EE5 in 2008 **Lecture notes**
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Approximate Methods

1. Variational Calculations

Few problems can be solved exactly analytically. This is true in Quantum Mechanics just as in Classical Mechanics. The variational method is one of the two most commonly used approximate methods in Quantum Mechanics. It is most often applied to bound states, and the discussion here will be restricted to those cases. (A variational method for scattering states, the Kohn variational principle, does exist and has become quite widely used in atom and molecule scattering calculations in the last few years.)

Given a time-independent Hamiltonian, H, with eigenstates $|\phi_n>$

$$H|\phi_n>=E_n|\phi_n>$$

where $n=0$ for the ground state, $n=1$ for excited state, etc, then for any arbitrary state vector $|\psi>$ in the space spanned by the eigenstates, i.e.

$$|\psi>=\sum_n c_n|\phi_n> ,$$

($|\psi>$ must satisfy the same boundary conditions as the $|\phi_n>$'s). We have

$$<H>=\frac{<\psi|H|\psi>}{<\psi|\psi>} \;\geq\; E_0 \; .$$

This says that the expectation value for the energy using the arbitrary state vector $|\psi>$ can never be lower than the true ground state energy E_0. This is called the *variational principle*. It can be used to get an estimate of E_0 and $|\phi_0>$.

'Proof:' We assume the eigenstates $|\phi_n>$ are normalized

$$<\phi_k|\phi_n>=\delta_{kn} \; .$$

Substituting the above expansion of $|\psi>$ into the expression for $<H>$, first the denom-

inator and then the numerator, gives

$$\begin{aligned}
< \psi|\psi > &= \sum_n c_n^* < \phi_n| \sum_k c_k|\phi_k >= \sum_n |c_n|^2 \\
< \psi|H|\psi > &= \sum_n c_n^* < \phi_n|H| \sum_k c_k|\phi_k > \\
&= \sum_n \sum_k c_n^* c_k < \phi_n|H|\phi_k > \\
&= \sum_n \sum_k c_n^* c_k E_k \delta_{nk} \\
&= \sum_n |c_n|^2 E_n = |c_0|^2 E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \ldots \\
&\geq |c_0|^2 E_0 + |c_1|^2 E_0 + |c_2|^2 E_0 + \ldots = E_0 \sum_n |c_n|^2 \ .
\end{aligned}$$

The inequality follows from using $E_0 \leq E_N$. Taking the ratio gives

$$< H > \geq \ \frac{E_0 \sum_n |c_n|^2}{\sum_n |c_n|^2} = E_0$$

The equality $< H >= E_0$ only holds when $c_1 = c_2 = c_3 \ldots = 0$. Then $|\psi >= |\phi_0 >$, i.e., $|\psi >$ *is* the true ground state.

The variational principle can be used to obtain an approximate ground state energy and wavefunction in the following way: Choose a family of functions $\psi_\alpha =< r|\psi_\alpha >$ that satisfy the right boundary conditions and depend on some parameter, α, for example,

$$\psi_\alpha(x) = e^{-\alpha x^2} \ ,$$

calculate $< H >_\alpha$ and find the value of α, say $\alpha = \alpha_m$, that minimizes $< H >_\alpha$. Then $< H >_{\alpha_m}$ is an estimate of the ground state $|\phi_0 >$. The family of functions $< x|\psi_\alpha >$ is called the *trial functions* and the more flexible it is, the better the estimates will be.

Example: Harmonic Oscillator:

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

A. First choice of trial functions:

$$< x|\psi_\alpha >= \psi_\alpha(x) = e^{-\alpha x^2} \quad (\alpha > 0).$$

The normalizing denomenator is

$$< \psi_\alpha|\psi_\alpha >= \int_{-\infty}^{\infty} dx e^{-2\alpha x^2} = \sqrt{\frac{\pi}{2\alpha}} \ .$$

The numerator is

$$< \psi_\alpha|H|\psi_\alpha >= \int_{-\infty}^{\infty} dx e^{-\alpha x^2}\Big[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2\Big]e^{-\alpha x^2}.$$

Perform the derivative in the first term of the integrand

$$\begin{aligned}\frac{d^2}{dx^2}e^{-\alpha x^2} &= \frac{d}{dx}\big(-2\alpha x e^{-\alpha x^2}\big) \\ &= -2\alpha e^{-\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2}\ .\end{aligned}$$

