \tag{15.23}$$

(even though H' is an operator, I leave the "hat" off of it since all calculations are carried out in the coordinate representation where the operators in $\hat{H}'$ are replaced by their functional values). The ground state has $n_1 = n_2 = 1$ and the lowest energy state for which $H'_{gn} \neq 0$ has $n_1 = n_2 = 2$.

The perturbation theory calculation is virtually identical to that in Chap. 14 with

$$E_g^{(0)} = E_{1,1}^{(0)} = -\frac{e^2}{4\pi\epsilon_0 a_0} \tag{15.24a}$$

$$E_1^{(0)} = E_{2,2}^{(0)} = -\frac{e^2}{4\pi\epsilon_0 a_0}\frac{1}{4}, \tag{15.24b}$$

where $E_{n_1,n_2}^{(0)}$ is the unperturbed energy for one atom having quantum number n_1 and the other n_2. The only difference from Chap. 14 is that I need to replace $1/\left(E_{1,1}^{(0)}\right)$ appearing in Eq. (14.41) by $1/\left(E_{1,1}^{(0)} - E_{2,2}^{(0)}\right)$, which multiplies the final result, Eq. (14.44), by a factor 4/3, namely

$$\Delta E_g = \Delta E_{1,1}^{(2)} \geq -\frac{8a_0^5 e^2}{4\pi\epsilon_0 R^6}. \tag{15.25}$$

Using a variational approach, I assume an (unnormalized) wave function of the form

$$\psi_t(\mathbf{r}_1, \mathbf{r}_2) = \psi_g(r_1)\psi_g(r_2)\left(1 + \beta H'\right) \tag{15.26}$$

where $\psi_g(r) = \psi_{100}(r)$ is the ground state wave function of an isolated hydrogen atom and H' is the perturbation energy, which is a function of $\mathbf{r}_1$ and $\mathbf{r}_2$. From the variational principle I know that

$$E_g + \Delta E_g \leq \frac{\int \psi_t^*(\mathbf{r}_1, \mathbf{r}_2)\left(\hat{H}_0 + H'\right)\psi_t(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2}{\int \psi_t^*(\mathbf{r}_1, \mathbf{r}_2)\psi_t(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2}. \tag{15.27}$$

I substitute Eqs. (15.22) and (15.23) into Eq. (15.27) and use the fact that

$$\int \left|\psi_g(r_1)\psi_g(r_2)\right|^2 H' d\mathbf{r}_1 d\mathbf{r}_2 = 0 \tag{15.28}$$

and that the unperturbed ground state wave functions are real to obtain

$$\begin{aligned} E_g &= E_g^{(0)} + \Delta E_g \\ &\leq \frac{\int \left(1 + \beta H'\right)\psi_g(r_1)\psi_g(r_2)\left(\hat{H}_0 + H'\right)\psi_g(r_1)\psi_g(r_2)\left(1 + \beta H'\right)d\mathbf{r}_1 d\mathbf{r}_2}{\int \left|\psi_g(r_1)\psi_g(r_2)\right|^2 (1 + \beta H')^2 d\mathbf{r}_1 d\mathbf{r}_2} \\ &= \frac{E_g^{(0)} + \int \psi_g(r_1)\psi_g(r_2)\left[2\beta H'^2 + \beta^2 H'\hat{H}_0 H'\right]\psi_g(r_1)\psi_g(r_2)d\mathbf{r}_1 d\mathbf{r}_2}{\int \left|\psi_g(r_1)\psi_g(r_2)\right|^2\left(1 + \beta^2 H'^2\right)d\mathbf{r}_1 d\mathbf{r}_2}. \end{aligned} \tag{15.29}$$

keeping terms up to order H'^2 only. The contributions to

$$\int \psi_g(r_1)\psi_g(r_2)\left[\beta^2 H'\hat{H}_0 H'\right]\psi_g(r_1)\psi_g(r_2)d\mathbf{r}_1 d\mathbf{r}_2, \tag{15.30}$$

from all the cross terms in the integrand (that is, terms varying as $z_1z_2x_1x_2$, $z_1z_2y_1y_2$, $x_1x_2y_1y_2$) vanish. Thus, Eq. (15.30) consists of a sum of three terms and each term contains a factor of the form

$$\int \psi_g(r)r_\alpha\left(-\frac{\hbar^2\nabla^2}{2m_e}-\frac{e^2}{4\pi\epsilon_0 r}\right)\left[r_\alpha\psi_g(r)\right]d\mathbf{r}, \tag{15.31}$$

