

7.) Chapter 7.The Rayleigh-Ritz Variational Method

So far our approximation schemes have depended on us knowing the solution to the unperturbed problem which physically describes the major aspects of the system. Of course one can seldom solve such a problem, for example in a multi-electron atom or in molecular physics we cannot ignore all the inter-electron interactions or even spin. The variational method does not rely on solving exactly any simpler Hamiltonian in order to approximate the energy levels.

The mathematical problem underlying the variational method is to find the conditions under which variations in the arbitrary states $|\varphi\rangle, |\chi\rangle$ leave the functional

$$L[\varphi, \chi] \equiv \langle \varphi | H | \chi \rangle - E \langle \varphi | \chi \rangle$$

stationary with H an operator and $E \in \mathbb{C}$.

The stationarity conditions are found by taking the variational derivatives of $\mathcal{L}$ with respect to $|\psi\rangle$ and $|\chi\rangle$. That is, suppose we allow $|\psi\rangle$ and $|\chi\rangle$ to vary from $|\psi_0\rangle$ & $|\chi_0\rangle$ infinitesimally in an independent way

$$|\psi\rangle = |\psi_0\rangle + a|\alpha\rangle$$

$$|\chi\rangle = |\chi_0\rangle + b|\beta\rangle$$

with a, b infinitesimal complex numbers and $|\alpha\rangle$ and $|\beta\rangle$ arbitrary states.

Then

$$\begin{aligned} \mathcal{L}[\psi, \chi] &= (\langle\psi_0| + a^*\langle\alpha|) H (|\chi_0\rangle + b|\beta\rangle) \\ &\quad - E (\langle\psi_0| + a^*\langle\alpha|) (|\chi_0\rangle + b|\beta\rangle) \end{aligned}$$

$$= \mathcal{L}[\psi_0, \chi_0] + a^*\langle\alpha|(H-E)|\chi_0\rangle$$

$$+ b\langle\psi_0|(H-E)|\beta\rangle$$

$$+ \cancel{a^*b\mathcal{L}[\alpha, \beta]}$$

→ neglect
second order
infinitesimal

Then the variation of L is zero

$$\begin{aligned}\delta L &= L[\psi, \chi] - L[\psi_0, \chi_0] \\ &= a^* \langle \alpha | (H - E) | \chi_0 \rangle + b \langle \psi_0 | (H - E) | \beta \rangle \\ &= 0\end{aligned}$$

if $(H - E) | \chi_0 \rangle = 0$ and

$$\langle \psi_0 | (H - E) = 0 \Rightarrow (H^\dagger - E^*) | \psi_0 \rangle = 0$$

Since a, b are independent.

Then L is stationary if $| \chi_0 \rangle$ is the right eigenvector of H and $| \psi_0 \rangle$ is the left eigenvector of H and E is the (complex) eigenvalue. If $H = H^\dagger$, as in our case (most of the time),

then $E = E^*$ and $| \psi_0 \rangle = | \chi_0 \rangle$.

Then $\forall L[\psi, \chi] = \langle \psi | (H - E) | \chi \rangle$. Of course we need only consider, but often useful to use $L[\psi, \chi]$, until we evaluate L at the stationary states $| \chi_0 \rangle$, it is not zero, i.e. $| \chi \rangle$ is arbitrary.

The idea of the method then is to choose any trial states $|\psi\rangle$ and $|\phi\rangle$ (guided by physical intuition) which in general depend on certain parameters which we vary until $L[\psi, \phi]$ is stationary. We then can extract approximate values for E , the energy levels of the system from this. This approach is encapsulated in the theorem:

These energy values are approx. since the space of trial functions is smaller than the full space.

Variational Theorem: If $H = H^\dagger$ and

E_0 is the ground state (lowest) energy eigenvalue of H , then for any state $|\psi\rangle$ the inequality is true

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

Proof: The proof is straightforward.

The eigenstates of H

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

are complete then we expand any $|\psi\rangle$ in terms of $\{|\psi_n\rangle\}$

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

which for orthonormal $|\psi_n\rangle$; $C_n = \langle \psi_n | \psi \rangle$

then

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

Since E_0 is the lowest value of E_n this is bounded by

$$\langle \psi | H | \psi \rangle \geq E_0 \sum_n |C_n|^2$$

Since $\langle \psi | \psi \rangle = \sum_n |C_n|^2$ we have

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

Clearly the equality holds only when $C_n = 0$, $n \neq 0$. But this implies

$|\psi\rangle = C_0 |\psi_0\rangle$ the true ground state

So the equality is true iff $|\psi\rangle = c|\psi_0\rangle$.

The expectation value of the Hamiltonian above is called the energy functional

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

Its lower bound is $E_0 \leq E[\psi]$, for any $|\psi\rangle$.

