Variational Method

H : $|u_n\rangle$, E_n, $E_0 < E_1 < E_2 \ldots$

and $\langle u_n | u_m \rangle = \delta_{nm}$

Eigen energies may be known from Exp. but not the eigenstate.

Trial ground state $|\psi(\lambda)\rangle$ may depend on one or more continuous real parameters.

$$|\psi\rangle = \sum_n |u_n\rangle\langle u_n|\psi\rangle$$

and $$\langle\psi|H|\psi\rangle = \sum_{n,m} \langle\psi|u_n\rangle\langle u_n|H|u_m\rangle\langle u_m|\psi\rangle$$

$$= \sum_{n,m} E\,\delta_{nm}\langle\psi|u_n\rangle\langle u_m|\psi\rangle$$

$$= \sum_n E_n |\langle\psi|u_n\rangle|^2$$

Now $$\sum_n E_n |\langle\psi|u_n\rangle|^2 \geq E_0 \sum_n |\langle\psi|u_n\rangle|^2 = E_0\langle\psi|\psi\rangle$$

Thus for ANY trial state $|\psi\rangle$

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

and equality $\Rightarrow$ $|\psi\rangle = |u_0\rangle$

Vary λ to seek a minimum in $\dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$

$\Rightarrow$ the best trial function of the particular functional form.

Eg. the ground state of a hydrogenic atom

$$E_1 = -\frac{Z^2}{2}, \quad \text{and} \quad u_{1s} = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} e^{-Zr}$$

Let's try $\psi = \underbrace{\left(\frac{\lambda^3}{\pi}\right)^{\frac{1}{2}}}_{\text{normalization factor}} e^{-\lambda r}$

$$\langle\psi|H|\psi\rangle = -\frac{1}{2}\langle\psi|\nabla^2|\psi\rangle - Z\langle\psi|\frac{1}{r}|\psi\rangle$$

$$= \frac{\lambda^2}{2} - \lambda Z$$

$$\frac{\partial}{\partial\lambda}\left(\frac{\lambda^2}{2} - \lambda Z\right) = \lambda - Z = 0 \quad \Rightarrow \quad \lambda = Z \;\&\; E_{min} = -\frac{Z^2}{2}$$

However, keep in mind there is a fundamental limitation.

A poor trial function can yield a rather close experimentally determined ground state energy.

$\Rightarrow$ So, finding a good energy does not necessarily indicate that we have a good trial function.

Suppose $|\psi\rangle = |u_0\rangle + \delta|u'\rangle$

where $\langle u_0|u_0\rangle = \langle u'|u'\rangle = 1, \quad \langle u_0|u'\rangle = 0$

Then

$$\langle\psi|H|\psi\rangle = \langle u_0 + \delta u'|H|u_0 + \delta u'\rangle$$

$$= \langle u_0|H|u_0\rangle + |\delta|^2\langle u'|H|u'\rangle + \delta\langle u_0|H|u'\rangle + \delta^*\langle u'|H|u_0\rangle$$

$$= E_0 + |\delta|^2\langle u'|H|u'\rangle$$

$\Rightarrow$ Although $|\psi\rangle$ is in error by first order in δ, $\langle\psi|H|\psi\rangle$ is in error only by second order in δ!

Static perturbation Theory

Time independent problem

$|\phi_0\rangle$, $|n_0\rangle$, E_{n_0}

$H_0 \to H_0 + \lambda H'$, eigenstate $|n\rangle$ & E_n ?

$$|n\rangle = |n_0\rangle + \lambda |n_1\rangle + \lambda^2 |n_2\rangle + \cdots$$

$$E_n = E_0 + \lambda E_{n_1} + \lambda^2 E_{n_2} + \cdots$$

$$(H_0 + \lambda H')\left[|n_0\rangle + \lambda|n_1\rangle + \lambda^2|n_2\rangle + \cdots\right]$$
$$= (E_{n_0} + \lambda E_{n_1} + \lambda^2 E_{n_2} + \cdots)\left[|n_0\rangle + \lambda|n_1\rangle + \lambda^2|n_2\rangle + \cdots\right]$$

λ^0 : $(H_0 - E_{n_0})|n_0\rangle = 0$

λ^1 : $(H_0 - E_{n_0})|n_1\rangle = (E_{n_1} - H')|n_0\rangle$

λ^2 : $(H_0 - E_{n_0})|n_2\rangle = E_{n_2}|n_0\rangle + (E_{n_1} - H')|n_1\rangle$

λ^3 : $(H_0 - E_{n_0})|n_3\rangle = E_{n_3}|n_0\rangle + E_{n_2}|n_1\rangle + (E_{n_1} - H')|n_2\rangle$

$\vdots$

Note that:

① $|n_k\rangle$ is expressed in terms of the previous orders $|n_{k-1}\rangle$, $|n_{k-2}\rangle$ ---

② LHS of the k-th order eq ($k>0$) is not altered if substracting from $|n_k\rangle$ <u>ANY</u> arbitraty multiple of $|n_0\rangle$

We replase $|n_k\rangle$ by

$$|n_k'\rangle = |n_k\rangle - |n_0\rangle\langle n_0|n_k\rangle$$

Such that $\langle n_0|n_k'\rangle = 0$ for all $k>0$.