where $r_\alpha = x$, y, or z. It is possible to show that all such integrals vanish as well. For example,

$$\begin{aligned}
&\int \psi_g(r)z\left(-\frac{\hbar^2\nabla^2}{2m_e}-\frac{e^2}{4\pi\epsilon_0 r}\right)\left[z\psi_g(r)\right]d\mathbf{r}\\
&=\frac{1}{\pi a_0^3}\int r\cos\theta e^{-r/a_0}\left(-\frac{\hbar^2\nabla^2}{2m_e}-\frac{e^2}{4\pi\epsilon_0 r}\right)\left[r\cos\theta e^{-r/a_0}\right]d\mathbf{r}\\
&=\frac{2}{a_0^3}\int_0^\infty r^2dr\int_0^\pi \sin\theta d\theta e^{-r/a_0}r\cos\theta\\
&\quad\times\left[-\frac{\hbar^2\cos\theta}{2m_e}\left(\frac{r-4a_0}{a_0^2}\right)e^{-r/a_0}-\frac{e^2\cos\theta}{4\pi\epsilon_0}e^{-r/a_0}\right]\\
&=\left(\frac{\hbar^2}{2m_e}-\frac{e^2a_0}{8\pi\epsilon_0}\right)=0.
\end{aligned} \tag{15.32}$$

As a consequence, Eq. (15.29) reduces to

$$\begin{aligned}
E_g^{(0)}+\Delta E_g &\le \frac{E_g^{(0)}+2\beta\int\psi_g(r_1)\psi_g(r_2)H'^2\psi_g(r_1)\psi_g(r_2)d\mathbf{r}_1d\mathbf{r}_2}{1+\beta^2\int\left|\psi_g(r_1)\psi_g(r_2)\right|^2H'^2d\mathbf{r}_1d\mathbf{r}_2}\\
&\approx E_g^{(0)}(1-\beta^2K)+2\beta K,
\end{aligned} \tag{15.33}$$

where

$$K=\int\psi_g(r_1)\psi_g(r_2)H'^2\psi_g(r_1)\psi_g(r_2)d\mathbf{r}_1d\mathbf{r}_2=\frac{6a_0^6\left(E_g^{(0)}\right)^2}{R^6}. \tag{15.34}$$

Minimizing with respect to β, I find

$$\beta = 1/E_g^{(0)}, \tag{15.35}$$

such that

$$\Delta E_g \leq K/E_g^{(0)} = \frac{6a_0^6 E_g^{(0)}}{R^6} = -\frac{6e^2 a_0^5}{4\pi\epsilon_0 R^6}. \tag{15.36}$$

The perturbation and variational results can be combined to provide both upper and lower limits for the shift,

$$-\frac{8e^2 a_0^5}{4\pi\epsilon_0 R^6} \leq \Delta E_g \leq -\frac{6e^2 a_0^5}{4\pi\epsilon_0 R^6}. \tag{15.37}$$

The result from a multi-parameter variational approach is $\Delta E \approx -\frac{6.50 e^2 a_0^5}{4\pi\epsilon_0 R^6}$.[1]

15.2 Helium Atom

The Hamiltonian for the helium atom is

$$\hat{H} = \frac{\hat{p}_1^2}{2m_e} + \frac{\hat{p}_2^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}\right) \tag{15.38}$$

where the two electrons are denoted by 1 and 2. Although the last term, which represents the electron–electron interaction is not much smaller than the attractive terms, I can still try to treat it by perturbation theory setting

$$\hat{H}_0 = \frac{\hat{p}_1^2}{2m_e} + \frac{\hat{p}_2^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right); \tag{15.39a}$$

$$H' = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{r}_1|}, \tag{15.39b}$$

where $Z = 2$ is the nuclear charge. The Hamiltonian $\hat{H}_0$ is the sum of two Hamiltonians, one for each particle. Each of these Hamiltonians is identical to that of hydrogen if the replacement $e^2 \rightarrow Ze^2 = 2e^2$ is made. This implies that the Bohr radius a_0 (which varies as $1/e^2$) must be replaced by

$$a = a_0/2 \tag{15.40}$$

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[1] Linus Pauling and J. Y. Beach, *The van der Waals Interaction of Hydrogen Atoms*, Physical Review **47**, 686–692 (1935).