Note that

$$\langle \psi | \psi \rangle E[\psi] = L[\psi, \psi] + E \langle \psi | \psi \rangle$$

or
$$L[\psi, \psi] = (E[\psi] - E) \langle \psi | \psi \rangle$$

hence

$$L[\psi, \psi] \geq (E_0 - E) \langle \psi | \psi \rangle$$

Further at the stationary points of $L[\psi, \psi]$

$E = E_n$ the eigenvalues, thus

For $\delta L = 0 \Rightarrow E[\psi_n] = E_n$ as is

clear from its definition.

The variation of the energy functional is found from

$$E[\psi] = \frac{(\langle \psi_0 | + a^* \langle \alpha |) H (\psi_0 + a |\alpha \rangle)}{\langle \psi_0 | \psi_0 \rangle + a^* \langle \alpha | \psi_0 \rangle + a \langle \psi_0 | \alpha \rangle + a^* a \langle \alpha | \alpha \rangle}$$

with $|\alpha\rangle$ arbitrary and a infinitesimal

$$= \frac{\langle \psi_0 | H | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} \left[1 - a^* \frac{\langle \alpha | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} - a \frac{\langle \psi_0 | \alpha \rangle}{\langle \psi_0 | \psi_0 \rangle} \right]$$

$$+ \frac{a^* \langle \alpha | H | \psi_0 \rangle + a \langle \psi_0 | H | \alpha \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$= E[\psi_0] + \frac{a^*}{\langle \psi_0 | \psi_0 \rangle} \langle \alpha | (H - E[\psi_0]) | \psi_0 \rangle$$

$$+ \frac{a}{\langle \psi_0 | \psi_0 \rangle} \langle \psi_0 | (H - E[\psi_0]) | \alpha \rangle .$$

$$\text{So for } \delta E \equiv E[\psi] - E[\psi_0] = 0$$

$$\Rightarrow H|\psi_0\rangle = E[\psi_0]|\psi_0\rangle$$

that is $|\psi_0\rangle$ is an eigenstate of H and $E[\psi_0]$ is the eigenenergy.

Thus the stationary points of $E[\psi]$ are the stationary points of $L[\psi, \bar{\psi}]$.

$\delta E[\psi] = 0 \iff \delta L[\psi] = 0$ and both conditions imply $H|\psi\rangle = E|\psi\rangle$, $|\psi\rangle$ is a solution to the Schrödinger equation.

(Note: We can use this as the dynamical postulate for quantum mechanics rather than the Schrödinger equation $\delta E[\psi] = 0$.)

So equivalently we can evaluate $E[\psi]$ for any trial state $|\psi\rangle$ which in practice depends on various parameters. The parameters can be varied and $E[\psi]$ can be made stationary. As with $L[\psi]$

The value of $E[\psi] = E$ is then an approximation to the eigenvalues of H . For the lowest $E[\psi]$ this gives an approximation to the ground state E_0 with

$E[\psi] \geq E_0$. The space of trial states over which we vary E (or L) is smaller than all H , so energy E is only an approximation to the true energy E_0 .

Suppose we consider excited state $E_n > E_0$, then if we know the exact eigenstates $|\psi_i\rangle$ below energy E_n we can form the trial states

$$|\phi_n\rangle = |\psi\rangle - \sum_{i=1}^{n-1} \langle \psi | \psi_i \rangle |\psi_i\rangle$$

$$\begin{aligned} E[\phi_n] &= \frac{\langle \phi_n | H | \phi_n \rangle}{\langle \phi_n | \phi_n \rangle} \\ &= \frac{\sum_{l \geq n} E_l |c_l|^2}{\sum_{l \geq n} |c_l|^2} \end{aligned}$$

$$E[\phi_n] \geq E_n, \text{ The equality holding iff } \phi_n = C\psi_n.$$

Thus each excited ^{energy eigen} state is a stationary point and with the above trial functions we can approximate the excited energy eigenvalues by the variational equation

$$\delta E[\phi_n] = 0, \text{ then } E[\phi_n] \approx E_n.$$

Of course we must know exactly the lower lying eigenstates in order to estimate E_n . The approximate eigenstates are all we really know and so each of those errors will compound when estimating E_n . Hence, only low lying excited states are generally determined with any degree of accuracy with this method.

Finally we can estimate the error in the energy eigenvalue when approximated by $|\phi_0\rangle$ which differs from the true eigenstate $|\psi_0\rangle$ by a small amount

$$|\psi_0\rangle = |\phi_0\rangle + a|\alpha\rangle, \quad a \ll 1.$$

We choose $|\phi_0\rangle$ so that $\delta E[\phi_0] = 0$ even though it is not the exact eigenstate

$$\begin{aligned} E[\psi_0] &= E_0 \\ &= E[\phi_0] + \cancel{\delta E} + O(a^2) \end{aligned}$$

Thus $E_0 = E[\phi_0] + O(a^2)$. The error in the energy is second order in smallness even though the error in the energy eigenstate is first order in smallness.

