

# G25.2666: Quantum Mechanics II

## Notes for Lecture 10

### I. VARIATIONAL THEORY AND THE VARIATIONAL PRINCIPLE

A very useful approximation method is known as the variational method. This is the basis of much of quantum chemistry, including Hartree-Fock theory, density functional theory, as well as variational quantum Monte Carlo. The underlying theorem of the method is the Ritz theorem, which states that, given a time-independent Hamiltonian,  $H$ , with a set of eigenvalues,  $E_n$  and eigenvectors,  $|\psi_n\rangle$  satisfying

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

then for any arbitrary ket vector  $|\psi\rangle$  in the Hilbert space, the expectation value of  $H$  in this ket must satisfy

$$\langle H \rangle \equiv \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0$$

where  $E_0$  is the exact ground state energy. Equality only holds if

$$|\psi\rangle = |\psi_0\rangle$$

The proof of the theorem is relatively simple. We expand  $|\psi\rangle$  in the eigenstates of  $H$ :

$$|\psi\rangle = \sum_n C_n |\psi_n\rangle$$

Then

$$\langle \psi | \psi \rangle = \sum_{m,n} C_n^* C_m \langle \psi_n | \psi_m \rangle = \sum_n |C_n|^2$$

and

$$\langle \psi | H | \psi \rangle = \sum_{m,n} C_n^* C_m \langle \psi_n | H | \psi_m \rangle = \sum_{m,n} C_n^* C_m E_n \delta_{mn} = \sum_n E_n |C_n|^2$$

Therefore, the expectation value of  $H$  in the arbitrary ket vector is

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_n E_n |C_n|^2}{\sum_n |C_n|^2}$$

Since  $|C_n|^2 \geq 0$  and  $E_n \geq E_0$ , it follows that

$$\frac{\sum_n E_n |C_n|^2}{\sum_n |C_n|^2} \geq \frac{E_0 \sum_n |C_n|^2}{\sum_n |C_n|^2} = E_0$$

Therefore, we have

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0$$

It is also clear that equality can only hold if  $C_0 = 1$  and  $C_n = 0$ ,  $n > 0$ , in which case,

$$|\psi\rangle = |\psi_0\rangle$$

The conclusion is that  $E_0$  is, therefore, a lower bound on the on  $\langle H \rangle$ , which means that we can approximate  $E_0$  by a minimization of  $\langle H \rangle$  with respect to any parameters that  $|\psi\rangle$  might depend on.

Note that

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

depends on *all* components of  $|\psi\rangle$ . If we write the expectation values as integrals (in one-dimension, for example), then we see that

$$\langle H \rangle = \frac{\int dx \psi^*(x) H \psi(x)}{\int dx \psi^*(x) \psi(x)}$$

which shows that  $\langle H \rangle$  depends on all values of the function  $\psi(x)$ , which is known as a *trial wave function*. We, therefore, call  $\langle H \rangle$  a *functional* of  $\psi(x)$ . Loosely speaking, a functional is a function of a function. We, therefore, denote the variational functional as

$$E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

from which it follows that

$$\begin{aligned} E[\psi] &\geq E_0 \\ E[\psi_0] &= E_0 \end{aligned}$$

The functional character of  $E[\psi]$  can be used to derive another important property of the functional, which is the stationarity property around any eigenstate of  $H$ . In order to derive the stationarity condition, we consider making a small variation of the trial ket according to

$$\begin{aligned} |\psi\rangle &\longrightarrow |\psi\rangle + |\delta\psi\rangle \\ \langle\psi| &\longrightarrow \langle\psi| + \langle\delta\psi| \end{aligned}$$

and we evaluate the functional  $E[\psi + \delta\psi]$ :

$$E[\psi + \delta\psi] = \frac{[\langle\psi| + \langle\delta\psi|] H [|\psi\rangle + |\delta\psi\rangle]}{[\langle\psi| + \langle\delta\psi|] [|\psi\rangle + |\delta\psi\rangle]}$$

