PH253: The Variational Method

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The Variational Method

We have solved the Schrödinger equation for the hydrogen atom exactly, in principle. However, most problems we will deal with cannot be solved exactly, and we must resort to approximations. One method used to find the approximate ground state of a system (its lowest energy state) is the *variational method*. Essentially, we come up with a decent guess for what the ground state wave function should look like, leaving a few free parameters. The ground state of a system by definition has the lowest possible energy. By minimizing the energy of the system with our trial wavefunction with respect to variations in the free parameters, we can find the form of the trial wavefunction that is closest to the true ground state. Of course, the quality of the optimized trial wavefunction depends on how good our guess was in the first place. First, we will outline the basis of the variational method, and then discuss a few examples of how to make clever choices.

Take the time-independent Schrödinger equation as our starting point:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \equiv H\psi = E\psi \tag{1.1}$$

Here we have defined an *operator* $H \equiv -\frac{\hbar^2}{2m}\nabla^2 + V$. When H operates on the wave function, $H\psi$, it returns the energy of the state ψ. This operator is called the *hamiltonian* of the system. For now, however, it is mainly a matter of simplifying notation.

Now take our Schrödinger equation, $H\psi = E\psi$, and multiply both sides by ψ^* (or just ψ if ψ is purely real). Then integrate over all space (dV), and you have

$$\int \psi^* H\psi \, dV = \int \psi^* E\psi \, dV = E \int |\psi|^2 \, dV \tag{1.2}$$

If the ψ we choose are actually solutions for this particular H, the ratio

$$E[\psi] = \frac{\int \psi^* H\psi \, dV}{\int |\psi|^2 \, dV} \tag{1.3}$$

will equal the associated energy E. The problem is, of course, that we don't know what ψ is for the ground state, so these mathematical manipulations have been of little use. However, one thing we can rely on is that the true ground state wave function will minimize E. The best choice for ψ if we are not sure it is an exact solution, therefore, will be the one that gives the lowest value of $E[\psi]$. The general approach, therefore, is to assume a reasonable form for ψ that conforms to the basic symmetries of the problem, but with several adjustable parameters $c_1, c_2, \cdots$, and adjust these parameters to minimize $E[\psi]$. Using experimental constraints, such as the ionization energy or optical spectra, we can see how close our guess was. Somewhat more formally, the variational theorem states that for *any* trial wave function ψ, $E[\psi] \geqslant E$, where E is the true ground state energy.

That is, any choice of ψ we make that isn't a true ground state solution will give us back an energy higher than the ground state energy, but for a clever choice we can get arbitrarily close. .

1.1 Hydrogen-like atom

For a hydrogen-like ion, with Z protons and a single electron, the energy operator may be written as

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Zke^2}{r} \tag{1.4}$$

The simplest thing to do is presume that the wave function of such an ion in its lowest energy state is functionally the same as the hydrogen atom. This seems reasonable given that the symmetry of the problem is identical, the only real change is the strength of the nuclear attraction. It seems entirely likely that the only important change will be the characteristic distance involved - rather than being a_o, the Bohr radius, we should expect it is a decreasing function of Z. No problem: we'll let the length scale be an adjustable constant, and add a second one to handle normalization, i.e.:

$$\psi = c_1 e^{-c_2 r} \tag{1.5}$$

Here c_1 and c_2 are adjustable constants, with $1/c_2$ representing the characteristic length scale and c_1 handling normalization. How can we use the variational principle and the normalization condition to find the values of c_1 and c_2 that give the minimum energy for this trial wave function? Given the optimum values of c_1 and c_2, we can check compare our answer to the ionization energy of H and the second ionization energy of He ($Z{=}2$), $-54.5\,\text{eV}$. *Note that since the trial function is spherically symmetric,* $dV{=}4\pi r^2\,dr$ *and* $\nabla^2\psi{=}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)$.

