VARIATIONAL METHODS

The perturbation theory developed in the previous section is, of course, of no help unless we already know exact solutions to a problem whose Hamiltonian is sufficiently similar.

The variational method we now discuss is very useful for estimating the ground state energy E_0 when such exact solutions are not available.

We attempt to guess the ground-state energy E_0 by considering a "trial ket" $|\tilde{0}\rangle$, which tries to imitate the true ground-state ket $|0\rangle$.

To this end we first obtain a theorem of great practical importance.

We define $\overline{H}$ such that

$$\overline{H} \equiv \frac{\langle \tilde{0} | H | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}$$

where we have accommodated the possibility that $|0\rangle$ might not be normalized.

Theorem: $\overline{H} \geq E_0$.

This means that we can obtain an upper bound to E_0 by considering various kinds of $|\tilde{0}\rangle$.

The proof of this is very straightforward.

Proof:

Even though we do not know the energy eigenket of the Hamiltonian H, we can imagine that $|\tilde{0}\rangle$ can be expanded as

$$|\tilde{0}\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\tilde{0}\rangle$$

where $|k\rangle$ is an exact energy eigenket of H:

$$H|k\rangle = E_k|k\rangle$$

$$
\begin{aligned}
\overline{H} &= \frac{\sum\limits_{k=0} |\langle k|\tilde{0}\rangle|^2 E_k}{\sum\limits_{k=0} |\langle k|\tilde{0}\rangle|^2} \\
&= \frac{\sum\limits_{k=1}^{\infty} |\langle k|\tilde{0}\rangle|^2 (E_k - E_0)}{\sum\limits_{k=0} |\langle k|\tilde{0}\rangle|^2} + E_0 \\
&\geq E_0,
\end{aligned}
$$

where we have used the fact that $E_k - E_0$ is necessarily positive.

It is also obvious from this proof that the equality sign in $\bar{H} \geq E_0$ holds only if $|\tilde{0}\rangle$ coincides exactly with $|0\rangle$, that is, if the coefficients $\langle k|\tilde{0}\rangle$ all vanish for $k \neq 0$. ■

The theorem $\bar{H} \geq E_0$ is quite powerful because H provides an upper bound to the true ground-state energy.

Furthermore, a relatively poor trial ket can give a fairly good energy estimate for the ground state because if $\langle k|\tilde{0}\rangle \sim O(\varepsilon)\, fork \neq 0$ then from $\bar{H}$ relation we have $\bar{H} - E_0 \sim O(\varepsilon^2)$.

We see an example of this in a moment.

Of course, the method does not say anything about the discrepancy between $\bar{H}$ and E_0; all we know is that $\bar{H}$ is larger than (or equal to) E_0.

Another way to state the theorem is to assert that $\bar{H}$ is stationary with respect to the variation

$$|\tilde{0}\rangle \to |\tilde{0}\rangle + \delta|\tilde{0}\rangle$$

that is, $\delta\bar{H} = 0$ when $|\tilde{0}\rangle$ coincides with $|0\rangle$.

By this we mean that if $|0\rangle + \delta|\tilde{0}\rangle$ is used in place of $|\tilde{0}\rangle$ in $\bar{H}$ equation and we calculate $\bar{H}$, then the error we commit in estimating the true ground-state energy involves $|\tilde{0}\rangle$ to order $\left(|\tilde{0}\rangle\right)^2$.

The variational method per se does not tell us what kind of trial kets are to be used to estimate the ground-state energy.

Quite often we must appeal to physical intuition—for example, the asymptotic behavior of wave function at large distances.

What we do in practice is to characterize trial kets by one or more parameters $\lambda_1, \lambda_2, \ldots$ and compute $\boldsymbol{\bar{H}}$ as a function of $\lambda_1, \lambda_2, \ldots$.

We then minimize $\boldsymbol{\overline{H}}$ by

(1) setting the derivative with respect to the parameters all zero, namely,

$$\frac{\partial \overline{H}}{\partial \lambda_1} = 0, \qquad \frac{\partial \overline{H}}{\partial \lambda_2} = 0, \ldots$$

(2) determining the optimum values of λ_1, λ_2, ...

(3) substituting them back to the expression for $\boldsymbol{\overline{H}}$.

If the wave function for the trial ket already has a functional form of the exact ground-state energy eigenfunction, we of course obtain the true ground-state energy function by this method.