in the hydrogenic wave functions. As a consequence, the unperturbed ground state wave function is

$$\psi^{(0)}\left(r_1,r_2\right)=\psi_g\left(r_1\right)\psi_g\left(r_2\right)=\frac{1}{\pi a^3}e^{-(r_1+r_2)/a} \tag{15.41}$$

and the unperturbed ground state energy is

$$E_g^{(0)}=2\left(\frac{-Ze^2}{8\pi\epsilon_0 a}\right)=2\left(\frac{-Ze^2}{4\pi\epsilon_0 a_0}\right)=-108.8\text{ eV}=8E_0, \tag{15.42}$$

where E_0 is the ground state energy of hydrogen. The ground state energy of helium, calculated using perturbation theory, is

$$E_g\approx 8E_0+\frac{e^2}{4\pi\epsilon_0}\int d\mathbf{r}_1\int d\mathbf{r}_2\frac{1}{\pi^2a^6}e^{-2(r_1+r_2)/a}\frac{1}{\left|\mathbf{r}_2-\mathbf{r}_1\right|}. \tag{15.43}$$

The integral in Eq. (15.43) can be evaluated by expanding $\frac{1}{|\mathbf{r}_2-\mathbf{r}_1|}$ in terms of spherical harmonics as[2]

$$\frac{1}{\left|\mathbf{r}_2-\mathbf{r}_1\right|}=4\pi\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{1}{2\ell+1}\frac{r_<^{\ell}}{r_>^{\ell+1}}\left[Y_\ell^m\left(\theta_1,\phi_1\right)\right]^*Y_\ell^m\left(\theta_2,\phi_2\right), \tag{15.44}$$

where $r_<$ is the lesser of r_1 and r_2 while $r_>$ is the greater of r_1 and r_2. With this expansion, only the $\ell=0$ term in the sum in Eq. (15.44) contributes to the integrals in Eq. (15.43) owing to the fact that

$$\int d\Omega Y_\ell^m\left(\theta,\phi\right)=\sqrt{4\pi}\delta_{\ell,0}\delta_{m,0}. \tag{15.45}$$

As a consequence, using Eqs. (15.43), (15.44), and (15.40), I find

$$\begin{aligned}E_g&\approx 8E_0+\frac{16e^2}{4\pi\epsilon_0a^6}\int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2\frac{e^{-2(r_1+r_2)/a}}{r_>}\\&=8E_0+\frac{16e^2}{4\pi\epsilon_0a^6}\int_0^\infty r_1^2dr_1\int_0^{r_1} r_2^2dr_2\frac{e^{-2(r_1+r_2)/a}}{r_1}\\&\quad+\frac{16e^2}{4\pi\epsilon_0a^6}\int_0^\infty r_1^2dr_1\int_{r_1}^{\infty} r_2^2dr_2\frac{e^{-2(r_1+r_2)/a}}{r_2}\\&=8E_0+\frac{16e^2}{4\pi a\epsilon_0}\left(\frac{5}{256}+\frac{5}{256}\right)=E_g^{(0)}+\frac{5}{8}\frac{e^2}{4\pi a\epsilon_0}\\&=8E_0-2.5E_0=-74.8\text{ eV}.\end{aligned} \tag{15.46}$$

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[2] See, for example, John David Jackson, *Classical Electrodynamics, Third Edition* (John Wiley and Sons, Inc., New York, 1999) Sect. 3.6.

The experimental result is -78.9 eV so I have done better than might be expected.

I can use the variational method to get an even better estimate. Since each electron is partially shielded from the nucleus by the other electron, I try a (normalized) trial wave function of the form

$$\psi_t(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\pi a^3} e^{-(r_1+r_2)/a} \tag{15.47}$$

where

$$a = a_0/Z_{\text{eff}} \tag{15.48}$$

and Z_{eff} is the parameter to be varied. I expect to find $1 < Z_{\text{eff}} < 2$, since Z_{eff} is the shielded nuclear charge seen by each electron. The Hamiltonian (15.38) can be written as $\hat{H} = \hat{H}_1 + \hat{H}_2$, with

$$\hat{H}_1 = \frac{\hat{p}_1^2}{2m_e} + \frac{\hat{p}_2^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z_{\text{eff}}}{r_1} + \frac{Z_{\text{eff}}}{r_2}\right); \tag{15.49a}$$

$$H_2 = \frac{e^2}{4\pi\epsilon_0 \left|\mathbf{r}_2 - \mathbf{r}_1\right|} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2-Z_{\text{eff}}}{r_1} + \frac{2-Z_{\text{eff}}}{r_2}\right), \tag{15.49b}$$

