

221A Lecture Notes

Variational Method

1 Introduction

Most of the problems in physics cannot be solved exactly, and hence need to be dealt with approximately. There are two common methods used in quantum mechanics: the perturbation theory and the variational method.

The perturbation theory is useful when there is a small dimensionless parameter in the problem, and the system is exactly solvable when the small parameter is sent to zero. The system is then studied in power series expansion in the small parameter. For instance, the quantum electrodynamics is a perfect example where the perturbation theory is useful. The small parameter is the fine-structure constant $\alpha = e^2/(4\pi\epsilon_0\hbar c) \simeq 1/137 \ll 1$. In the limit where $\alpha \rightarrow 0$, the photons and electrons are free particles and there is no interaction; hence the system is exactly solvable. Physical quantities are calculated in power series in α .

The variational method is useful to study the ground state, but not very useful for the study of excited states. On the other hand, it is not required that the system has a small parameter, nor that the system is exactly solvable in a certain limit. Therefore it has been useful in studying strongly correlated systems, such as the fractional Quantum Hall effect. The study of multi-electron atoms relies on the Hartree–Fock theory based on the variational method. Certain systems also exhibit drastic difference between the perturbative ground state and true ground state, such as the superconductivity. The Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity is based on the variational method. On the other hand, the success of the variational method depends on the initial “guess” what the ground-state wave function looks like, and an excellent physical intuition is required for a successful application.

2 Fundamentals

By definition, the ground state has the lowest energy eigenvalue of a given system,

$$H|0\rangle = E_0|0\rangle, \tag{1}$$

while any other states have higher energy eigenvalues,

$$H|n\rangle = E_n|n\rangle, \quad E_n > E_0. \quad (2)$$

Suppose we have a Hamiltonian we cannot solve for eigenstates and eigenvalues exactly. Based on a physical intuition, we try to come up with a guess what the ground state looks like: $|\tilde{0}\rangle$. Many prefer to call it an “ansatz” or a “trial” wave function instead of a “guess” to make it sound scientific, but a guess is nonetheless a guess. If the ansatz is not exactly right, it is a linear combination of different Hamiltonian eigenstates,

$$|\tilde{0}\rangle = \sum_{n=0}^{\infty} |n\rangle \langle n|\tilde{0}\rangle = \sum_{n=0}^{\infty} c_n |n\rangle. \quad (3)$$

The ansatz is exact if $c_0 = 1$ and $c_n = 0$ for all $n \neq 0$. The proper normalization requires $|c_0|^2 + \sum_{n \neq 0} |c_n|^2 = 1$.

The expectation value of the energy with the ansatz is

$$\langle \tilde{0}|H|\tilde{0}\rangle = |c_0|^2 E_0 + \sum_{n \neq 0} |c_n|^2 E_n \geq |c_0|^2 E_0 + \sum_{n \neq 0} |c_n|^2 E_0 = E_0. \quad (4)$$

Namely the expectation value must be always greater than or equal to the ground state energy. This way, one can obtain an *upper limit* on the ground-state energy eigenvalue by employing an arbitrary trial ket. Clearly a better upper limit is obtained by a better trial ket, namely a better overlap with the true ground state (*e.g.*, c_0 as close to unity as possible). The converse is also true: a state with a lower expectation value of the Hamiltonian should have a better overlap with the true ground state.

Given this observation, one can look for a ground state wave function by introducing parameters to the trial ket $|\tilde{0}(\lambda_1, \lambda_2, \dots)\rangle$, calculating the energy expectation value

$$\bar{E}(\lambda_1, \lambda_2, \dots) = \langle \tilde{0}(\lambda_1, \lambda_2, \dots)|H|\tilde{0}(\lambda_1, \lambda_2, \dots)\rangle, \quad (5)$$

and looking for as low expectation value as possible, namely minimizing it:

$$\frac{\partial \bar{E}}{\partial \lambda_1} = \frac{\partial \bar{E}}{\partial \lambda_2} = \dots = 0. \quad (6)$$

The success of this method still depends on having a good trial ket with the good set of parameters. This is what is called the variational method: you vary the parameters within the ansatz and find the parameter set that minimizes the energy expectation value. If the ansatz is close enough to the true ground state, so is the minimum energy expectation value. If the ansatz has the correct functional form, it leads to the exact ground state.

3 Examples

If the functional form of the ground-state wave function is guessed correctly, then the variational method gives the true ground-state wave function.