For example, suppose somebody has the foresight to guess that the wave function for the ground state of the hydrogen atom must be of the form

$$\langle \mathbf{x} | 0 \rangle \propto e^{-r/a}$$

where a is regarded as a parameter to be varied.

We then find, upon minimizing $\overline{\boldsymbol{H}}$ with $\langle x|0\rangle \propto e^{-r/a}$, the correct ground-state energy $-\dfrac{e^2}{2a_0}$.

Not surprisingly, the minimum is achieved when a coincides with the Bohr radius a_0.

As a second example, we attempt to estimate the ground state of the infinite-well (one-dimensional box) problem defined by

$$V = \begin{cases} 0, & \text{for } |x| < a \\ \infty, & \text{for } |x| > a. \end{cases}$$

The exact solutions are, of course, well known:

$$\langle x|0\rangle = \frac{1}{\sqrt{a}}\cos\left(\frac{\pi x}{2a}\right),$$

$$E_0 = \left(\frac{\hbar^2}{2m}\right)\left(\frac{\pi^2}{4a^2}\right)$$

Evidently the wave function must vanish at x = ± a; furthermore, for the ground state the wave function cannot have any wiggles.

The simplest analytic function that satisfies both requirements is just a parabola going through x = ± a:

$$\langle x|\tilde{0}\rangle = a^2 - x^2$$

where we have not bothered to normalize $|\tilde{0}\rangle$.

Here there is no variational parameter.

We can compute $\overline{H}$ as follows:

$$\overline{H} = \frac{\left(\frac{-\hbar^2}{2m}\right)\int_{-a}^{a}(a^2 - x^2)\frac{d^2}{dx^2}(a^2 - x^2)dx}{\int_{-a}^{a}(a^2 - x^2)^2\,dx}$$

$$= \left(\frac{10}{\pi^2}\right)\left(\frac{\pi^2\hbar^2}{8a^2m}\right) \simeq 1.0132\ E_0.$$

It is remarkable that with such a simple trial function we can come within 1.3% of the true ground-state energy.

A much better result can be obtained if we use a more sophisticated trial function. We try

$$\langle x|\tilde{0}\rangle = |a|^{\lambda} - |x|^{\lambda}$$

where λ is now regarded as a variational parameter. Straightforward algebra gives

$$\overline{H} = \left[\frac{(\lambda + 1)(2\lambda + 1)}{(2\lambda - 1)}\right]\left(\frac{\hbar^2}{4ma^2}\right)$$

which has a minimum at

$$\lambda = \frac{(1+\sqrt{6})}{2} \simeq 1.72$$

not far from $\lambda = 2$ (a parabola) considered earlier. This gives

This gives

$$\overline{H}_{\min} = \left(\frac{5+2\sqrt{6}}{\pi^2} \right) E_0 \simeq 1.00298 E_0$$

So the variational method with $\langle x|\tilde{0}\rangle = |a|^2 - |x|^2$ gives the correct ground-state energy within 0.3%—a fantastic result considering the simplicity of the trial function used.

How well does this trial function imitate the true ground-state wave function?

It is amusing that we can answer this question without explicitly evaluating the overlap integral $\langle 0|\tilde{0}\rangle$.

Assuming that $|\tilde{0}>$ is normalized, we have

$$\overline{H}_{\min} = \sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2 E_k$$

$$\geq |\langle 0|\tilde{0}\rangle|^2 E_0 + 9E_0(1 - |\langle 0|\tilde{0}\rangle|^2)$$

where $9E_0$ is the energy of the second excited state; the first excited state (k = 1) gives no contribution by parity conservation.

Departure from unity characterizes a component of $|\tilde{0}\rangle$ in a direction orthogonal to $|0\rangle$.

If we are talking about "angle" θ defined by

$$\langle 0|\tilde{0}\rangle = \cos\theta$$

then the before last equation corresponds to

$$\theta \lesssim 1.1^\circ$$

so $|0\rangle$ and $|\tilde{0}\rangle$ are nearly "parallel."

One of the earliest applications of the variational method involved the ground-state energy of the helium atom, which we will discuss in Section 6.1. We can also use the variational method to estimate the energies of first excited states; all we need to do is work with a trial ket orthogonal to the ground-state wave function—either exact, if known, or an approximate one obtained by the variational method.