The solution is somewhat lengthy, so it is best to tackle it systematically, step by step. First, let us calculate $\nabla^2\psi$:

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(-r^2 c_1 c_2 e^{-c_2 r}\right) = \frac{1}{r^2}\left(-2r c_1 c_2 e^{-c_2 r} + r^2 c_1 c_2^2 e^{-c_2 r}\right) \tag{1.6}$$

$$= c_1 c_2 e^{-c_2 r}\left(c_2 - \frac{2}{r}\right) \tag{1.7}$$

With that in hand, we can calculate $H\psi$, the energy operator H operating on the wave function ψ:

$$H\psi = -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Zke^2}{r}\psi = -\frac{\hbar^2}{2m}c_1 c_2 e^{-c_2 r}\left(c_2 - \frac{2}{r}\right) - \frac{kZe^2}{r}c_1 e^{-c_2 r} \tag{1.8}$$

Finally, we can calculate $\psi H\psi$ by multiplying through by the wavefunction:

$$\psi H \psi = -\frac{\hbar^2}{2m} c_1^2 c_2 e^{-2c_2 r} \left(c_2 - \frac{2}{r} \right) - \frac{kZe^2}{r} c_1^2 e^{-2c_2 r} \tag{1.9}$$

Next, we must integrate this over all space to find the numerator in our energy expression. Since the wavefunction is spherically symmetric, we may use $dV = 4\pi r^2$ and let r run from 0 to ∞:

$$\int \psi H \psi \, dV = -\frac{2\pi\hbar^2}{m} c_1^2 \int_0^\infty e^{-2c_2 r} r^2 \left(c_2^2 - \frac{2c_2}{r} \right) \, dr - 4\pi Z k e^2 c_1^2 \int_0^\infty r e^{-2c_2 r} \, dr \tag{1.10}$$

$$= -\frac{2\pi\hbar^2}{m} c_1^2 \left(c_2^2 \frac{2}{(2c_2)^3} - \frac{2c_2}{(2c_2)^2} \right) - Z k e^2 c_1^2 \frac{\pi}{(2c_2)^2} = \frac{\pi\hbar^2 c_1^2}{2mc_2} - \frac{Zke^2\pi c_1^2}{c_2^2} \tag{1.11}$$

The denominator of our energy expression is just a reflection of the normalization condition:

$$\int \psi^2 \, dV = \int_0^\infty 4\pi r^2 c_1^2 e^{-2c_2 r} \, dr = \frac{\pi c_1^2}{c_2^3} \tag{1.12}$$

Combining,

$$E[\psi] = \frac{\int \psi^* H \psi \, dV}{\int |\psi|^2 \, dV} = \frac{c_2^3}{\pi c_1^2} \left(\frac{\pi\hbar^2 c_1^2}{2mc_2} - \frac{Zke^2\pi c_1^2}{c_2^2} \right) = \frac{\hbar^2 c_2^2}{2m} - Zke^2 c_2 \tag{1.13}$$

The best we can do with this wave function is to minimize the energy with respect to our parameters c_1 and c_2. The energy does not explicitly depend on c_1 – sensible, since it is only a normalization constant – so we can minimize with respect to c_2 to find the minimum ground state energy with this trial wave function:

$$\frac{\partial E}{\partial c_2} = \frac{\hbar^2 c_2}{m} - Zke^2 = 0 \qquad \Longrightarrow \qquad c_2 = \frac{Zke^2 m}{\hbar^2} = \frac{Z}{a_o} \tag{1.14}$$

Here a_o is the Bohr radius. This is a sensible result: the characteristic length scale is a_o/Z, meaning the larger that Z is, the stronger the attraction of the electron to the nucleus, and the more short-range the wave function becomes. We can find c_1 from normalization, which gives

$$c_1 = \sqrt{\frac{Z^3}{\pi a_o^3}} \tag{1.15}$$

The best-case trial wavefunction is thus

$$\psi = \sqrt{\frac{Z^3}{\pi a_o^3}} e^{-Zr/a_o} \tag{1.16}$$

Given our value of c_2, we may find the energy of the ground state:

$$E = \frac{\hbar^2 c_2^2}{2m} - Zke^2c_2 = \frac{\hbar^2 Z^2}{2ma_o^2} - \frac{kZ^2e^2}{a_o} = \frac{-\hbar^2 Z^2}{2ma_o^2} \tag{1.17}$$

Here the last relationship relies on the definition of the Bohr radius, $a_o = \hbar/kmc^2$. For H, with $Z=1$, we find $E \approx -13.6 \, \text{eV}$, which we know to be the correct answer. For He^+, with $Z=2$, we find $E \approx -54 \, \text{eV}$, in very good agreement with experiments and exact calculations. We should not be too surprised, since our 'trial wavefunction' was exactly the correct one. The next problem shows how close one can get if the trial wavefunction is not chosen quite as cleverly.