This gives

$$\begin{aligned}< \psi_\alpha|H|\psi_\alpha > &= \int_{-\infty}^{\infty} dx\left[\frac{\hbar^2 2\alpha}{2m} + \big(-\frac{\hbar^2 4\alpha^2}{2m} + \frac{m\omega^2}{2}\big)x^2\right]e^{-2\alpha x^2} \\ &= \frac{\hbar^2\alpha}{m}\sqrt{\frac{\pi}{2\alpha}} + \Big(-\frac{2\hbar^2\alpha^2}{m} + \frac{m\omega^2}{2}\Big) \underbrace{\frac{1}{4\alpha}\sqrt{\frac{\pi}{2\alpha}}}_{\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2}dx} \\ &= \Big(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\Big)\sqrt{\frac{\pi}{2\alpha}}\ .\end{aligned}$$

Taking the ratio gives

$$< H >_\alpha = \frac{\big(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\big)\sqrt{\frac{\pi}{2x}}}{\sqrt{\frac{\pi}{2\alpha}}} = \frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\ .$$

Figure 1. $< H >_\alpha$ as a function of α. The minimum corresponds to the best approximation.

Now we need to minimize $< H >_\alpha$ with respect to α. For any extremum we have

$$\begin{aligned}\frac{d}{d\alpha} < H >_\alpha \Big|_{\alpha=\alpha_m} &= 0 \\ \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha_m^2} &= 0\ .\end{aligned}$$

This gives an optimal value for α

$$\alpha_m^2 = \frac{m^2\omega^2}{4\hbar^2}$$
$$\alpha_m = \frac{m\omega}{2\hbar} \ .$$

This value of α indeed gives a minimum in $< H >_\alpha$. An estimate for the ground state energy can now be obtained by using the optimal value $\alpha = \alpha_m$

$$\begin{aligned} < H >_{\alpha_m} &= \frac{\hbar^2}{2m}\Big(\frac{m\omega}{2\hbar}\Big) + \frac{m\omega^2}{8}\ \Big(\frac{2\hbar}{m\omega}\Big) \\ &= \frac{\hbar\omega}{2} \\ &= \frac{1}{2}\ \hbar\omega \ . \end{aligned}$$

Here we happen to get exactly the right ground state energy because the family of trial functions we chose, $\psi_\alpha(x) = e^{-\alpha x^2}$, includes the exact wave function.

B. Second choice of trial functions:

$$< x|\psi_\alpha >= \frac{1}{x^2+\alpha} \qquad (\alpha > 0)$$

$$< \psi_\alpha|\psi_\alpha > = \int_{-\infty}^{\infty} \frac{dx}{(x^2+\alpha)^2} = \frac{\pi}{2\alpha\sqrt{\alpha}}$$
$$< H >_\alpha = \frac{\hbar^2}{4m}\ \frac{1}{\alpha} + \frac{1}{2}\ m\omega^2\alpha \ .$$

Minimizing with respect to α

$$\frac{d < H >_\alpha}{d\alpha}\Big|_{\alpha=\alpha_m} = 0$$

gives

$$\alpha_m = \frac{1}{\sqrt{2}}\ \frac{\hbar}{m\omega}$$

and

$$< H >_{\alpha_m} = \frac{1}{\sqrt{2}}\hbar\omega \ .$$

Here the estimate of the ground state energy is off by 20% of the $\hbar\omega$ quantum. Considering how different the trial wave functions are from the true ground state wave function, this is perhaps a surprisingly good estimate of the energy. It turns out that it is always much easier to get good estimates of the energy than the wavefunction. This is because the energy extrema are insensitive to small changes in the wave function, $\delta < H > /\delta\psi = 0$.

The quality of the approximation provided by the variational method is determined by how well the chosen family of trial functions can mimic the true eigenfunction. Experience and intuition are important in making a good choice of trial functions.

How about excited states?

Given an estimate of the ground state wave function, $|\psi_{\alpha_m^0}>$, we can choose a family of functions $|\psi'_\alpha>$ that satisfy

$$<\psi_{\alpha_m^0}|\psi'_\alpha>=0.$$

Carrying out similar analysis as above, but now with $c_0 = 0$, gives

$$<H>=\frac{<\psi'|H|\psi'>}{<\psi'|\psi'>} \;\geq\; E_1 \;.$$

Example: Continuing with case A in the harmonic oscillator example, we can now choose

$$\psi'_\alpha(x) = xe^{-\alpha x^2}$$

as trial functions. These functions are odd, so they are guaranteed to be orthogonal to the ground state wave function, which is even,

$$<\psi_{\alpha_m^0}|\psi'_\alpha>=\int_{-\infty}^{\infty} dx\; xe^{-(\alpha+\alpha_m^0)x^2}=0\;.$$

