

VARIATIONAL METHOD

[H7.3, G8]

In many cases it is not possible to separate the Hamiltonian H into a solvable part and a small perturbation, making perturbation theory unsuitable. For such problems the variational method can be very useful, especially for the ground state.

The method hinges on the following fact: For any state vector $|4\rangle$,

$$\boxed{\frac{\langle 4|H|4\rangle}{\langle 4|4\rangle} \geq E_0,}$$

(1)

where E_0 is the ground state energy. If $|4\rangle$ is normalized, the above simplifies to

$$\langle 4|H|4\rangle \geq E_0.$$

Proof:

Since the unknown eigenfunctions ψ_n of H form a complete set, we can write

$$|\psi\rangle = \sum_n |\psi_n\rangle \langle \psi_n| \psi\rangle = \sum_n c_n |\psi_n\rangle,$$

with

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

and $\langle \psi_m | \psi_n \rangle = \delta_{mn}$. Hence,

$$\langle \psi | \psi \rangle = \sum_{m,n} c_m^* c_n \delta_{mn} = \sum_n |c_n|^2,$$

and

$$\langle \psi | H | \psi \rangle = \sum_{m,n} c_m^* E_n c_n \delta_{mn} = \sum_n |c_n|^2 E_n.$$

Since the ground state energy, by definition is the smallest eigenvalue, $E_0 \leq E_n$, we get

$$\langle \psi | H | \psi \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 = E_0 \langle \psi | \psi \rangle$$

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

Since this holds for any $|4\rangle$, we can use trial states or wave functions with free parameters, and minimize the left hand side of (1) with respect to these parameters in order to get as close as possible to the ground state energy.

EXAMPLE - Harmonic Oscillator [G p. 328]

Suppose we want to find the ground state energy of the harmonic oscillator,

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2,$$

which we of course already know to be $E_0 = \hbar\omega/2$. We pick a Gaussian trial wavefunction

$$\psi(x) = Ae^{-bx^2},$$

with some constant $b > 0$. We now calculate

$$\langle 4|4\rangle = \int_{-\infty}^{\infty} dx \psi^*(x) \psi(x) = |A|^2 \sqrt{\frac{\pi}{2b}}$$

and

$$\begin{aligned}\langle \psi | H | \psi \rangle &= \int_{-\infty}^{\infty} dx \psi''(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right] \psi(x) \\ &= |A|^2 \left[+ \frac{\hbar^2}{2m} \sqrt{\frac{\pi b}{2}} + \frac{1}{8} m \omega^2 \sqrt{\frac{\pi}{2 b^3}} \right].\end{aligned}$$

Hence

$$\begin{aligned}E_0 \leq E(b) &= \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \frac{\frac{\hbar^2 b}{2m} + \frac{m \omega^2}{8b}}{1},\end{aligned}$$

see Griffiths p. 328 for details.

Since $E_0 \leq E(b)$, we minimize $E(b)$ with respect to b :

$$\frac{dE(b)}{db} = \frac{\hbar^2}{2m} - \frac{m \omega^2}{8b^2} = 0 \Rightarrow b_{\min} = \frac{m \omega}{2 \hbar}.$$

Hence,

$$E_0 \leq E(b_{\min}) = \frac{1}{2} \hbar \omega,$$

the exact solution! We were "lucky" with our choice of trial wavefunction. (157)

The Gaussian is a popular trial function because it is easy to work with, even when it does not greatly resemble the true ground state.

The variational method is very powerful, and easy to use. For instance, to find the ground state energy of a molecule, one could use a trial wavefunction ψ with a large number of adjustable parameters, calculate $\langle 41\text{f}1/2 \rangle / \langle 41\text{f} \rangle$, and tweak the parameters to minimize the ground state estimate. One can then often get very close to the true E_0 , even though ψ has little resemblance with the true wavefunction.

The only problem with the method is that one cannot tell how close to the true ground state the approximation is. (188)

EXAMPLE - Ground state of Helium

[G 8.2]

We have already discussed helium, with Hamiltonian

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{|r_1 - r_2|} \right]$$

both in the lectures and exercise set 10.

By neglecting $\text{He}-\text{el}$, the electron-electron repulsion and using hydrogenic wavefunctions, we found $E_0 = 8E_1^{\text{hydr}} = -109$ eV, which is far off the experimental value

$$E_0^{\text{exp}} = -78.975 \text{ eV.}$$

We want to estimate E_0 , including the effects of $\text{He}-\text{el}$, using the variation method, and the hydrogenic wavefunction

$$\psi_0(\vec{r}_1, \vec{r}_2) = \frac{8}{\pi a_0^3} e^{-2(r_1 + r_2)/a_0},$$

where a_0 is the Bohr radius.

