

Lecture 20 Highlights Phys 402

The Variational Method

The Variational Method is another approximation method that is very useful for estimating the ground state energy of a complicated Hamiltonian. The idea is very simple. Given a Schrödinger problem to solve $H\Psi = E\Psi$ (we know H , but cannot solve the TISE exactly), make your best guess for the ground state wavefunction $\Psi_{GS,Guess}(\vec{r})$ (make sure it is normalized: $\langle \Psi_{GS,Guess} | \Psi_{GS,Guess} \rangle = 1$) and calculate the expectation value of the Hamiltonian with this wavefunction: $\langle \Psi_{GS,Guess} | H | \Psi_{GS,Guess} \rangle$. The true ground state energy is guaranteed to be less than or equal to this expectation value: $E_{GS} \leq \langle \Psi_{GS,Guess} | H | \Psi_{GS,Guess} \rangle$. Basically this is true because your guess wavefunction is in general a linear combination of the true ground state wavefunction and many excited states. Hence the expectation of energy is bounded below by the true ground state energy.

To improve the guess wavefunction, one can add many adjustable parameters to it, call them $\lambda_1, \lambda_2, \lambda_3, \dots$. These are often physically motivated quantities, such as the width of the wavefunction in real-space, or the effective charge of the nucleus as seen by an electron in an atom, or perhaps the distance between two nuclei in a molecule, etc. Your intuition about the ground state wavefunction is important for choosing the original guess and the parameter dependence. Once again, normalize the new guess wavefunction $\Psi_{GS,Guess}(\vec{r}, \lambda_1, \lambda_2, \lambda_3, \dots)$ and calculate the expectation value of the Hamiltonian. Now we can minimize the expectation value of H with respect to variations in the parameter values.

In other words, set
$$\frac{\partial \langle \Psi_{GS,Guess}(\vec{r}, \lambda_1, \lambda_2, \lambda_3, \dots) | H | \Psi_{GS,Guess}(\vec{r}, \lambda_1, \lambda_2, \lambda_3, \dots) \rangle}{\partial \lambda_i} = 0 \quad \text{for all}$$

parameters λ_i . This will give a closer estimate of the ground state energy. How close? Unfortunately, there is no way to estimate how far the result is from the true ground state energy.

There are some ground rules for guess wavefunctions. We should make sure the curvature of the wavefunction is appropriate for the region of space in which it is used. For example in classically forbidden regions it should be concave away from the axis, while in classically-allowed regions it should curve towards the axis. Since kinetic energy is proportional to the curvature of the wavefunction, ground state wavefunctions should be gently varying in space. Another rule of thumb is that one can often add a parameter to the wavefunction that trades off the effects of kinetic and potential energy contributions to the total energy, allowing for energy optimization through the minimization process discussed above. Bottom line: the intuition that you have gained about quantum wavefunctions in 1D and 3D over the course of Phys 401 and 402 will guide your approach to creating the guess wavefunctions.

In class, we did the example of a 1D problem of an infinite delta function well $V(x) = -\alpha \delta(x)$ bound state. We guessed a parameterized ground state wavefunction of the form: $\Psi_{GS,Guess}(x, b) = Ae^{-bx^2}$, which is a Gaussian centered on the well. The parameter $1/\sqrt{b}$ is basically the width of the wavefunction in real space. If the width is too small, the

particle will be bound to a very small interval, creating a large uncertainty in its momentum, leading to a large expectation value of kinetic energy. If the width is too big, then the particle will not take sufficient advantage of the attractive potential well, which is confined to the origin. Hence, there must be a compromise between these two tendencies. We found

that $A = \left(\frac{2b}{\pi}\right)^{1/4}$ from normalization. The rest of the discussion followed pages 328-331

of Griffiths. Note that the expectation of kinetic energy of the particle $\langle T \rangle = \frac{\hbar^2 b}{2m}$ scales

inversely with the square of the width of the wavefunction. More narrow-in-space wavefunctions “force” the particle to have a greater uncertainty in momentum and therefore a larger expectation value of kinetic energy. The expectation value of potential

energy is $\langle V \rangle = -\alpha \sqrt{\frac{2b}{\pi}}$, showing that narrow wavefunctions (large b) are favored. The

expectation value of the Hamiltonian $\langle H \rangle = \langle T \rangle + \langle V \rangle$ is minimized for the special value of

$b_{\min} = \frac{2m^2 \alpha^2}{\pi \hbar^4}$, giving a minimum expectation value of $\langle H \rangle_{\min} = -\frac{m \alpha^2}{\pi \hbar^2}$, which is close

to (but larger than) the true ground state energy of $E_{GS} = -\frac{m \alpha^2}{2 \hbar^2}$. The true ground state

wavefunction is an exponential (see page 66 of Griffiths) centered on the origin. Our choice of a Gaussian guess wavefunction is different, but we still get a decent estimate of the ground state energy, illustrating the power of this method. (Note that the Gaussian has the wrong curvature near the origin! Despite this built-in deficiency, we still get a reasonable estimate of the ground state energy.) This example also illustrates how a physically-motivated choice of parameter can lead to deeper insights into the properties of the ground state wavefunction.

We also briefly discussed the Helium atom problem covered in detail in section 8.2 of Griffiths, and introduced the effective charge of the nucleus, $+Ze$. This is a 3-body Coulomb interaction problem that cannot be solved analytically in either classical or quantum mechanics. The variational principle is useful for estimating the ground state energy. Note that the variational method does not change the Hamiltonian of the problem - that is given by nature. Instead it allows us to embellish the guess wavefunctions with additional parameters to improve our estimate of the ground state energy. In this case, we posit that the two electrons partially screen the Helium nucleus, creating an effective nuclear charge $Z < 2$ for the electron-nucleus Coulomb attraction terms in the Hamiltonian. By using Hydrogen atom ground state wavefunctions with nuclear charge Z for the two electrons, we can find how the expectation value of the Hamiltonian depends on Z . We can then vary Z to minimize the total energy of the atom. This results in an effective nuclear charge experienced by the electrons of $Z = 1.69 < 2$, and gives us a better estimate of the ground state energy of the Helium atom.

The variational method is remarkably tolerant and gives very good estimates of ground state energies even with guessed wavefunctions that are not that similar to the true ground state wavefunction. As long as the guessed wavefunction has the correct general character, it seems to work quite well.

One can also calculate upper-bound estimates of excited state energies. This can be done by first making a best variational guess at the ground state wavefunction and then constructing an excited state wavefunction guess $\Psi_{FES,Guess}$ that is orthogonal to the ground state guess, $\langle \Psi_{GS,BestGuess} | \Psi_{FES,Guess} \rangle = 0$ with $\langle \Psi_{FES,Guess} | \Psi_{FES,Guess} \rangle = 1$. Based on our studies of 1D quantum mechanics, we might expect that each higher state will have one additional node in the wavefunction, compared to the previous state. Also, for potentials that are symmetric ($V(-x) = +V(x)$) we know that consecutive wavefunctions must have opposite parity. This provides a convenient way to “orthogonalize” two neighboring wavefunctions.