Now, we work to first order in  $|\delta\psi\rangle$  or  $\langle\delta\psi|$ . Thus, we expand the functional:

$$E[\psi + \delta\psi] = E[\psi] + \frac{\partial E}{\partial \langle\psi|} \langle\delta\psi| + \frac{\partial E}{\partial |\psi\rangle} |\delta\psi\rangle + \dots$$

and the right side becomes

$$\begin{aligned} \frac{\langle\psi|H\psi\rangle + \langle\delta\psi|H|\psi\rangle + \langle\psi|H|\delta\psi\rangle + \dots}{\langle\psi|\psi\rangle + \langle\psi|\delta\psi\rangle + \langle\delta\psi|\psi\rangle + \dots} &= \frac{\langle\psi|H\psi\rangle + \langle\delta\psi|H|\psi\rangle + \langle\psi|H|\delta\psi\rangle}{\langle\psi|\psi\rangle} \left[ 1 - \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} \right] \\ &= \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\delta\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|H|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} \\ &= E[\psi] + \frac{\langle\delta\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|H|\delta\psi\rangle}{\langle\psi|\psi\rangle} - E[\psi] \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} - E[\psi] \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} \\ &= E[\psi] + \langle\delta\psi| \left[ \frac{H|\psi\rangle}{\langle\psi|\psi\rangle} - \frac{E[\psi]|\psi\rangle}{\langle\psi|\psi\rangle} \right] + \left[ \frac{\langle\psi|H}{\langle\psi|\psi\rangle} - \frac{\langle\psi|E[\psi]}{\langle\psi|\psi\rangle} \right] |\delta\psi\rangle \end{aligned}$$

Now, comparing the left and right sides, we have

$$\begin{aligned} \frac{\partial E}{\partial \langle\psi|} &= \frac{H|\psi\rangle}{\langle\psi|\psi\rangle} - \frac{E[\psi]|\psi\rangle}{\langle\psi|\psi\rangle} \\ \frac{\partial E}{\partial |\psi\rangle} &= \frac{\langle\psi|H}{\langle\psi|\psi\rangle} - \frac{\langle\psi|E[\psi]}{\langle\psi|\psi\rangle} \end{aligned}$$

The stationarity condition is now obtained by setting the two first derivatives of  $E[\psi]$  to zero, which yields to conditions:

$$\begin{aligned} H|\psi\rangle &= E[\psi]|\psi\rangle \\ \langle\psi|H &= \langle\psi|E[\psi] \end{aligned}$$

which are equivalent, being simply adjoints of each other.

Thus, the stationary condition is

$$H|\psi\rangle = E[\psi]|\psi\rangle$$

which can be satisfied only if  $|\psi\rangle$  is an eigenvector of  $H$  with eigenvalue  $E[\psi]$ . This suggests that any eigenvector of  $H$  can be found by searching the functional  $E[\psi]$  for extrema. Although possible, in principle, this is very difficult to implement in practice unless the dimensionality of the system is very low. However, if anyone were able to come up with an efficient algorithm for doing so, the variational theory guarantees that the process will yield the eigenvectors of  $H$ .

### A. Example I: The harmonic oscillator

We will use the harmonic oscillator Hamiltonian in order to illustrate the procedure of using the variational theory. The Hamiltonian we wish to consider, therefore, is

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

Suppose that we do not know the exact ground state solution of this problem, but, using intuition and knowledge of the shape of the potential, we postulate the shape of the wavefunction:

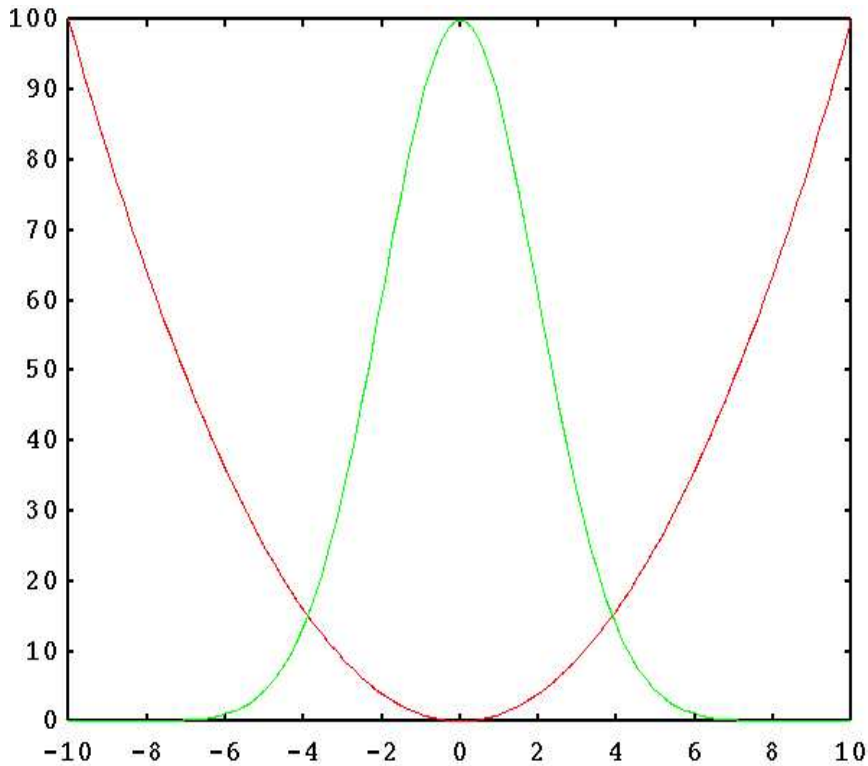


FIG. 1.

and postulate a form for the ground state wave function as

$$\psi(x) = e^{-\alpha x^2} \equiv \psi(x; \alpha)$$

We view  $\alpha$  as a variational parameter with respect to which we can minimize  $\langle H \rangle$ .

Thus, we compute

$$E(\alpha) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

Clearly,

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} dx e^{-2\alpha x^2} = \sqrt{\frac{\pi}{2\alpha}}$$

The quantity

$$\langle \psi | H | \psi \rangle = \int_{-\infty}^{\infty} dx e^{-\alpha x^2} \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right] e^{-\alpha x^2}$$

can be easily shown to be

$$\langle \psi | H | \psi \rangle = \left( \frac{\alpha \hbar^2}{2m} + \frac{m \omega^2}{8\alpha} \right) \sqrt{\frac{\pi}{2\alpha}}$$

There, the ratio of these gives

$$E(\alpha) = \left( \frac{\alpha \hbar^2}{2m} + \frac{m \omega^2}{8\alpha} \right)$$

We then compute the best approximation to  $E_0$  by minimizing  $E(\alpha)$  with respect to  $\alpha$ :

$$\begin{aligned} E'(\alpha) &= \frac{dE}{d\alpha} = 0 \\ \frac{\hbar^2}{2m} - \frac{m \omega^2}{8\alpha^2} &= 0 \\ \alpha^2 &= \frac{m^2 \omega^2}{2\hbar^2} \\ \alpha &= \frac{m\omega}{2\hbar} \end{aligned}$$

Then the energy is obtained from

$$E(\alpha_{\min}) = \frac{\hbar^2}{2m} \frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \frac{2\hbar}{m\omega} = \frac{\hbar\omega}{2} = E_0$$

In this case, the exact ground state energy is obtained because we assumed the correct functional form for the trial wave function. Thus, the ground state wavefunction is clearly given by

$$\psi_0(x) = \left( \frac{m\omega}{\pi \hbar} \right)^{1/4} e^{-m\omega x^2 / 2\hbar}$$

## B. Example II: The harmonic oscillator revisited

Suppose we guessed, instead, a trial wave function of the form:

$$\psi(x) = \frac{1}{x^2 + a^2} \equiv \psi(x; a)$$

The potential and this trial wavefunction are illustrated in the figure below:

