Variational Methods

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Introduction

So far, we have concentrated on problems that were analytically solvable, such as the simple harmonic oscillator, the hydrogen atom, and square well type potentials. In fact, we shall soon be confronted with situations where an exact analytic solution is unknown: more general potentials, or atoms with more than one electron. To make progress in these cases, we need approximation methods. The best known method is perturbation theory, which has proved highly successful over a wide range of problems (but by no means all). We shall soon be discussing perturbation methods at length. First, though, we shall review two other approximation methods: in this lecture, the variational method, then in the next lecture the semiclassical WKB method. The variational method works best for the ground state, and in some circumstances (to be described below) for some other low lying states; the WKB method is good for higher states.

Variational Method for Finding the Ground State Energy

The idea is to guess the ground state wave function, but the guess must have an adjustable parameter, which can then be varied (hence the name) to minimize the expectation value of the energy, and thereby find the best approximation to the true ground state wave function. This crude sounding approach can in fact give a surprisingly good approximation to the ground state energy (but usually not so good for the wave function, as will become clear).

We'll begin with a single particle in a potential, $H = p^2/2m + V(\vec{r})$. If the particle is restricted to one dimension, and we're looking for the ground state in any fairly localized potential well, we can start with the family of normalized Gaussians, $|\psi,\alpha\rangle = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$: just find $\langle\psi,\alpha|H|\psi,\alpha\rangle$, differentiate the result with respect to α, setting this to zero (and checking that you have in fact found a minimum.) Not surprisingly, this gives the exact ground state for the simple harmonic oscillator potential, and for nothing else. What is perhaps surprising is that the result is only off by 30% or so for the attractive delta-function potential, even though the wave function looks a lot different (solved in detail in Griffiths, page 258). Obviously, the Gaussian family cannot be used if there is an infinite wall anywhere: one must find a family of wave functions vanishing at the wall.

To gain some insight into what we're doing, suppose the Hamiltonian $H = p^2/2m + V(\vec{r})$ has the set of (unknown to us) eigenstates

$$H|n\rangle = E_n|n\rangle.$$

Since the Hamiltonian is Hermitian, these states span the space of possible wave functions, including our variational family, so:

$$|\psi,\alpha\rangle = \sum a_n(\alpha)|n\rangle.$$

From this,

$$\frac{\langle\psi,\alpha|H|\psi,\alpha\rangle}{\langle\psi,\alpha|\psi,\alpha\rangle} = \sum |a_n|^2 E_n \geq E_0$$

for *any* $|\psi,\alpha\rangle$. (We don't need the denominator if we've chosen a family of normalized wave functions, as we did with the Gaussians above.) Evidently, minimizing $\frac{\langle\psi,\alpha|H|\psi,\alpha\rangle}{\langle\psi,\alpha|\psi,\alpha\rangle}$ as a function of α gives us an upper bound on the ground state energy, hopefully not too far from the true value.

We can see immediately that this will probably be better for finding for the ground state energy than for mapping the ground state wave function: suppose the optimum state in our family is actually $|\alpha_{\min}\rangle = N(|0\rangle + 0.2|1\rangle)$, with the normalization constant $N \cong 0.98$, a 20% admixture of the first excited state. Then the wave function is off by of order 20%, but the energy estimate will be too high by $0.04(E_1 - E_0)$ usually a much smaller error.

To get some idea of how well this works, Messiah applies the method to the ground state of the hydrogen atom. We know it's going to be spherically symmetric, so it amounts to a one-dimensional problem: just the radial wave function. Using standard notation,

$$a_0 = \hbar^2/me^2,\ E_0 = me^4/2\hbar^2, \quad \rho = r/a_0$$

and for a trial wave function *u*

$$E(u) = -E_0 \frac{\int u\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho}\right)u d\rho}{\int u^2 d\rho}$$

(we're going to take *u* real).

Messiah tries three families:

$$u_1 = \rho e^{-\alpha\rho}$$

$$u_2 = \frac{\rho}{\alpha^2 + \rho^2}$$

$$u_3 = \rho^2 e^{-\alpha\rho}$$

and finds $\alpha_{\min} = 1, \quad \pi/4, \quad 3/2$ respectively. The first family, u_1, includes the exact result, and the minimization procedure finds it.

For the three families, then the energy of the best state is off by 0, 25%, 21% respectively.