1.2   Gaussian approximation for Hydrogen

Pretend we didn't know the ground state wave function for hydrogen, but attempted a trial solution of

$$\psi = c_1 e^{-c_2 r^2} \tag{1.18}$$

How far off is the ground state energy using this trial wavefunction? We follow the same procedure we did for the previous question, and calculate step by step. First, $\nabla^2 \psi$:

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = 4c_1 c_2^2 r^2 e^{-c_2 r^2} - 6c_1 c_2 e^{-c_2 r^2} \tag{1.19}$$

Using the energy operator from the previous problem with $Z=1$ for hydrogen,

$$H\psi = -\frac{\hbar^2}{2m} \left(4c_1 c_2^2 r^2 e^{-c_2 r^2} - 6c_1 c_2 e^{-c_2 r^2} \right) - \frac{ke^2}{r} c_1 e^{-c_2 r^2} \tag{1.20}$$

Multiplying through by the wave function,

$$\psi H\psi = -\frac{\hbar^2}{2m} c_1^2 e^{-2c_2 r^2} \left(4c_2^2 r^2 - 6c_2 \right) - \frac{ke^2}{r} c_1^2 e^{-2c_2 r^2} \tag{1.21}$$

Integrating over all space (noting again that the wave function is spherically symmetric),

$$\int \psi H\psi \, dV = \int_0^\infty -\frac{4\pi \hbar^2 c_1^2}{m} \left(2c_2^2 r - 3c_2 r^2 \right) e^{-2c_2 r^2} - 4\pi ke^2 c_1^2 re^{-2c_2 r^2} \, dr \tag{1.22}$$

$$= -\frac{4\pi \hbar^2 c_1^2}{m} \left(2c_2^2 \frac{3\sqrt{\pi}}{8 \left(2c_2 \right)^{3/2}} - 3c_2 \frac{\sqrt{\pi}}{4} \frac{1}{\left(2c_2 \right)^{3/2}} \right) - \frac{\pi ke^2 c_1^2}{c_2} \tag{1.23}$$

$$= \frac{3\pi^{3/2} \hbar^2 c_1^2}{2^{5/2} m \sqrt{c_2}} - \frac{\pi ke^2 c_1^2}{c_2} \tag{1.24}$$

The denominator in our energy expression gives

$$\int \psi^2 \, dV = \int_0^\infty 4\pi r^2 c_1^2 e^{-2c_2 r^2} \, dr = \frac{\sqrt{\pi}}{4} \frac{4\pi c_1^2}{(2c_2)^{3/2}} = \frac{c_1^2 \pi^{3/2}}{2^{3/2} c_2^{3/2}} \tag{1.25}$$

Combining, we have our energy:

$$E[\psi] = \frac{2^{3/2} c_2^{3/2}}{c_1^2 \pi^{3/2}} \left(\frac{3\pi^{3/2} \hbar^2 c_1^2}{2^{5/2} m \sqrt{c_2}} - \frac{\pi k e^2 c_1^2}{c_2} \right) = \frac{3\hbar^2 c_2}{2m} - \frac{2^{3/2} k e^2 \sqrt{c_2}}{\sqrt{\pi}} \tag{1.26}$$

Again, the energy does not depend on the normalization constant c_1. Minimizing with respect to c_2,

$$\frac{\partial E}{\partial c_2} = \frac{3\hbar^2}{2m} - \sqrt{\frac{2}{\pi}} \frac{k e^2}{\sqrt{c_2}} = 0 \qquad \Longrightarrow \qquad \sqrt{c_2} = \frac{2k e^2 m}{3\hbar^2} \sqrt{\frac{2}{\pi}} \tag{1.27}$$

