

# **Perturbation Theory**

Chem 2430

$H = H^{(0)} + \lambda V$ , where  $V$  is the perturbation and  $\lambda$  a variable introduced for bookkeeping

$$\begin{array}{l} \psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \\ E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{array} \quad \left| \quad \text{Here, } n \text{ refers to the state.} \right.$$

Assume  $\psi_n^{(0)}$  normalized and  $\langle \psi_n^{(0)} | \psi_n \rangle = 1$  (intermediate normalization)

$$H\psi_n = E_n\psi_n \rightarrow$$

$$(H^0 + \lambda V)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) \cdot (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots)$$

Gather together terms of the same power of  $\lambda$

$$\lambda^0: H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad \left| \quad \text{The problem we have already solved.} \right.$$

$$\lambda^1 \left| H^{(0)}\psi_n^{(1)} + V\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \right.$$

Multiply on left by  $\psi_n^{(0)*}$  and  $\int$

$$\underbrace{\langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(1)} \rangle}_0 + \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle = E_n^{(0)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}_0 + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$$

$$E_n^{(1)} = \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle \quad \text{First-order connection to energy}$$

Might be zero by symmetry

$$\lambda^2: \left| H^{(0)}\psi_n^{(2)} + V\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)} \right.$$

Multiply on the left by  $\psi_m^{(0)*}$  and  $\int$

$$\langle \psi_m^{(0)} | H^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_m^{(0)} | V | \psi_n^{(1)} \rangle = E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + E_n^{(2)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle$$

If  $m = n$ ,  $\langle \psi_n^{(0)} | V | \psi_n^{(1)} \rangle = E_n^{(2)}$

But what is  $\psi_n^{(1)}$  ?

Lets go back to the expression linear in  $\lambda$

$$H^{(0)}\psi_n^{(1)} + V\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$$

Multiply on the left by  $\psi_m^{(0)*}$  and  $\int$

$$\langle \psi_m^{(0)} | H^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle}_0$$

This simplifies to

$$(E_n^{(0)} - E_m^{(0)}) \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle$$

$\psi_n^{(1)}$  can be expressed in terms of  $\psi_j^{(0)}$ :  $\psi_n^{(1)} = \sum_{j \neq n} c_j \psi_j^{(0)}$

Then 
$$c_m = \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

There should be another index on  $c_j$  to make it clear these are coefficients for the  $n^{\text{th}}$  state

$$\sum_{j \neq n} c_j (E_n^{(0)} - E_m^{(0)}) \langle \psi_m^{(0)} | \psi_j^{(0)} \rangle = \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle$$

$$c_m = \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle / (E_n^{(0)} - E_m^{(0)})$$

Recall that  $\langle \psi_n^{(0)} | V | \psi_n^{(1)} \rangle = E_n^{(2)}$

and that  $\psi_n^{(1)} = \sum_{j \neq n} c_j \psi_j^{(0)}$

Hence 
$$E_n^{(2)} = \sum_{j \neq n} \frac{\langle \psi_n^{(0)} | V | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_j^{(0)}}$$

or 
$$E_n^{(2)} = \sum_{j \neq n} \frac{|\langle \psi_n^{(0)} | V | \psi_j^{(0)} \rangle|^2}{E_n^{(0)} - E_j^{(0)}}$$

If  $n = 0$ , the ground state,  $E_0^{(2)}$  is necessarily negative.

These results can be extended to determine higher order corrections to the energy and wave function

## Things to note.

(1) PT is not variational

e.g.,  $E^{(0)} + E^{(1)} + E^{(2)}$  can be below the true energy

(2) The above treatment assumes that we don't have degeneracies (need degenerate PT in that case.)

(3) Relation between variational and PT approaches

Consider  $\phi_1$  and  $\phi_2$  are eigenfunctions of  $H^{(0)}$

Further assume there is no first-order correction to E.

$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \rightarrow E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \frac{1}{2} \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}$$

Now if  $|H_{11} - H_{22}| > 2|H_{12}|$

$$E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \frac{(H_{11} - H_{22})}{2} \sqrt{1 + 4H_{12}^2 / (H_{11} - H_{22})^2}$$

Still exact

Series expansion

$$E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \frac{(H_{11} - H_{22})}{2} \left[ 1 + \frac{2H_{12}^2}{(H_{11} - H_{22})^2} + \dots \right]$$

$$E_{+} \approx H_{11} + \frac{H_{12}^2}{H_{11} - H_{22}} \quad \left( H_{11} - H_{22} \text{ is negative} \right)$$

This is identical to our result from PT (if there is no first order correction)

Note: we can derive the 3<sup>rd</sup>, 4<sup>th</sup> etc. order PT results from the Taylor series expansion of the CI result.