Here we can use symmetry to choose a valid family of trial functions without having to know the exact ground state wavefunction. After evaluating the numerator and denominator, we get

$$<H>_\alpha=\frac{<\psi'_\alpha|H|\psi'_\alpha>}{<\psi'_\alpha|\psi'_\alpha>}=\frac{3\hbar^2}{2m}\;\alpha+\frac{3}{8}\;\frac{m\omega^2}{\alpha}\;.$$

Minimizing this expectation value of the energy with respect to α gives

$$<H>_{\alpha_m}=\frac{3}{2}\hbar\omega\;.$$

Again, the variational calculation gives exactly the right value here, because we happened to choose a set of trial functions that includes the true eigenfunction.

General variation of the trial function

It is possible to minimize the expectation value of the energy without reference to any explicit form of the wavefunction. We then need to minimize with respect to a function, namely the wave function, rather than a variable. The value of the function at each point on a grid of points becomes a variational parameter. This can be done with the so called calculus of variation. If we make an infinitesimal change in the function

$$|\psi> \rightarrow\; |\psi> + |\delta\psi>$$

then the expectation value $<H>$ will change

$$<H> \rightarrow <H> + \delta <H>\;.$$

Figure 2. An arbitrary, infinitesimal change $|\delta\psi>$ to the trial function.

We will show now that if $|\psi>$ is such that $\delta< H >= 0$ for *any* small change in the function, $|\delta\psi>$, then

$$H|\psi>=< H > |\psi>$$

i.e., $|\psi>$ is an eigenvector of H with an eigenvalue $< H >$. Note that this is true for the excited states as well as the ground state. Therefore, any extremum in $< H >$ is an eigenvalue.

'Proof:' By definition of $< H >$ we have:

$$< H >< \psi|\psi >=< \psi|H|\psi >$$

for any $|\psi>$. After a small change in $|\psi>$ to a state $|\psi + \delta\psi>$ this becomes

$$\big(< H > +\delta < H > \big) < \psi + \delta\psi|\psi + \delta\psi >=< \psi + \delta\psi|H|\psi + \delta\psi > .$$

Multiply this out:

$$\big(< H > +\delta < H > \big)\big(< \psi|\psi > + < \delta\psi|\psi > + < \psi|\delta\psi > + < \delta\psi|\delta\psi > \big)$$
$$= < \psi|H|\psi > + < \delta\psi|H|\psi > + < \psi|H|\delta\psi > + < \delta\psi|H|\delta\psi >$$

The change $\delta\psi$ is infinitesimal so second order terms, such as $< \delta\psi|\delta\psi >$ and $< \delta\psi|H|\delta\psi >$ can be neglected,

$$< H >< \psi|\psi > + \delta < H >< \psi|\psi > + < H > \big(< \delta\psi|\psi > + < \psi|\delta\psi > \big)$$
$$=< \psi|H|\psi > + < \delta\psi|H|\psi > + < \psi|H|\delta\psi >$$
$$\delta < H >= \frac{1}{< \psi|\psi >}\big(< \delta\psi|H|\psi > + < \psi|H|\delta\psi > \big) - < H > \big(< \delta\psi|\psi > + < \psi|\delta\psi > \big).$$

So, if $\delta < H >= 0$ we get the condition

$$< \delta\psi|H - < H > |\psi > + < \psi|H - < H > |\delta\psi >= 0.$$

This is true for any infinitesimal $|\delta\psi>$. In particular we can choose

$$|\delta\psi >= \delta\lambda \ |\chi >$$

with $|\chi>$ defined to be

$$|\chi >\equiv (H - < H >)|\psi > .$$

Using the fact that H is hermitian, $H^\dagger = H$, we can write

$$< \psi|(H - < H >) \equiv< \chi|.$$

The above condition then becomes

$$2\delta\lambda \ < \chi|\chi >= 0,$$

that is

$$< \chi|\chi >= 0.$$

When the modulus is zero, the vector itself must be zero, so $|\chi >= 0$. By definition of $|\chi>$ this means

$$(H - < H >)|\psi >= 0.$$

Since this result is independent of $|\delta\psi>$ it must be true irrespective of what choice we make for $|\delta\psi>$. Therefore

$$H|\psi >=< H > |\psi > .$$