Plugging this back into our energy expression,

$$E = \frac{3\hbar^2}{2m} \frac{4k^2 e^4 m}{9\hbar^4} - \frac{3\hbar^2 k e^2}{2k e^2 m} = \frac{4k^2 e^4 m}{3\pi\hbar^2} - \frac{8k^2 e^4 m}{3\pi\hbar^2} = -\frac{8}{3\pi} \left(\frac{k^2 e^4 m}{2\hbar^2} \right) = \frac{8}{3\pi} E_1 \tag{1.28}$$

Recognizing that $E_1 = \frac{k^2 e^4 m}{2\hbar^2}$ is the correct $n = 1$ ground state energy for Hydrogen, our trial wave function is just a factor of $8/3\pi$ off (or about 15%) at $E \approx -11.5 \, \text{eV}$

1.3   Another approximation for Hydrogen

Pretend again we don't know the ground state wave function for hydrogen, but decided to guess the following form for ψ:

$$\psi(r) = \frac{\beta}{\alpha^2 + r^2} \tag{1.29}$$

This is a Lorentzian function, and it has the right symmetries - radially symmetric, peaked about the origin, and strongly decaying as r increases. Plausible. Let us use the variational principle and normalization to find the values of α and β that give the minimum energy for this trial wave function, and compare this result to the correct ground state energy of hydrogen.

Let there be no confusion: this variational stuff is messy. Highly effective, but messy. Let's get started. First, let us compute $H\psi$.

$$\mathsf{H}\psi = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) - \frac{ke^2}{r}\psi = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\frac{\beta}{\alpha^2+r^2}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} \tag{1.30}$$

$$= -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{-2r\beta}{(\alpha^2+r^2)^2}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(\frac{-2r^3\beta}{(\alpha^2+r^2)^2}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} \tag{1.31}$$

$$= -\frac{\hbar^2}{2mr^2}\left(\frac{8r^4\beta}{(\alpha^2+r^2)^3} - \frac{6r^2\beta}{(\alpha^2+r^2)^2}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} \tag{1.32}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{8r^2\beta-6\beta\alpha^2-6\beta^2}{(\alpha^2+r^2)^3}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} = -\frac{\hbar^2}{2m}\left(\frac{2r^2\beta-6\beta\alpha^2}{(\alpha^2+r^2)^3}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} \tag{1.33}$$

Yes, that was just terrible. Now we multiply through by ψ again to get $\psi\mathsf{H}\psi$. Since $\psi(x)$ is real for all x, we need not worry about complex conjugates and such.

$$\psi\mathsf{H}\psi = -\frac{\hbar^2\beta}{2m}\left(\frac{2\beta r^2-6\beta\alpha^2}{(\alpha^2+r^2)^4}\right) - \frac{ke^2\beta^2}{r\left(\alpha^2+r^2\right)^2} \tag{1.34}$$

Now we integrate that over all space, using the volume element $4\pi r^2\,dr$ with r ranging from 0 to ∞. In this process, we either remember some obscure integrals or use Wolfram Alpha (http://wolframalpha.com).

$$\int\psi\mathsf{H}\psi = \int_0^\infty -\frac{4\pi\hbar^2\beta^2}{2m}\left(\frac{2r^4-6\alpha^2r^2}{(\alpha^2+r^2)^4}\right) - \frac{4\pi ke^2\beta^2 r}{(\alpha^2+r^2)^2} \tag{1.35}$$

$$= -\frac{4\pi\hbar^2\beta^2}{m}\left(2\frac{\pi}{32\alpha^3} - 6\alpha^2\frac{\pi}{32\alpha^5}\right) - 4\pi ke^2\beta^2\frac{1}{2\alpha^2} \tag{1.36}$$

$$= -\frac{4\pi^2\hbar^2\beta^2}{2m}\left(\frac{1}{16\alpha^2} - \frac{3}{16\alpha^2}\right) - \frac{2\pi ke^2\beta^2}{\alpha^2} = \frac{\pi^2\hbar^2\beta^2}{4m\alpha^3} - \frac{2ke^2\beta^2}{\alpha^2} \tag{1.37}$$