In this form, the the trial wave function is the ground state eigenfunction of the Hamiltonian $\hat{H}_1$, while H_2 can be considered as a small perturbation. Since $\hat{H}_1$ corresponds to a Hamiltonian in which each electron moves independently in the field of a nucleus having change Z_{eff}, it follows immediately that

$$\iint d^3r_1 d^3r_2 \psi_t^*(\mathbf{r}_1,\mathbf{r}_2)\hat{H}_1\psi_t(\mathbf{r}_1,\mathbf{r}_2) = -\frac{2Z_{\text{eff}}e^2}{8\pi\epsilon_0 a} = -\frac{2Z_{\text{eff}}^2 e^2}{8\pi\epsilon_0 a_0}. \tag{15.50}$$

Moreover, I have already shown in Eq. (15.46) that

$$\iint d^3r_1 d^3r_2 \psi_t^*(\mathbf{r}_1,\mathbf{r}_2)\frac{e^2}{4\pi\epsilon_0\left|\mathbf{r}_2-\mathbf{r}_1\right|}\psi_t(\mathbf{r}_1,\mathbf{r}_2) = \frac{5}{8}\frac{e^2}{4\pi a\epsilon_0} = \frac{5}{8}\frac{Z_{\text{eff}}e^2}{4\pi\epsilon_0 a_0}. \tag{15.51}$$

Thus I need only calculate

$$\begin{aligned} &-\frac{e^2}{4\pi\epsilon_0}\iint d^3r_1 d^3r_2 \psi_t^*(\mathbf{r}_1,\mathbf{r}_2)\left(\frac{2-Z_{\text{eff}}}{r_1} + \frac{2-Z_{\text{eff}}}{r_2}\right)\psi_t(\mathbf{r}_1,\mathbf{r}_2) \\ &= -\frac{2e^2\left(2-Z_{\text{eff}}\right)}{4\pi\epsilon_0 a} = -\frac{e^2 Z_{\text{eff}}\left(2-Z_{\text{eff}}\right)}{2\pi\epsilon_0 a_0}. \end{aligned} \tag{15.52}$$

Combining Eqs. (15.50)–(15.52), I find

$$\begin{aligned}
E &= \iint d^3r_1 d^3r_2 \psi_t^* (\mathbf{r}_1, \mathbf{r}_2) \hat{H} \psi_t (\mathbf{r}_1, \mathbf{r}_2) \\
&= \frac{e^2}{8\pi a_0 \epsilon_0} \left(-2Z_{\text{eff}}^2 + \frac{5}{4} Z_{\text{eff}} - 4Z_{\text{eff}} (2 - Z_{\text{eff}}) \right) \\
&= |E_0| \left(2Z_{\text{eff}}^2 - \frac{27}{4} Z_{\text{eff}} \right). \qquad (15.53)
\end{aligned}$$

Minimizing this expression with respect to Z_{eff}, I find $Z_{\text{eff}} = 27/16$ and

$$E_g \le 5.695 E_0 = -77.46 \text{ eV}, \qquad (15.54)$$

which is about 2% from the experimental value of −78.9 eV. By writing the Hamiltonian as the sum of the two terms given in Eqs. (15.49), I was able to obtain a good guess for the ground state wave function.

15.3 Summary

The variational method is an extremely powerful method for obtaining the ground state energy of quantum systems. It is the preferred method for approximating the ground state energy of atoms such as helium. In certain cases, the variational method can be combined with perturbation theory to obtain both lower and upper bounds for the ground state energy.

15.4 Problems

1. Use the variational method to estimate the ground state energy E_0 of the potential $V = mgz$, $z > 0$; $V = \infty$, $z < 0$. Use the (normalized) trial wave function

$$\psi_t = \left(\frac{128\alpha^3}{\pi} \right)^{1/4} z e^{-\alpha z^2},$$

which satisfies the boundary condition at $z = 0$. Compare your answer with the value, $E_0 = 2.3381(\hbar^2 m g^2/2)^{1/3}$, obtained from an exact solution of the Schrödinger equation.

