Lecture 40 Highlights

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 $\mathrm{H}\Psi = E\Psi$ (which cannot be solved 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: $\langle \Psi_{GS,Guess} | \mathrm{H} | \Psi_{GS,Guess} \rangle$. The true ground state energy is guaranteed to be less than or equal to this expectation value: $E_{GS} \le \langle \Psi_{GS,Guess} | \mathrm{H} | \Psi_{GS,Guess} \rangle$. 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 $\lambda_1, \lambda_2, \lambda_3, \ldots$ 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. Once again normalize the new guess wavefunction $\Psi_{GS,Guess}(\vec{r}, \lambda_1, \lambda_2, \lambda_3, \ldots)$ 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 $\frac{\partial \langle \Psi_{GS,Guess}(\vec{r}, \lambda_1, \lambda_2, \lambda_3, \ldots) | \mathrm{H} | \Psi_{GS,Guess}(\vec{r}, \lambda_1, \lambda_2, \lambda_3, \ldots) \rangle}{\partial \lambda_i} = 0$ 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.

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. We found that $A = \left(\frac{2b}{\pi}\right)^{1/4}$ from normalization. The rest of the discussion followed pages 294-296 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 $\langle V \rangle = -\alpha\sqrt{\frac{2b}{\pi}}$. The expectation value of the Hamiltonian $\langle \mathrm{H} \rangle = \langle T \rangle + \langle V \rangle$ is minimized for the special value of $b_{\min} = \frac{2m^2\alpha^2}{\pi\hbar^4}$, giving a minimum expectation value of $\langle \mathrm{H} \rangle_{\min} = -\frac{m\alpha^2}{\pi\hbar^2}$, which is close to (but larger than) the true ground state energy of $E_{GS} = -\frac{m\alpha^2}{2\hbar^2}$.

We also briefly discussed the Helium atom problem covered in detail in section 7.2 of Griffiths, and introduced the effective charge of the nucleus, $+Ze$. 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.

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.