Now the denominator in our energy expression:

$$\int|\psi|^2\,dV = \int_0^\infty \frac{4\pi\beta^2 r^2}{(\alpha^2+r^2)^2}\,dr = 4\pi\beta^2\frac{\pi}{4\alpha} = \frac{\pi^2\beta^2}{\alpha} \tag{1.38}$$

This implies that for the wave function to be normalized, such that $\int|\psi|^2\,dV = 1$, we require $\beta^2 = \alpha/\pi^2$. Putting it all together, we can find our expression for energy:

$$E = \frac{\alpha}{\pi^2\beta^2}\left(\frac{\pi^2\hbar^2\beta^2}{4m\alpha^3} - \frac{2\pi ke^2\beta^2}{\alpha^2}\right) = \frac{\hbar^2}{4m\alpha^2} - \frac{2ke^2}{\pi\alpha} \tag{1.39}$$

Note that the energy is independent of β, which makes again makes sense as β is just the nor-

malization constant. Our variational condition is that this energy is minimized with respect to the parameter α, thus

$$0 = \frac{\partial E}{\partial \alpha} = 2\frac{2\hbar^2}{4m\alpha^3} = \frac{2ke^2}{\pi\alpha^2} \tag{1.40}$$

$$\frac{\hbar^2}{2m\alpha^3} = \frac{2ke^2}{\pi\alpha^2} \tag{1.41}$$

$$\alpha = \frac{\pi\hbar^2}{4mke^2} = \frac{\pi}{4}a_o \tag{1.42}$$

Here a_o is the Bohr radius, $a_o = \hbar^2/kme^2$. Thus, we can interpret α as a characteristic distance of the electron cloud, about 20% smaller than the exact solution gives us. Plugging this in our energy equation, we have

$$E = -\frac{-4\hbar^2}{\pi^2 ma_o^2} \approx -11.1\,\mathrm{eV} \tag{1.43}$$

This is about 19% off of the exact value for the ground state energy. The plots of ψ for the variational and correct ground state wavefunctions are left as an exercise for the reader ...

1.4 Simple Harmonic Oscillator Approximation

The energy operator for a simple harmonic oscillator in *one dimension* is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \tag{1.44}$$

Presume we don't know the proper wave function, but guessed a wave function of the form

$$\psi(r) = \frac{\beta}{\alpha^2 + x^2} \tag{1.45}$$

Again, this Lorentzian function has all the right properties of being localized near the origin, rapidly decaying, etc. We can use the variational principle and normalization to find the values of α and β that give the minimum energy for this trial wave function, and compare this result to the correct ground state energy of the simple harmonic oscillator.

Much like the last one, except here $dV = dx$ and x runs from $-\infty$ to ∞, which changes all the integrals.

$$H\psi = -\frac{\hbar^2}{2m}\left(\frac{d}{dx}\frac{\beta}{\alpha^2+x^2}\right)+\frac{1}{2}m\omega^2 x^2\frac{\beta}{\alpha^2+x^2} \tag{1.46}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{-2\beta}{(\alpha^2+x^2)^2}+\frac{8x^2\beta}{(\alpha^2+x^2)^3}\right)+\frac{1}{2}\frac{m\omega^x\beta x^2}{\alpha^2+x^2} \tag{1.47}$$

$$= -\frac{\hbar^2\beta}{2m}\left(\frac{3x^2-\alpha^2}{(\alpha^2+x^2)^3}\right)+\frac{1}{2}\frac{m\omega^x\beta x^2}{\alpha^2+x^2} \tag{1.48}$$

Now $H\psi H$:

$$\psi H\psi = -\frac{\hbar^2\beta^2}{m}\left(\frac{3x^2-\alpha^2}{(\alpha^2+x^2)^4}\right)+\frac{1}{2}\frac{m\omega^2\beta^2 x^2}{(\alpha^2+x^2)^2} \tag{1.49}$$