Example: Let's return to the example of Helium like atoms and approximate the ground state energy by the variational method. As a trial wave function we use the zeroth order perturbation theory wavefunction

$$\psi_n(r_1, r_2) \equiv \langle \vec{r}_1, \vec{r}_2 | \psi_n \rangle = \frac{1}{\pi a^3} e^{-\frac{r_1 + r_2}{a}} \quad (\text{page } \dots)$$

but now let "a" be a variational parameter rather than $a = a_0/Z$.

$$\text{So since } \langle \psi_n | \psi_n \rangle = \int d^3r_1 d^3r_2 |\langle \vec{r}_1, \vec{r}_2 | \psi_n \rangle|^2 = 1$$

we have

$$\begin{aligned} E[\psi_n] &= \langle \psi_n | H | \psi_n \rangle \\ &= \int d^3r_1 d^3r_2 \psi_n^*(r_1, r_2) H \psi_n(r_1, r_2) \end{aligned}$$

where recall

$$H(r_1, r_2) = \frac{-\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2}$$

$$H' = \frac{e^2/4\pi\epsilon_0}{|\vec{r}_1 - \vec{r}_2|} + H'$$

Recall the $\psi_n = \psi_{100}^a(r_1) \psi_{100}^a(r_2)$

with $\psi_{100}^a(r)$ the ground state eigenfunction for an electron in the Coulomb field of charge $Z'e$ with $Z' = \frac{a_0}{a}$.

Hence the total energy of such an electron is

$$-Z'^2 E_H = -Z'^2 \frac{m e^4 \hbar^{-2}}{2 \hbar^2} = -Z'^2 13.6 \text{ eV},$$

which, recalling from our study of H-atom,

$$\langle \psi_{100}^a | \frac{\vec{p}^2}{2m} | \psi_{100}^a \rangle = +Z'^2 E_H$$

$$\langle \psi_{100}^a | \frac{-Z'e^2}{4\pi\epsilon_0 r} | \psi_{100}^a \rangle = -2Z'^2 E_H.$$

Now the He atom potential has $\frac{-Ze^2}{4\pi\epsilon_0 r}$, so

$$\begin{aligned} \langle \psi_{100}^a | \frac{-Ze^2}{4\pi\epsilon_0 r} | \psi_{100}^a \rangle &= \frac{Z}{Z'} (-2Z'^2 E_H) \\ &= -2ZZ' E_H. \end{aligned}$$

Finally we recall the perturbation calculation of $\langle \psi_n | H' | \psi_n \rangle$ page - - -

$$\langle \psi_n | H' | \psi_n \rangle = \frac{5}{4} Z' E_H$$

Putting this altogether, we get

$$\begin{aligned} E[\psi_n] &= \langle \psi_n | H | \psi_n \rangle \\ &= 2E_H \left[Z'^2 - 2Z'(Z - \frac{5}{16}) \right] \end{aligned}$$

recalling that $Z' = \frac{a_0}{a}$, then we vary $E[\psi_n]$ as a function of a or equivalently Z' to minimize it.

$$\frac{\partial E[\psi_n]}{\partial Z'} = 0 = [2Z' - 2(Z - \frac{5}{16})] 2E_H$$

$$\Rightarrow \boxed{Z' = Z - \frac{5}{16}}$$

At this minimum value we find

$$E[\psi_n] \Big|_{Z'=Z-\frac{5}{16}} \equiv E^{\text{var}} = -2\left(Z - \frac{5}{16}\right)^2 E_H$$

This is the variational method's approximation of the He-atom ground state energy

$$\boxed{E^{\text{var}} = -2\left(Z - \frac{5}{16}\right)^2 E_H}$$

Recalling our table on page -19-

	Z	E^{R-S} (eV)	E^{exp} (eV)	E^{var} (eV)
He	2	-74.8	-78.8	-77.5
Li ⁺	3	-193.8	-197.1	-195.1
Be ⁺⁺	4	-367.1	-370.0	-367.1

Thus E^{var} is closer to E^{exp} than E^{R-S} in fact,

$$E^{var} = E^{R-S} - \underbrace{\frac{25}{128} E_H}_{= 2.66 \text{ eV}},$$

Of course $E^{var} \geq E^{exp}$ as the Variational theorem requires.

The variational trial state $|\psi\rangle$ is interpreted as the state for 2 independent electrons moving in a Coulomb field with charge $Z'e$. $eZ' = (Z - \frac{5}{16})e$ is smaller than the nuclear charge Ze . The difference $\frac{5}{16}e$ represents the screening of the nuclear charge felt by each e^- due to the presence of the other electron.