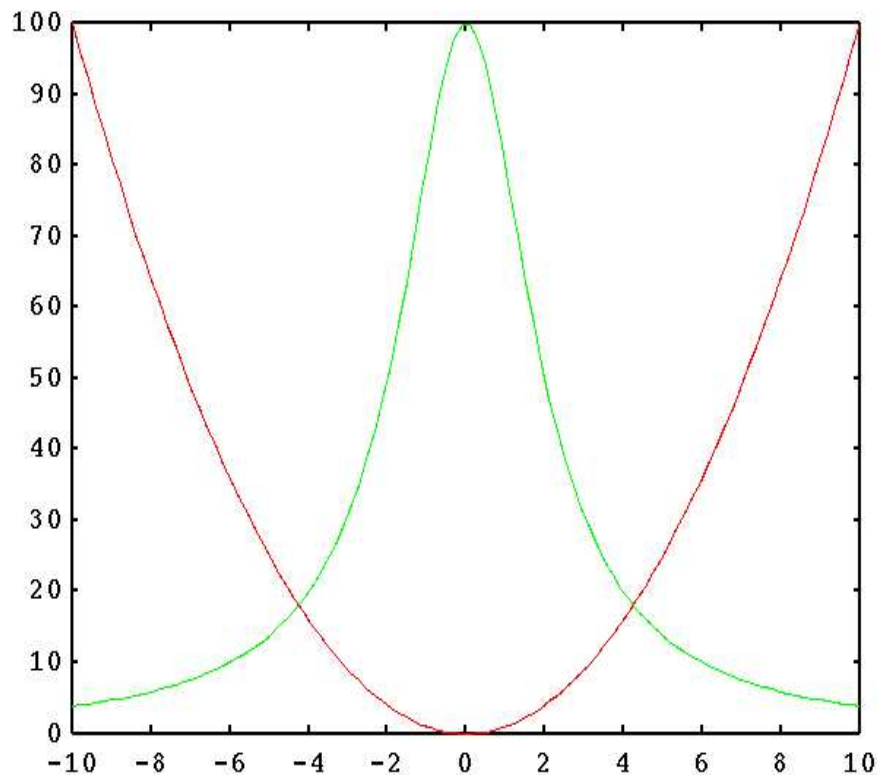


FIG. 2.

We now regard  $a$  as a variational parameter. Thus,

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} dx \frac{1}{(x^2 + a^2)^2}$$

This integral can be evaluated easily by a trigonometric substitution:

$$\begin{aligned} x &= a \tan \theta \\ dx &= a \sec^2 \theta \end{aligned}$$

from which

$$\begin{aligned} \langle \psi | \psi \rangle &= \int_{-\pi/2}^{\pi/2} \frac{a \sec^2 \theta d\theta}{a^4 (1 + \tan^2 \theta)^2} \\ &= \frac{1}{a^3} \int_{-\pi/2}^{\pi/2} \cos^2 \theta d\theta = \frac{\pi}{2a^3} \end{aligned}$$

With a little algebra, it can be similarly shown that

$$\langle \psi | H | \psi \rangle = \frac{\pi \hbar^2}{8ma^5} + \frac{\pi m\omega^2}{4a}$$

Thus,

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\hbar^2}{4ma^2} + \frac{1}{2}m\omega^2 a^2 = E(a)$$

Now, minimizing with respect to  $a$ , we find

$$\begin{aligned}
 E'(a) &= \frac{dE}{da} = 0 \\
 -\frac{\hbar^2}{2ma^3} + m\omega^2 a &= 0 \\
 a^2 &= \hbar\sqrt{2}m\omega
 \end{aligned}$$

and the energy is obtained by

$$\begin{aligned}
 E(a_{\min}) &= \frac{\hbar^2}{4m} \frac{\sqrt{2}m\omega}{\hbar} + \frac{1}{2}m\omega^2 \frac{\hbar}{\sqrt{2}m\omega} \\
 &= \frac{\hbar\omega}{\sqrt{2}} > \frac{\hbar\omega}{2}
 \end{aligned}$$

The result is larger than the true ground state energy, as expected. The error made by this trial wavefunction is

$$\frac{E(a_{\min}) - E_0}{E_0} = \frac{\hbar\omega/\sqrt{2} - \hbar\omega/2}{\hbar\omega/2} = \sqrt{2} - 1 \approx 0.41 = 41\%$$

which is a relatively large error.