And, the full numerator:

$$\int \psi H\psi\, dx = \int_{-\infty} \frac{\hbar^2\beta^2}{m}\left(\frac{\alpha^2-3x^2}{(\alpha^2+x^2)^4}\right)+\frac{1}{2}\frac{m\omega^x\beta^2 x^2}{(\alpha^2+x^2)^2} = \frac{\hbar^2\beta^2}{2m}\left(\frac{5\pi}{16\alpha^5}-\frac{3\pi}{16\alpha^5}\right)+\frac{m\omega^2\beta^2}{2}\frac{\pi}{2\alpha} \tag{1.50}$$

$$= \frac{\pi\beta^2\hbar^2}{8m\alpha^5}+\frac{\pi m\beta^2\omega^2}{4\alpha} \tag{1.51}$$

And the denominator:

$$\int |\psi|^2\, dx = \int_{-\infty}^{\infty}\frac{\beta^2}{(\alpha^2+x^2)^2}\,dx = \frac{\pi\beta^2}{2\alpha^3} \tag{1.52}$$

This implies that for a normalized wavefunction we require $\beta^2 = 2\alpha^3/\pi$. Now the energy expression in full:

$$E = \frac{2\alpha^3}{\pi\beta^2}\left(\frac{\pi\beta^2\hbar^2}{8m\alpha^5}+\frac{\pi m\beta^2\omega^2}{4\alpha}\right) = \frac{\hbar^2}{4m\alpha^2}+\frac{\alpha^2 m\omega^2}{2} \tag{1.53}$$

Once again, the energy is independent of β as it should be, and the optimal solution is when $dE/d\alpha = 0$.

$$\frac{dE}{d\alpha} = 0 = -\frac{2\hbar^2}{4m\alpha^3}+m\alpha\omega^2 \qquad \Longrightarrow \qquad \alpha^2 = \frac{\hbar}{\sqrt{2}m w} \tag{1.54}$$

The minimum energy for this guess at the wavefunction is then

$$E = \frac{\hbar^2}{4m} \frac{\sqrt{2}m\omega}{\hbar} + \frac{m\omega^2}{2} \frac{\hbar}{\sqrt{2}m\omega} = \frac{\sqrt{2}}{2}\hbar\omega = \frac{1}{2}\hbar\omega\left(\sqrt{2}\right) \tag{1.55}$$

Our variational approach with a plausible guess at the wavefunction yields a ground state energy that is a factor $\sqrt{2}\approx 1.4$ times higher than the exact value. Not bad for a guess.

1.5 Anharmonic oscillator

For another example, we can estimate the ground state energy for the anharmonic oscillator,

$$H = \frac{p^2}{2m} + \lambda x^4 \qquad \text{i.e., } H\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \lambda x^4\psi \tag{1.56}$$

The exact result is known for comparison:

$$E_o = 1.060\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3} \tag{1.57}$$

Note that this is a one-dimensional problem, so we can take $dV = dx$. The easiest thing to do is see how bad the normal harmonic oscillator solution is, presuming the anharmonic x^4 term is relatively small and doesn't cause too large a perturbation. The harmonic oscillator solution is known to be $\psi = e^{-cx^2}$. First we need to find $H\psi$.

$$H\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \lambda x^4\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}e^{-cx^2} + \lambda x^4 e^{-cx^2} \tag{1.58}$$

$$= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left(-2cxe^{-cx^2}\right) + \lambda x^4 e^{-cx^2} = -\frac{\hbar^2}{2m}\left(2ce^{-cx^2}\right)\left(2cx^2 - 1\right) + \lambda x^4 e^{-cx^2} \tag{1.59}$$

Next, we multiply by ψ again to get $\psi H\psi$, and integrate that over all space. Multiplying by ψ just makes the exponents all $-2cx^2$.

$$\int \psi H\psi \, dV = \int_{-\infty}^{\infty} -\frac{\hbar^2}{2m}\left(2ce^{-2cx^2}\right)\left(2cx^2 - 1\right) + \lambda x^4 e^{-2cx^2} \, dx \tag{1.60}$$

$$= \int_{-\infty}^{\infty} e^{-2cx^2}\left(\lambda x^4 - \frac{2\hbar^2 c^2}{m}x^2 + \frac{\hbar^2 c}{m}\right) \tag{1.61}$$

