Variational Method

Only a 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 Chemistry. It is used in the Hartree-Fock approximation, the configuration interaction method and density functional theory. But, before dealing with systems of many electrons, it is better to get to know the method by applying it to simpler systems.

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 denominator and then the numerator, gives

$$\begin{aligned}
<\psi|\psi> &= \sum_n c_n^* <\phi_n| \sum_k c_k|\phi_k >= \sum_n\sum_k c_n^* c_k \delta_{kn} = \sum_n |c_n|^2 \\
<\psi|H|\psi> &= \sum_n c_n^* <\phi_n|H| \sum_k c_k|\phi_k> \\
&= \sum_n \ \sum_k \ c_n^* c_k <\phi_n|H|\phi_k> \\
&= \sum_n \ \sum_k \ c_n^* c_k E_k \delta_{nk} \\
&= \sum_n |c_n|^2 E_n = |c_0|^2E_0 + |c_1|^2E_1 + |c_2|^2E_2 + \dots \\
&\geq |c_0|^2E_0 + |c_1|^2E_0 + |c_2|^2E_0 + \cdots = E_0 \sum_n |c_n|^2 \ .
\end{aligned} \tag{1}$$

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 $c_1 = c_2 = c_3 \cdots = 0$. 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 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

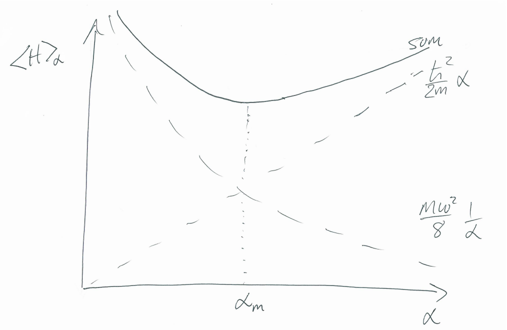
$$\begin{aligned} \frac{d^2}{dx^2}e^{-\alpha x^2} &= \frac{d}{dx}\big(-2\alpha x e^{-\alpha x^2}\big) \\ &= -2\alpha e^{-\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2} \ . \end{aligned} \tag{2}$$

This gives

$$\begin{aligned} < \psi_\alpha|H|\psi_\alpha > &= \int_{-\infty}^{\infty} dx\left[\frac{\hbar^2 2\alpha}{2m} + \big(-\frac{\hbar^2 4\alpha^2}{2m} + \frac{m\omega^2}{2}\big)x^2\right]e^{-2\alpha x^2} \\ &= \frac{\hbar^2\alpha}{m}\sqrt{\frac{\pi}{2\alpha}} + \Big(-\frac{2\hbar^2\alpha^2}{m} + \frac{m\omega^2}{2}\Big)\quad \underbrace{\frac{1}{4\alpha}\sqrt{\frac{\pi}{2\alpha}}}_{\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx} \\ &= \Big(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\Big)\sqrt{\frac{\pi}{2\alpha}} \ . \end{aligned} \tag{3}$$

Taking the ratio gives the expectation value of the energy as a function of α

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



Expectation value of the energy, $< H >_\alpha$, as function of the width of the Gaussian trial function, α, (solid line) and its two contributions(dashed lines). The minimum represents the optimal value according to the variational principle.

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

$$\begin{aligned} \frac{d}{d\alpha} < H >_\alpha \Big|_{\alpha=\alpha_m} &= 0 \\ \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha_m^2} &= 0 \quad . \end{aligned} \tag{4}$$

This gives an optimal value for α

$$\begin{aligned} \alpha_m^2 &= \frac{m^2\omega^2}{4\hbar^2} \\ \alpha_m &= \frac{m\omega}{2\hbar} \ . \end{aligned} \tag{5}$$

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 $\alpha = \alpha_m$

$$\begin{aligned} < H >_{\alpha_m} &= \frac{\hbar^2}{2m}\left(\frac{m\omega}{2\hbar}\right) + \frac{m\omega^2}{8}\left(\frac{2\hbar}{m\omega}\right) \\ &= \frac{\hbar\omega}{2} \\ &= \frac{1}{2}\ \hbar\omega \ . \end{aligned} \tag{6}$$