Sakurai discusses the example of the hydrogen atom, where the ground state wave function is

$$\psi = \frac{1}{\sqrt{4\pi}} \frac{Z^{3/2}}{a_0} 2e^{-Zr/a_0}, \quad (7)$$

where $a_0 = \hbar^2/(m_e e^2)$ is the Bohr radius (in Gaussian unit). The energy eigenvalue is

$$E_0 = -\frac{Ze^2}{2a_0} = -\frac{Z^2 e^4 m_e}{2\hbar^2}. \quad (8)$$

See Appendix A.6 of Sakurai.

Suppose you didn't know this exact form, but guessed that the ground-state wave function is spherical and exponentially damping, $\psi \propto e^{-r/d}$. The properly normalized wave function is then

$$\psi_{\bar{0}} = \frac{1}{\sqrt{\pi d^3}} e^{-r/d}. \quad (9)$$

Now we calculate the expectation value of the Hamiltonian

$$H = \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r}. \quad (10)$$

The kinetic energy term gives

$$\langle \frac{\vec{p}^2}{2m} \rangle = \frac{1}{\pi d^3} \frac{-\hbar^2}{2m} \int 4\pi r^2 dr e^{-r/d} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) e^{-r/d} = \frac{1}{\pi d^3} \frac{-\hbar^2}{2m} \frac{-1}{d^2} \pi d^3 = \frac{\hbar^2}{2md^2}. \quad (11)$$

The potential energy term, on the other hand, gives

$$\langle -\frac{Ze^2}{r} \rangle = \frac{1}{\pi d^3} (-Ze^2) \int 4\pi r dr e^{-2r/d} = \frac{1}{\pi d^3} (-Ze^2) 4\pi \left(\frac{d}{2} \right)^2 = -\frac{Ze^2}{d}. \quad (12)$$

By minimizing the expectation value,

$$\frac{\partial \bar{E}(d)}{\partial d} = \frac{\partial}{\partial d} \left(\frac{\hbar^2}{2md^2} - \frac{Ze^2}{d} \right) = -2\frac{\hbar^2}{2md^3} + \frac{Ze^2}{d^2} = 0, \quad (13)$$

we find $d = \hbar^2/(Zm_e e^2)$, the exact result. Note that this is the theoretically justified version of the HW #3, problem 2.

Suppose, however, you didn't guess it correctly and instead tried a Gaussian,

$$\psi = \left(\frac{2}{\pi d^2}\right)^{3/2} e^{-r^2/d^2}. \quad (14)$$

The expectation value of the kinetic energy is

$$\begin{aligned} \langle \frac{\vec{p}^2}{2m} \rangle &= \left(\frac{2}{\pi d^2}\right)^{3/2} \frac{-\hbar^2}{2m} \int 4\pi r^2 dr e^{-r^2/d^2} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr}\right) e^{-r^2/d^2} \\ &= \left(\frac{2}{\pi d^2}\right)^{3/2} \frac{-\hbar^2}{2m} \int 4\pi r^2 dr e^{-2r^2/d^2} \left(\frac{4r^2}{d^4} - \frac{6}{d^2}\right) \\ &= \frac{3\hbar^2}{2md^2}. \end{aligned} \quad (15)$$

That of the potential energy is

$$\begin{aligned} \langle \frac{-Ze^2}{r} \rangle &= -Ze^2 \left(\frac{2}{\pi d^2}\right)^{3/2} \int 4\pi r^2 dr e^{-2r^2/d^2} \frac{1}{r} \\ &= -\frac{Ze^2 2\sqrt{2}}{d \sqrt{\pi}}. \end{aligned} \quad (16)$$

The minimization of the expectation value yields

$$\frac{\partial \bar{E}}{\partial d} = \frac{\partial}{\partial d} \left(\frac{3\hbar^2}{2md^2} - \frac{Ze^2 2\sqrt{2}}{d \sqrt{\pi}} \right) = -\frac{3\hbar^2}{md^3} + \frac{Ze^2 2\sqrt{2}}{d^2 \sqrt{\pi}} = 0, \quad (17)$$

and hence

$$d = \frac{3\sqrt{\pi} \hbar^2}{2\sqrt{2} Zm_e e^2}, \quad \bar{E}_{min} = -\frac{4}{3\pi} \frac{Z^2 e^4 m_e}{\hbar^2} = 0.85 E_0. \quad (18)$$

Even though the functional form is *quite* wrong, we still got a good answer within 15%! Indeed the expectation value is larger in the absolute value (less in magnitude) than the true ground-state energy.

