

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 $|4\rangle$,

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

(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 $|f\rangle$, 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

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

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.

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 $\langle 41\text{H}1/2 \rangle / \langle 414 \rangle$, 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.

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

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

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 ;

$$A|\psi_0\rangle = a|\psi_0\rangle.$$

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,

[Reminder: If $A|\psi_0\rangle = \alpha_0|\psi_0\rangle$ and $A|\psi\rangle = \alpha|\psi\rangle$, with $\alpha_0 \neq \alpha$, and A is Hermitian,

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

$$= \alpha_0 \langle\psi|\psi_0\rangle = \alpha^* \langle\psi_0|\psi\rangle^* = \alpha^* \langle\psi|\psi_0\rangle.$$

Since A is Hermitian $\alpha_0, \alpha \in \mathbb{R} \Rightarrow \langle\psi|\psi_0\rangle = 0.$]

EXAMPLE - The Helium atom

The only atom we have studied so far is the hydrogen atom, for which we could find the energy eigenvalues analytically. We will now consider heavier atoms, and more specifically the helium atom.

In general, a neutral atom of atomic number Z , with a nucleus of charge Ze and Z electrons (mass m_e and charge $-e$) is described by the Hamiltonian

$$H = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right. \\ \left. + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \sum_{l \neq j} \frac{e^2}{|r_j - r_l|} \right) \right\} \text{el-el interaction}$$

due to double
Counting

We need to solve $H\psi = E\psi$ for

Wave function $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z)$.

This can only be solved exactly for $Z=1$ — hydrogen! Let's still try to find approximate solutions for $Z=2$, helium.

With $Z=2$, the Hamiltonian simplifies to

$$\begin{aligned} H = & -\frac{\hbar^2}{2me} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \\ & - \frac{\hbar^2}{2me} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{1}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \\ \equiv & H_1 + H_2 + H_{12}. \end{aligned}$$

H_1 and H_2 are hydrogenic Hamiltonians with nuclear charge $2e$, for electron 1 and 2. H_{12} describes the repulsion between the electrons, and causes all the problems!

If we ignore H_{12} , the SE separates, resulting in solutions

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{nlm}(\vec{r}_1) \psi_{n'l'm'}(\vec{r}_2)$$

(must be antisym.)

where ψ_{nlm} are hydrogen wavefunctions.
However, since $e \rightarrow 2e$, the Bohr radius is halved $a_0 \rightarrow a_0/2$, and

$$E_n^{Z=2} = 4E_n^{Z=1}$$

for each electron, giving total energy

$$E = 4(E_n + E_{n'})$$

with $E_n = -13.6/n^2$ eV.

Ground state

For the ground state we would get

$$E_0 = -109 \text{ eV},$$

and

$$\begin{aligned} \psi_0(\vec{r}_1, \vec{r}_2) &= \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) \quad (\text{spin singlet}) \\ &= \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0}, \end{aligned}$$

where a_0 is the Bohr radius.

The experimentally measured ground state energy is

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

which is quite a lot higher than our approximation. This is because we ignored the electron-electron H_{12} , which is positive and therefore should increase the ground state energy.

Let's now use the variational method to estimate the ground state energy, using ψ_0 as our trial wavefunction

Since ψ_0 is normalized, we get:

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

$$\leq \underbrace{8E_1}_{E_0}^{\text{hydr}} + \langle \psi_0 | H_{12} | \psi_0 \rangle.$$

where

$$\langle \psi_0 | H_{12} | \psi_0 \rangle = \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_{a0}} \right)^2 \int d\vec{r}_1 \int d\vec{r}_2 \frac{e^{-4r_{1a0}} e^{-4r_{2a0}}}{|\vec{r}_1 - \vec{r}_2|}$$

(see Griffiths pp. 333 - 335.)

$$= \frac{5}{2} \frac{e^2}{8\pi\epsilon_0 Z a_0} = - \frac{5}{2} E_1^{\text{hydro}} = 34 \text{ eV.}$$

$$\Rightarrow E_0 \leq -74.8 \text{ eV.}$$

This is a quite good estimate, but we can improve it by adding a variable parameter to our trial wavefunction:

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

The motivation for allowing Z to deviate from 2 is that the electrons could partially screen the nuclear charge, thus reducing Z .

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

$$H = -\frac{t^2}{2m} \left[\nabla_1^2 + \nabla_2^2 \right] - \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z}{r_1} + \frac{Z}{r_2} \right] + \frac{e^2}{4\pi\epsilon_0} \left[\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right]$$

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

We now get:

$$\begin{aligned} \langle H \rangle(Z) &= \langle \phi | H | \phi \rangle \\ &= 2Z^2 E_1^{\text{hydr}} + \frac{2(Z-2)e^2}{4\pi\epsilon_0} \langle \phi | \frac{1}{r} | \phi \rangle \\ &\quad + \langle \phi | H_{1,2} | \phi \rangle. \end{aligned}$$

Using

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

and

$$\langle \phi | H_{12} | \phi \rangle = -\frac{5Z}{4} E_1^{\text{hydr}}$$

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 $\langle H \rangle(z)$:

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

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

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

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

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

What about excited states? The excited states consist of one electron in the $n=1$ state and the other with $n>1$, $\neq 1$.

There are two ways to construct antisymmetric states

$$|p\rangle = [\text{sym. } \Psi] [\text{spin singlet}] - \text{parallel}$$

$$|0\rangle = [\text{antisym. } \Psi] [\text{spin triplet}] - \text{orthogonal}$$

Both are possible for the excited states. Experimentally, one finds

$$E_{1,p}^{\text{exp}} = E_0 + 22.55 \text{ eV},$$

$$E_{1,0}^{\text{exp}} = E_0 + 19.77 \text{ eV},$$

For the first excited states. Why is there a difference?

If the wavefunction is symmetric ("boson-like"), we saw earlier that the expectation value for the separation is smaller than for the antisymmetric wavefunction ("fermion-like"). Hence, the interaction energy due to H_{12} should be higher for $|1p\rangle$ than for $|10\rangle$:

$$\langle E_{1,S} = \langle S | H | S \rangle$$

$$= \langle S | H_1 + H_2 | S \rangle + \langle S | H_{12} | S \rangle$$

with $S = p, 0$. We write

$$|10\rangle = \frac{1}{\sqrt{2}}(|200\rangle - |110\rangle) \pm \frac{1}{\sqrt{2}}(|100\rangle - |210\rangle) \equiv \frac{|(2,1)\pm 1,2\rangle}{\sqrt{2}}$$

where we have neglected the spin part

and get

$$E_{1,3} \leq 4E_1^{\text{hydr}} + 4E_2^{\text{hydr}}$$
$$+ \frac{1}{2} \left[\langle 2,1 | H_{1,2} | 2,1 \rangle + \langle 1,2 | H_{1,2} | 1,2 \rangle \right.$$
$$\left. \pm \langle 2,1 | H_{1,2} | 1,2 \rangle \pm \langle 1,2 | H_{1,2} | 2,1 \rangle \right]$$

Calculating this numerically we get

$$E_p = -55.4 \text{ eV} \quad \text{vs} \quad \sim -58 \text{ eV}$$
$$E_0 = -57.8 \text{ eV} \quad \sim -59. \text{ eV.}$$

which is in decent agreement
with the experimental values.