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:

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

$$\begin{aligned} < \psi_\alpha|\psi_\alpha > &= \int_{-\infty}^{\infty} \frac{dx}{(x^2+\alpha)^2} = \frac{\pi}{2\alpha\sqrt{\alpha}} \\ < H >_\alpha &= \frac{\hbar^2}{4m}\ \frac{1}{\alpha} + \frac{1}{2}\ m\omega^2\alpha \ . \end{aligned} \tag{7}$$

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 basis vectors $|\psi'_\alpha>$ that are orthogonal to the ground state, i.e. they 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

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

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

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

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

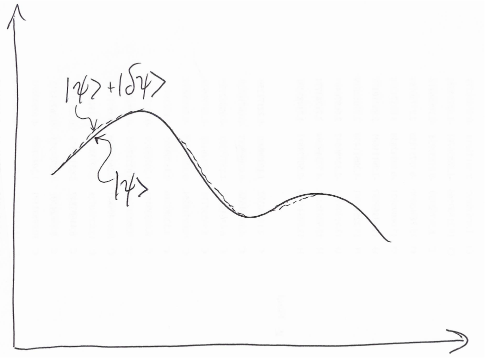
It is possible to minimize the expectation value of the energy, $< H >$, without reference to any explicit form of the trial wavefunction. We then need to minimize $< H > = < \psi | H | \psi > \ / \ < \psi | \psi >$ with respect to any arbitrary infinitesimal change in $|\psi>$ rather than with respect to a parameter in a predefined form of the trial function. Or, if we represent the trial function by its numerical values on a dense grid of the variable(s), the value of the function at each point on the grid becomes a variational parameter. The expectation value of the energy is an example of a *functional*. While a function is an operation where the input is a number and the output is a number, a functional has a function as input and the output is a number. An integral is an example of a functional. Just like we find a minimum of a function by differentiating the function with respect to the variable and setting the derivative to zero, a functional is minimized by making an arbitrary, infinitesimal change to the input function and setting the change in the functional to zero. This is referred to as calculus of variation. If we make an infinitesimal change in the function

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

then the expectation value $<H>$ will change by $\delta<H>$, that is

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

It is good to go through this general derivation of the variational principle for two reasons. One is to see how the variational principle can be applied to excited states, not just to the ground state. The second is to see this technique of finding the extremum of a functional with respect to a function because this is how Hartree-Fock is derived, the central concept in computational chemistry.



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

We will show now that if $|\psi>$ is such that $\delta<H>=0$ for *any* infinitesimal 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 $<H>$ with respect to an arbitrary, infinitesimal change in $|\psi>$ is an eigenvalue of H.

'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

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

By making use of the fact that the integration, $<\cdots>$, and the operator H are linear, we get

$$\begin{aligned}\big(<H>+\delta<H>\big)\big(<\psi|\psi>+<\delta\psi|\psi>+<\psi|\delta\psi>+<\delta\psi|\delta\psi>\big)\\ =<\psi|H|\psi>+<\delta\psi|H|\psi>+<\psi|H|\delta\psi>+<\delta\psi|H|\delta\psi>\end{aligned} \tag{8}$$

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,

$$\begin{aligned}<H><\psi|\psi>+\delta<H><\psi|\psi>+<H>\big(<\delta\psi|\psi>+<\psi|\delta\psi>\big)\\ =<\psi|H|\psi>+<\delta\psi|H|\psi>+<\psi|H|\delta\psi>\\ \delta<H>=\frac{1}{<\psi|\psi>}\big[\big(<\delta\psi|H|\psi>+<\psi|H|\delta\psi>\big)-<H>\big(<\delta\psi|\psi>+<\psi|\delta\psi>\big)\big].\end{aligned} \tag{9}$$

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

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

and

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

So, $|\psi >$ must be one of the eigenstates and it corresponds to eigenvalue $< H >$. This is not necessarily the ground state. Any stationary function in the sense that an arbitrary change to the function does not change the expectation value of the energy, is a solution to the Schrödinger equation. Note that a stationary point is not necessarily a minimum, it can be a saddle point or maximum on the energy surface.