All the integrals are known (you can ask Wolfram):

$$\int \psi H \psi \, dV = \lambda \frac{3}{16} \sqrt{\frac{\pi}{2c^5}} - \frac{2\hbar^2 c^2}{m} \frac{1}{4} \sqrt{\frac{\pi}{2c^3}} + \frac{\hbar^2 c}{m} \sqrt{\frac{\pi}{2c}} = \frac{3\lambda}{16} \sqrt{\frac{\pi}{2c^5}} + \frac{\hbar^2}{2m} \sqrt{\frac{\pi c}{2}} \tag{1.62}$$

$$= \sqrt{\frac{\pi}{2c}} \left(\frac{3\lambda}{16} \frac{1}{c^2} + \frac{\hbar^2}{2m} c \right) \tag{1.63}$$

The denominator in the variational expression is simpler:

$$\int\limits_{-\infty}^{\infty} \psi^2 \, dx = \int\limits_{-\infty}^{\infty} e^{-2cx^2} \, dx = \sqrt{\frac{\pi}{2c}} \tag{1.64}$$

Our energy expression is thus

$$E[\psi] = \frac{\int \psi^* H \psi \, dV}{\int |\psi|^2 \, dV} = \frac{3\lambda}{16c^2} + \frac{\hbar^2 c}{2m} \tag{1.65}$$

To minimize the energy with this wavefunction, we require $dE/dc = 0$.

$$\frac{dE}{dc} = -\frac{6\lambda}{16c^3} + \frac{\hbar^2}{2m} = 0 \tag{1.66}$$

$$\implies \quad c = \sqrt[3]{\frac{3\lambda m}{4\hbar^2}} \tag{1.67}$$

Now we plug that back in our expression for E to find the minimum energy and simplify.

$$E_{min} = \frac{3\lambda}{16c^2} + \frac{\hbar^2 c}{2m} = \frac{3\lambda}{16} \left(\frac{4\hbar^2}{3\lambda m} \right)^{2/3} + \frac{\hbar^2}{2m} \left(\frac{3\lambda m}{4\hbar^2} \right)^{1/3} \tag{1.68}$$

$$= \frac{3}{16} \lambda^{1/3} \left(\frac{\hbar^2}{2m} \right)^{2/3} \left(\frac{8}{3} \right)^{2/3} + \frac{1}{2} \lambda^{1/3} \left(\frac{\hbar^2}{2m} \right)^{2/3} 3^{1/3} = \left(\frac{3\sqrt[3]{3}}{4} \right) \lambda^{1/3} \left(\frac{\hbar^2}{2m} \right)^{2/3} \tag{1.69}$$

$$\approx 1.082 \lambda^{1/3} \left(\frac{\hbar^2}{2m} \right)^{2/3} \tag{1.70}$$

This differs from the exact result by only $\sim 2\%$. Not bad!

1.6 Anharmonic oscillator, redux

Let's repeat that problem with a different trial wave function. We know physically a trial function must be peaked around $x = 0$ and must be normalizable (i.e., $\int_{-\infty}^{\infty} \psi^2 \, dx$ is finite). Such functions would include $e^{-c|x|}$ or $1/(c + x^2)$, for instance. Choose wisely, and the mathematics will be far simpler.

How do we pick an appropriate function? What properties should your wave function have for the ground state? We can come up with a few rules by looking at the potential and thinking about the generic properties of wavefunctions. First, for the lowest energy state the wave function should be an even function and peaked near $x = 0$, just like it is for the simple harmonic oscillator. Second, it should be normalizable (i.e., in rough terms the integral of the function squared over all space should be finite). Third, for the variational integral to converge, the square of the wavefunction must decay faster than x^4, since we have to integrate $|\psi|^2 x^4$ over all space and come up with a finite answer.

This is already pretty restrictive, when you get down to it. For instance, $1/(x^2 + a^2)$ will not work, since when squared and multiplied by x^4, its integral will not converge. You'll run in to weirder problems trying things like e^{-x^4}, pushing the analogy with the harmonic oscillator. Just to cut to the chase, one thing that does work is $1/(x^2 + a)^2$. (It is not even that messy if you let Wolfram do the heavy lifting.) This isn't the only possibility, certainly. You might just try two Gaussians with two adjustable parameters, or possibly $e^{-a|x|}$. We'll try $\psi = 1/(x^2 + a^2)^2$. First, we need the second derivative.