(189)

Since ψ_0 is normalized, we get:

$$E_0 \leq \langle \psi_0 | H | \psi_0 \rangle$$

$$\leq 8E_1^{\text{hydro}} + \langle \psi_0 | \text{H}_{\text{el-el}} | \psi_0 \rangle.$$

The last term is exactly the same as the first order correction calculated in problem set 10 with the (uncritical) use of perturbation theory. The result is

$$E_0 \leq -74.8 \text{ eV},$$

see solution to problem set 10, or Griffiths pp. 333–335. This is a quite good estimate, but we can improve it by adding a variable parameter to our trial wavefunction:

$$\psi_1(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}.$$

The motivation for allowing Z to deviate from 2 is that the electrons could (190)

partially screen the nuclear charge,
thus reducing Z .

The wavefunction ψ_1 is an eigenstate
of an "unperturbed" Hamiltonian
with nuclear charge Z instead of 2.
We therefore rewrite the Hamiltonian:

$$H = -\frac{\hbar^2}{2m} \left[\nabla_1^2 + \nabla_2^2 \right] - \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z}{r_1} + \frac{Z}{r_2} \right]$$

$$+ \frac{e^2}{4\pi\epsilon_0} \left[\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right]$$

It's important to note that we do
not change the Hamiltonian itself.

We now get:

$$\langle H \rangle(Z) = \langle \psi_1 | H | \psi_1 \rangle$$

$$= 2Z^2 E_1^{\text{hydr}} + \frac{2(Z-2)e^2}{4\pi\epsilon_0} \langle \psi_1 | \frac{1}{r} | \psi_1 \rangle$$

$$+ \langle \psi_1 | H_{\text{el-el}} | \psi_1 \rangle.$$

Using

$$\langle \psi_1 | \frac{1}{r} | \psi_1 \rangle = \frac{Z}{a_0}$$

and

$$\langle \psi_1 | H_{\text{el-el}} | \psi_1 \rangle = -\frac{5Z}{4} E_1^{\text{hydr}}$$

we get

$$\begin{aligned}\langle H \rangle(z) &= \left[2z^2 - 4z(z-2) - \frac{5z}{4} \right] E_1^{\text{hydr}} \\ &= \left[-2z^2 + \frac{27}{4}z \right] E_1^{\text{hydr.}} \\ &\geq E_0.\end{aligned}$$

Since this should always hold according to the variational principle, we minimize $\langle H \rangle(z)$:

$$\frac{d \langle H \rangle}{dz} = \left[-4z + \frac{27}{4} \right] E_1^{\text{hydr}}$$

$$\Rightarrow z_{\min} = \frac{27}{16} \approx 1.69 < 2.$$

Hence, we find a new upper bound for the ground state energy,

$$E_0 \leq \langle H \rangle_{\min} = \frac{1}{2} \left(\frac{3}{2} \right)^6 E_1^{\text{hydr}} = -77.5 \text{ eV},$$

which is only 2% off the experimental value. It could be calculated even more accurately by using more complicated trial functions with more parameters, as was done by Egil Hylleraas in the late 1920's.

EXCITED STATES

[H 7.3.3]

We can also use the variational method for excited states, at least in principle, if we are able to construct test functions that are orthogonal to all the wavefunctions of the lower energy levels.

In other words, if we have a set of energies

$$\{E_n\} = \{E_0, E_1, \dots\} \text{ with } E_{n+1} > E_n \quad \forall n \in \{0, 1, \dots\}$$

with corresponding ψ_n ($n=0, 1, 2, \dots$), then a test function ψ for ψ_N must fulfill

$$\langle \psi | \psi_n \rangle = 0 \quad \forall n < N.$$

The difficulty is of course that we often don't know ψ_n ($n=0, 1, 2, \dots$) exactly, but might themselves be approximated by test wavefunctions using the variational method. Hence, we have to deal with intrinsic errors that we cannot evade.

In many cases, we can use symmetry to help us choose orthogonal trial functions. For instance, for a symmetric potential in one dimension, the ground state is always symmetric. We can then

estimate the first excited state using antisymmetric trial functions.

More generally, if there exists a Hermitian operator A such that $[A, H] = 0$, the ground state must be an eigenstate of A ;

$$A|\psi_0\rangle = \alpha|\psi_0\rangle$$

If we choose a trial state $|\psi\rangle$ that is an eigenstate of A ,

$$A|\psi\rangle = \alpha|\psi\rangle$$

with $\alpha \neq \alpha_0$, we know that $|\psi_0\rangle$ and $|\psi\rangle$ are orthogonal.* Using $|\psi\rangle$ will therefore give an upper bound for an excited state,

* see next page.

[Reminder: If $A\psi_0 = a_0 \psi_0$ and $A\psi = a\psi$, with $a_0 \neq a$, and A is Hermitian,

$$\langle \psi | A | \psi_0 \rangle = \langle \psi_0 | A | \psi \rangle^*$$

$$= a_0 \langle \psi | \psi_0 \rangle = a^* \langle \psi_0 | \psi \rangle^* = a^* \langle \psi | \psi_0 \rangle.$$

Since A is Hermitian $a_0, a \in \mathbb{R} \Rightarrow \langle \psi | \psi_0 \rangle = 0.$]