Actually, with some thinking, we would not choose a Gaussian. It is useful to think about the asymptotic behavior of the wave function. Because the Coulomb potential goes to zero at the infinity, the bound state wave function satisfies (asymptotically)

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} \psi = -|E| \psi \quad (19)$$

whose solution is

$$\psi \propto e^{-\kappa r}, \quad (20)$$

where $\kappa = \sqrt{2m|E|/\hbar}$. Therefore, we know that Gaussian was not a very good guess, but nonetheless it did quite well. On the other hand, this type of consideration does suggest an exponential form, which turns out to be the *correct* ansatz, and then the variational method fixes the exponent.

Sakurai discusses a particle in the box problem. Instead of the exact ground-state wave function

$$\psi = \frac{1}{\sqrt{a}} \cos \frac{\pi x}{2a}, \quad (21)$$

he tries

$$\psi = |a|^\lambda - |x|^\lambda, \quad (22)$$

and finds the result $\bar{E}_{min} = 1.00298E_0$, a remarkable agreement. In coming up with this guess, the main argument was to make sure the boundary condition, $\psi(\pm a) = 0$, is satisfied. Again, having some thoughts about the boundary conditions turn out to be useful.

4 Excited States

In general, the application of the variational method is difficult for excited states, but it is not impossible. One such way is to identify a quantum number that distinguishes the excited state from the ground state; then one can look for the lowest energy state with that quantum number. Because of the different quantum numbers, the trial wave function is guaranteed to be orthogonal to the ground state. The variational method gives a rigorous upper limit on the lowest energy state with a given quantum number.

For instance, one can look for the $2p$ state of the hydrogen atom because it is the lowest energy state with $l = 1$. Using a trial wave function that involves Y_1^m , it is guaranteed to be orthogonal to the ground-state wave function due to its distinct angular momentum quantum numbers. The true wave function is

$$\psi = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{\sqrt{3}a_0} e^{-Zr/2a_0} Y_1^m, \quad (23)$$

with the energy eigenvalue

$$E_1 = -\frac{Ze^2}{8a_0}. \quad (24)$$

On general grounds, the radial wave functions start with the power r^l because of the centrifugal barrier $-\frac{\hbar^2 l(l+1)}{2mr^2}$. Therefore, we can “guess”

$$\psi = \left(\frac{4}{3d^5}\right)^{1/2} r e^{-r/d} Y_1^m. \quad (25)$$

The prefactor is determined to make it properly normalized. The kinetic energy term has the expectation value

$$\left\langle \frac{\vec{p}^2}{2m} \right\rangle = -\frac{\hbar^2}{2m} \left\langle \frac{d}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right\rangle = \frac{\hbar^2}{2md^2}, \quad (26)$$

while the potential energy term gives

$$\left\langle -\frac{Ze^2}{r} \right\rangle = -\frac{Ze^2}{2d}. \quad (27)$$

The minimization of the expectation value

$$\frac{\partial \bar{E}(d)}{\partial d} = \frac{\partial}{\partial d} \left(\frac{\hbar^2}{2md^2} - \frac{Ze^2}{2d} \right) = -\frac{\hbar^2}{md^3} + \frac{Ze^2}{2d^2} = 0 \quad (28)$$

gives

$$d = \frac{\hbar^2}{2Ze^2 m_e} \quad (29)$$

and the energy

$$E_{min} = -\frac{Ze^2 m_e}{8\hbar^2}. \quad (30)$$

This is the exact result as expected, because we had the correct functional form.

It is interesting to see that the variational method may also give the correct result for excited states even when there is no distinct quantum number. By extending the trial function for $l = 0$ to include a polynomial,

$$\psi = N(1 + kr)e^{-r/d} Y_0^0, \quad (31)$$

where

$$N^{-2} = \int r^2 dr (1 + kr)^2 e^{-2r/d} = \frac{1}{4} d^3 (1 + 3dk + 3d^2 k^2), \quad (32)$$

we compute the expectation value of the energy. We find

$$\bar{E}(d, k) = \langle H \rangle = \frac{1}{1 + 3dk + 3d^2k^2} \left(\frac{\hbar^2(1 + dk + d^2k^2)}{2md^2} - \frac{Ze^2(2 + 4dk + 3d^2k^2)}{2d} \right). \quad (33)$$