PT fails when  $|H_{11} - H_{22}| < 2|H_{12}|$  while the variational treatment does not have that problem..

Can have more than one perturbation

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)}$$

$$\text{or } H = H^{(0)} + \lambda H_a^{(1)} + \beta H_b^{(1)}$$

E.g. for a potential energy curve described as  $\frac{1}{2}kx^2 + \gamma x^3 + \delta x^4$ ,  
we would associate  $\gamma x^3$  with  $H^{(1)}$  and  $\delta x^4$  with  $H^{(2)}$

If we have continuum functions in the basis set

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{H_{mn} \psi_m^{(0)}}{E_n^{(0)} - E_m^{(0)}} + \int \frac{H_{E,n} \psi_E^{(0)} dE^{(0)}}{E_n^{(0)} - E^{(0)}}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|H_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \int \frac{|H_{E,n}|^2 dE^{(0)}}{E_n^{(0)} - E^{(0)}}$$



## Helium atom

$$\hat{H} = \frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze'^2}{r_1} - \frac{Ze'^2}{r_2} + \frac{e'^2}{r_{12}}$$

$$\hat{H}' = \frac{e'^2}{r_{12}} \text{ prevents the SE from being separated}$$

$$\begin{array}{l} \hat{H}^\circ = \hat{H} - \hat{H}' \\ \hat{H}^\circ = \hat{H}_1^\circ + \hat{H}_2^\circ \end{array} \left| \begin{array}{l} \hat{H}_1^\circ \text{ and } \hat{H}_2^\circ \\ \text{are He}^+ \text{ Hamiltonians.} \end{array} \right.$$

electron 1      electron 2

$$\psi^{(0)} = F_1(r_1, \theta_1, \phi_1) F_2(r_2, \theta_2, \phi_2)$$

$$E^{(0)} = E_1 + E_2 = -\frac{4e'^2}{2a_0} - \frac{4e'^2}{2a_0}$$

$$\psi_{1s^2}^{(0)} = \frac{1}{\pi} \left( \frac{2}{a_0} \right)^3 e^{-2r_1/a_0} e^{-2r_2/a_0} = 1s(1)1s(2)$$

$E_{1s^2}^{(0)} = -108.83\text{eV}$  which is far too large in magnitude.

$$\text{First order correction } \left\langle \psi_{1s^2}^{(0)} \left| \frac{e^{\prime 2}}{r_{12}} \right| \psi_{1s^2}^{(0)} \right\rangle = \frac{10}{8} \left( \frac{e^{\prime 2}}{a_0} \right) = 34.01\text{eV}$$

$$E^{(0)} + E^{(1)} = -108.83 + 34.01 = -74.82\text{eV}$$

Exact answer is **-79.01eV**

What if we now use  $\psi \sim e^{-\zeta r_1/a_0} e^{-\zeta r_2/a_0}$

and treat  $\zeta$  as a variation parameter?

$$E = -77.84\text{eV}$$

Error only about 1.2 eV. This error is due to the neglect of the correlated motion of the electrons.

How do you think we could try to improve on the above wave function?

Could evaluate the 2<sup>nd</sup> order PT correction

$1s^2 \rightarrow 2s^2, 2p^2, 2s3s, 2p3p, 3d^2$ , etc.

$2s3s$  – radial correlation;  $2p^2$ , angular correlation, tends to put electrons on opposite side of the nucleus

This expansion converges slowly. Difficulty in describing the cusp due to  $1/r^2$  using products of  $f(r_1)g(r_2)$

Third-order PT contains terms of the form  $\langle 0|V|i\rangle\langle i|Vj\rangle\langle j|V|0\rangle/[E_0-E_i)(E_0-E_j)$

E.g.  $\langle 1s^2|V|2p^2\rangle\langle 2p^2|V|3d^2\rangle\langle 3d^2|V|1s^2\rangle$  in the numerator