The wave function error is defined as how far the square of the overlap with the true ground state wave function falls short of unity. For the three families, $\varepsilon = 1 - \left|\langle \psi_0 | \psi_{\text{var}} \rangle\right|^2$:0, 0.21, 0.05. Notice here that our hand waving argument that the energies would be found much more accurately than the wave functions comes unstuck. The third family has far better wave function overlap than the second, but only a slightly better energy estimate. Why? A key point is that the potential is singular at the origin, there is a big contribution to potential energy from a rather small region, and the third family wave function is the least accurate of the three there. The second family functions are very inaccurate at large distances: the expectation value $\langle r \rangle = 1.5a_0, \infty, 1.66a_0$ for the three families. But at large distances, both kinetic and potential energies are small, so the result can still look reasonable. These examples reinforce the point that the variational method should be used cautiously.

Variational Method for Higher States

In some cases, the approach can be used easily for higher states: specifically, in problems having some symmetry. For example, if the one dimensional attractive potential is symmetric about the origin, and has more than one bound state, the ground state will be even, the first excited state odd. Therefore, we can estimate the energy of the first excited state by minimizing a family of odd functions, such as $\psi(x,\alpha) = \left(\sqrt{\pi}/2\alpha^{3/2}\right) x e^{-\alpha x^2/2}$.

Ground State Energy of the Helium Atom by the Variational Method

We know the ground state energy of the hydrogen atom is 1 Ryd, or 13.6 ev. The He^+ ion has $Z = 2$, so will have ground state energy, proportional to Z^2, equal to 4 Ryd. Therefore for the He atom, if we neglect the electron-electron interaction, the ground state energy will be 8 Ryd, 109 ev., the two electrons having opposite spins will both be in the lowest spatial state. Actually, experimentally, the He atom ground state energy is only 79 ev, because the repulsion between the electrons loosens things.

To get a better value for the ground state energy still using tractable wave functions, we change the wave functions from the ionic wave function $\left(Z^3/\pi a_0^3\right)^{1/2} e^{-Zr/a_0}$ with $Z = 2$ to $\left(Z'^3/\pi a_0^3\right)^{1/2} e^{-Z'r/a_0}$ with Z' now a variable parameter. In other words, we are trying to allow for the electron-electron repulsion, which must push the wave functions out a bit, by keeping exactly the same shaped wave function but lessening the effective nuclear charge as reflected in the spread of the wave function from Z to Z', and we'll determine Z' by varying it to find the minimum total energy, including the term from electron-electron repulsion.

To find the potential energy from the nuclear-electron interactions, we of course use the actual nuclear charge $Z = 2$, but the Z' wave function, so the nuclear *P.E.* for the two electrons is:

$$P.E. = -2Ze^2 \int_0^\infty \frac{1}{r} 4\pi r^2 dr \left(Z'^3 / \pi a_0^3 \right) e^{-2Z'r/a_0}$$
$$= -4ZZ' \left(e^2 / 2a_0 \right)$$
$$= -8Z' \text{ Ryd} \quad (Z = 2).$$

This could have been figured out from the formula for the one-electron ion, where the potential energy for the one electron is $2Z^2$ Ryd, one factor of Z being from the nuclear charge, the other from the consequent shrinking of the orbit.

The kinetic energy is even easier: it depends entirely on the shape of the wave function, not on the actual nuclear charge, so for our trial wave function it has to be Z'^2 Ryds per electron.

The tricky part is the *P.E.* for the electron-electron interaction. This is positive.

Each electron has a wave function $\left(Z'^3 / \pi a_0^3 \right)^{1/2} e^{-Z'r/a_0}$, a spherical charge probability distribution.

Denoting charge probability density by $\rho(r)$, we need

$$I = \int\int d\vec{r}_1 d\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$
$$= 16\pi^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{\rho(r_1)\rho(r_2)}{r_>},$$
$$r_> = \max(r_1, r_2).$$

This integral must be done in two stages:

$$I = 16\pi^2 \int_0^\infty \rho(r_1) r_1 dr_1 \left(\int_0^{r_1} \rho(r_2) r_2^2 dr_2 + r_1 \int_{r_1}^\infty \rho(r_2) r_2 dr_2 \right).$$

The result is $(5/4)Z'$ (see Messiah page 691).

Collecting terms, the total energy (for $Z = 2$) is:

$$E = -2\left(4Z' - Z'^2 - \tfrac{5}{8} Z' \right) \text{ Ryd}$$

and this is minimized by taking $Z' = 2 - \frac{5}{16}$, giving an energy of 77.5 ev, off the true value by about 1 ev, so indeed the presence of the other electron is taken care of as far as total energy is concerned by shielding the nuclear charge by an amount $(5/16)e$.