By minimizing it, Mathematica finds two real solutions

$$(d, k) = \left(\frac{\hbar^2}{Ze^2m_e}, 0 \right), \left(\frac{2\hbar^2}{Ze^2m_e}, -\frac{Ze^2m_e}{2\hbar^2} \right) \quad (34)$$

with energies

$$\bar{E} = -\frac{Z^2e^4m_e}{2\hbar^2}, -\frac{Z^2e^4m_e}{8\hbar^2}, \quad (35)$$

respectively. Indeed, the second solution is precisely that for the excited $n = 2$ state,

$$\psi = \left(\frac{Z}{2a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} Y_0^0, \quad (36)$$

with the energy eigenvalue

$$E_1 = -\frac{Ze^2}{8a_0}. \quad (37)$$

What is going on here is clear: the excited state does not quite minimize the expectation value, but it gives a *local* minimum for the function $\bar{E}(d, k)$.

Of course, this example is a cheat, because we used the exact form. In general, the variational method can give a good approximation to the ground-state wave function, and then one can try to find another wave function carefully chosen to be orthogonal to the (approximate) ground-state wave function. The better approximation the groundstate is, namely that it is high in the true ground-state content, whatever that is orthogonal to it is low in the ground-state content, and has a good chance of being an excited state. If the groundstate had been obtained poorly, so is the excited state, presumably even worse. There is no guarantee that this method works in general, but this example shows it is worth a shot.

5 Caveat

One word of caution about the variational method is that there is no way to judge how *close* your result is to the true result. The only thing you can

do is to try out many Ansätze and compare them. For example, the Laughlin’s paper on the Fractional Quantum Hall Effect, R.B. Laughlin, *Phys. Rev. Lett.* **50**, 1395–1398 (1983); <http://link.aps.org/abstract/PRL/v50/p1395>, proposed a trial wave function that *beat* other wave functions that had been proposed earlier, such as “Wigner crystal.” (Of course there were many other reasons why his wave function was “right” to deserve the Nobel Prize.) Once your wave function gives a lower energy than your rival’s, you won the race (for a moment, at least).

6 Why Not Full Variation?

One of you were smart to ask: why don’t we do the full arbitrary variation without taking a specific ansatz? Unfortunately, you will be brought back to where you started, namely the time-independent Schrödinger equation.

One can set up an analog of the action, which is the expectation value of the Hamiltonian,

$$\bar{E}[\psi^*, \psi] = \langle H \rangle = \int dx \psi^* H \psi. \quad (38)$$

We can regard \bar{E} as a functional of the wave function ψ , and try to minimize it. Because ψ is complex, we can regard ψ and ψ^* as independent. We can take an arbitrary variation without respect to ψ^* and require that the expectation value is stationary.

At the first sight, it leads to a wrong result:

$$0 = \delta \bar{E} = \int dx \delta \psi^* H \psi, \quad (39)$$

and hence

$$H \psi = 0. \quad (40)$$

We got this wrong result because the expectation value must be varied subject to the requirement that the wave function stays properly normalized. One way to enforce this requirement is to use the Lagrange multiplier,

$$\bar{E}[\psi^*, \psi, \lambda] = \int dx \psi^* H \psi - \lambda \left(\int dx \psi^* \psi - 1 \right). \quad (41)$$

We regard this expression as a functional of ψ , ψ^* , and a function of the Lagrange multiplier λ . The stationary condition with respect to λ obviously

requires the terms in the parentheses vanish; hence the properly normalized wave function. There is an important additional effect: the stationary condition with respect to ψ^* also changes,

$$\delta\bar{E} = \int dx \delta\psi^* H\psi - \lambda \int dx \delta\psi^* \psi = 0. \quad (42)$$

Now that we can treat $\delta\psi^*$ arbitrary, we find

$$H\psi - \lambda\psi = 0. \quad (43)$$

In other words, the Lagrange multiplier, introduced as a mathematical tool to enforce the proper normalization of the wave function, ends up being the energy eigenvalue! This is the correct result. On the other hand, we are back to square one. The reason we chose the variational method was because we *couldn't* solve the Schrödinger equation exactly. We unfortunately didn't gain anything.

By the way, the use of Lagrange multiplier that ends up being the energy comes back prominently when we discuss the Hartree–Fock method of multi-electron atoms in 221B.