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{4\left(5x^2 - a^2\right)}{\left(a^2 + x^2\right)^4} \tag{1.71}$$

With that, we can find $H\psi$

$$H\psi = -\frac{\hbar^2}{2m}\frac{4\left(5x^2 - a^2\right)}{\left(a^2 + x^2\right)^4} + \lambda x^4 \frac{1}{\left(a^2 + x^2\right)^2} \tag{1.72}$$

Now, $\psi H\psi$ just means multiplying through by ψ again:

$$\psi H\psi = -\frac{\hbar^2}{2m}\frac{4\left(5x^2 - a^2\right)}{\left(a^2 + x^2\right)^6} + \lambda x^4 \frac{1}{\left(a^2 + x^2\right)^4} \tag{1.73}$$

With Wolfram's help, we can integrate it over all space[i]

$$\int \psi H\psi \, dV = \int_{-\infty}^{\infty} -\frac{\hbar^2}{2m}\frac{4\left(5x^2 - a^2\right)}{\left(a^2 + x^2\right)^6} + \lambda \frac{x^4}{\left(a^2 + x^2\right)^4} \, dx$$

$$= -\frac{2\hbar^2}{m}\left(\frac{35\pi}{256a^9} - \frac{63\pi a^2}{256a^{11}}\right) + \lambda\frac{\pi}{16a^3} = \frac{-\hbar^2}{128ma^9}\left(35\pi - 63\pi\right) + \frac{\pi\lambda}{16a^3}$$

$$= \frac{7\pi\hbar^2}{32ma^9} + \frac{\pi\lambda}{16a^3} = \frac{\pi}{16a^3}\left(\lambda + \frac{7\hbar^2}{2ma^6}\right) \tag{1.74}$$

Now we need the denominator in our variational expression, the normalization condition:

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[i]Note that you can tell Wolfram to include limits to the integral, which simplifies things a lot. Compare typing in `integral of x^2/(a =^2+x^2)^6 from -infinity to infinity` to `integral of x^2/(a^2+x^2)^6`. Nice, right?

$$\int |\psi|^2 \, dV = \int\limits_{-\infty}^{\infty} \frac{1}{(x^2 + a)^4} \, dx = \frac{5\pi}{16a^7} \tag{1.75}$$

Combining and factoring a bit,

$$E[\psi] = \frac{\int \psi^* H \psi \, dV}{\int |\psi|^2 \, dV} = \frac{\pi}{16a^3}\left(\lambda + \frac{7\hbar^2}{2ma^6}\right) \cdot \frac{16a^7}{5\pi} = \frac{a^4}{5}\left(\lambda + \frac{7\hbar^2}{2ma^6}\right) = \frac{1}{5}a^4\lambda + \frac{7\hbar^2}{10ma^2} \tag{1.76}$$

To minimize the energy with this wavefunction, we require $dE/da=0$.

$$\frac{dE}{da} = \frac{4}{5}a^3\lambda - \frac{7\hbar^2}{5ma^3} \tag{1.77}$$

$$\implies \quad a = \sqrt[6]{\frac{7\hbar^2}{4m\lambda}} \tag{1.78}$$

Inserting this into our energy expression, we have the minimum energy

$$E_{min} = \frac{1}{5}a^4\lambda + \frac{7\hbar^2}{10ma^2} = \frac{\lambda}{5}\left(\frac{7\hbar^2}{4m\lambda}\right)^{2/3} + \frac{7\hbar^2}{10m}\left(\frac{4m\lambda}{7\hbar^2}\right)^{1/3} \tag{1.79}$$

$$= \lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3}\left[\frac{1}{5}\left(\frac{7}{2}\right)^{2/3} + \frac{7}{10}\left(\frac{16}{7}\right)^{1/3}\right] = \lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3}\left[\frac{3}{5}\left(\frac{7}{2}\right)^{2/3}\right] \tag{1.80}$$

$$\approx 1.38\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3} \tag{1.81}$$

This trial wave function is off by about 30%, not nearly as good as just using the harmonic oscillator solution as our guess. Still, it is amazing we can get that close with a guess based only on a few simple symmetry arguments.