We can choose $|n_k\rangle$ that

$$\langle n_0|n_0\rangle = 1, \quad \langle n_0|n_1\rangle = \langle n_0|n_2\rangle = \cdots = 0$$

To find E_{n_1}, first consider the case where the $|n_0\rangle$ are non-degenerate then

$$\langle n_0 | (H_0 - E_{n_0}) | n_1 \rangle = \langle n_0 | E_{n_1} - H' | n_0 \rangle$$

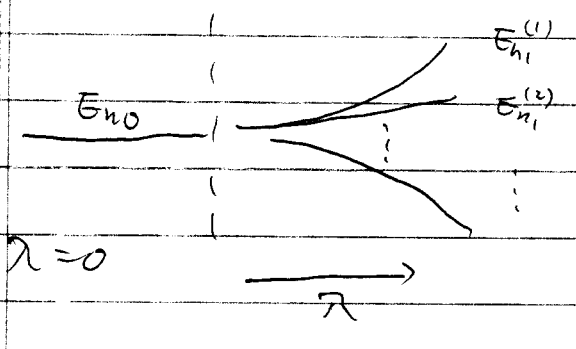
$$0 = E_{n_1} - \langle n_0 | H' | n_0 \rangle \Rightarrow \boxed{E_{n_1} = \langle n_0 | H' | n_0 \rangle}$$

* For the degenerate case, say s-fold degeneracy

all $|n_0^1\rangle, |n_0^2\rangle \cdots |n_0^s\rangle$ have the same energy E_{n_0} of H_0

Any linear combination of them is also an eigenvector corresponding to E_{n_0}.

Turn on $\lambda H'$, in general, this causes some of the degeneracy to be lifted.



eigenvalues ?

eigenvectors ?

Ans: Form the matrix

$$M = \langle n_0^{(i)} | H' | n_0^{(j)} \rangle \qquad i, j = 1 \cdots s$$

and diagonalize it.

If all the eigenvalues $E_{n_1}^{(1)}, \cdots E_{n_1}^{(i)} \cdots$ are all distinct, the degeneracy has been lifted completely in first order.

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go back to the non-degenerate case for simplicity.

$$\langle m_0 | (H_0 - E_{n_0}) | n_1 \rangle = \langle m_0 | E_{n_1} - H' | n_0 \rangle$$

$$(E_{m_0} - E_{n_0}) \langle m_0 | n_1 \rangle = E_{n_1} \delta_{m_0 n_0} - \langle m_0 | H' | n_0 \rangle$$

makes sense only for $m_0 \neq n_0$, also since we require that $\langle n_1 | n_0 \rangle = 0$

$$\Rightarrow \quad \langle m_0|n_1\rangle = \frac{\langle m_0|H'|n_0\rangle}{E_{n_0} - E_{m_0}}$$

and

$$\boxed{|n_1\rangle = \sum_{m_0 \neq n_0} |m_0\rangle\langle m_0|n_1\rangle = \sum_{m_0 \neq n_0} |m_0\rangle \frac{\langle m_0|H'|n_0\rangle}{E_{n_0} - E_{m_0}}}$$

$\Rightarrow$ first order change in the state vector

The next one,

$\langle n_0|\ (E_2(\lambda^2))\ \Rightarrow\ E_{n_2} = \langle n_0|H'|n_1\rangle$

by using the solution of $|n_1\rangle$

$$\Rightarrow E_{n_2} = \sum_{m_0 \neq n_0} \langle n_0|H'|m_0\rangle \frac{\langle m_0|H'|n_0\rangle}{E_{n_0} - E_{m_0}}$$

$$\boxed{= \sum_{m_0 \neq n_0} \frac{|\langle m_0|H'|n_0\rangle|^2}{E_{n_0} - E_{m_0}}}$$

Basically these 3 results are all we need.

We will apply the tool to analyse fine structure, hyperfine structure the Zeeman effect, the Stark effect in atomic hydrogen, and study the van der Waals interaction between 2 H atoms.

$E_{ne} = -\frac{E^2}{2n^2}$ Balmer formular, $\psi_{nem}(r,\theta,\varphi) = R_{ne}(r)\, Y_e^m(\theta,\varphi)$

$J = S + L$ (the total electronic angular momentum), $j = \ell \pm \frac{1}{2}$

A given state : $\{n, \ell\ m_\ell, s, m_s\}$

or $\{n, \ell, s, j, m_j\}$ in the $J\ m_j$ representation

Standard spectroscopic notation $n\,{}^{2s+1}\ell_j$, $\ell = 0, 1, 2 \cdots$ s, p, d $\cdots$

Ground state of hydrogen : $|\,{}^2_{S\frac{1}{2}}$