2–3. Use the variational method to estimate an upper bound $E_{0\mu}$ to the ground state energy of a particle having mass m moving in a potential $V(x) = V_0 \left| x/a \right|^{\mu}$, using a Gaussian trial wave function, $\psi_t = e^{-x^2/b^2}$. You can assume that μ, V_0, and a are greater than zero and use the fact that

$$\int_0^\infty z^\mu e^{-z^2} dz = \Gamma\left(\frac{1+\mu}{2}\right),$$

where Γ is the gamma function. Show that your result yields $E_{0\mu} = \hbar\omega_0/2$ when $\mu = 2$ and $V_0 = m\omega_0^2/2$. Why does the upper bound give the exact result in this case? Plot E_u/V_0 as a function of μ for $\beta^2 = 2mV_0a^2/\hbar^2 = 1$ and $0 \le \mu \le 5$. As $\mu \to \infty$, show that the potential approaches that of an infinite square well having width $2a$, but that the variational upper bound for the energy diverges. This shows that the choice of a Gaussian trial function for large values of μ is not a good choice. Why not? [Note: The exact ground state energies are given by $(E_{\text{exact}}/V_0)\,\beta^{\mu/(\mu+2)} = 1.0188, 1, 1.02295, 1.06036, 1.1023$ for $\mu = 1, 2, 3, 4, 5$.]

4. Repeat the previous calculation to estimate an upper bound $E_{1\mu}$ to the first excited state energy of a particle having mass m moving in the potential $V(x) = V_0\,|x/a|^\mu$, where μ is a positive integer. Now you must take a trial wave function that is consistent with the parity of the first excited state.

5. The Hamiltonian of a quantum system is given by $\hat{H} = \hat{H}_0 + \hat{H}'$, where $\hat{H}'$ can be considered as a perturbation. If the first order perturbation theory contribution to the ground state energy $E_0^{(1)}$ vanishes, prove that the second order correction satisfies

$$E_0^{(2)} \ge \frac{1}{E_0^{(0)} - E_1^{(0)}} \langle 0|\,\hat{H}'^2\,|0\rangle .$$

where $E_1^{(0)}$ is the first excited state energy. Use this result to get a lower bound for the Stark shift of the ground state of hydrogen when the atom is put into an external, constant electric field $\mathcal{E}$ along the z axis for which $\hat{H}' = e\mathcal{E}\hat{z}$. It turns out that the second order correction can be evaluated exactly and is given by

$$\Delta E = -\frac{9}{4}\,(4\pi\epsilon_0)\,\mathcal{E}^2 a_0^3.$$

How does your bound compare?

6–7. Now do a variational calculation to get an upper bound for the ground state energy of hydrogen in a static electric field. Since the field couples states with opposite parity, you can try a trial wave function of the form

$$\psi_t = \frac{e^{-r/a_0}}{\sqrt{\pi}a_0^{3/2}}(1 + \beta H'),$$

with $H' = e\mathcal{E}z$, and vary β to get the upper bound. Combine this result with that of Problem 15.5 and show that the exact solution fits between your two bounds.

[Hint: Follow the same procedure used in the text for the variational calculation of the van der Waals energy. You can use the fact that

$$\int \psi_t^* H' \hat{H}_0 \left[H' \psi_t \right] d\mathbf{r} = 0$$

(you can try to prove this if you wish, but it is not required)].

8. Starting with a (normalized) trial wave function $\psi_t = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$ with $\alpha > 0$, use the variational method to prove that, for a one-dimensional potential that is attractive in the sense that

$$\int_{-\infty}^{\infty} dx V(x) < 0$$

and for which $V(x) \to 0$ as $|x| \to \infty$, there is always a bound state (that is, an eigenstate with $E < 0$). [Hint: Consider the limit that $\alpha \sim 0$ for the energy associated with the trial wave function.]

9–10. Obtain an upper bound for the ground state energy of a particle having mass m confined to a square well potential having depth V_0 located between $-a/2$ and $a/2$. Use normalized trial wave functions

$$\psi_t^{(1)} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2};$$

$$\psi_t^{(2)} = \left(\frac{\alpha}{2}\right)^{1/2} \operatorname{sech}(\alpha x),$$

with $\alpha > 0$. In the limit that $\beta^2 = 2mV_0 a^2/\hbar^2 \ll 1$, show that the upper bound to the energy is always greater than that given in Eq. (6.96). Why does the second trial function provide a better limit for the exact energy?