Chapter 6: METHODS OF APPROXIMATION

Perturbation Theory

$$H = \underbrace{H^{(0)}}_{\text{simpler problem}} + \underbrace{H^{(1)}}_{\text{perturbation}} \qquad (\text{or } \; H^{(0)} + V \;)$$

Suppose $H^{(0)}$ is two level $\psi_1^{(0)}, \quad \psi_2^{(0)}$

$$H^{(0)}\psi_m^{(0)} = E_m^{(0)}\psi_m^{(0)}, \quad m = 1, 2$$

I.e., $\psi_1^{(0)}, \quad \psi_2^{(0)}$ is a complete basis set

$$H\psi = E\psi \rightarrow$$

$$\left[H^{(0)} + \lambda H^{(1)}\right]\left[\psi_1^{(0)} + \lambda \psi^{(1)}\right] = \left[E_1^{(0)} + \lambda E^{(1)}\right]\left[\psi_1^{(0)} + \lambda \psi^{(1)}\right]$$

$$H^{(0)}\psi_1^{(0)} + H^{(0)}\lambda\psi^{(1)} + \lambda H^{(1)}\psi_1^{(0)} + \lambda^2 H^{(1)}\psi^{(1)} = E_1^{(0)}\psi_1^{(0)} + \lambda E_1^{(0)}\psi^{(1)} + \lambda E^{(1)}\psi_1^{(0)} + \lambda^2 E^{(1)}\psi^{(1)}$$

$$H^{(0)}\psi^{(1)} + H^{(1)}\psi_1^{(0)} = E_1^{(0)}\psi^{(1)} + E^{(1)}\psi_1^{(0)} \quad \Bigg| \quad \lambda$$

multiply on left by $\psi_1^{(0)*}$ and $\int$

$$\underbrace{\left\langle \psi_1^{(0)} \middle| H^{(0)} \middle| \psi^{(1)} \right\rangle}_{0} + \left\langle \psi_1^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle = \underbrace{E_1^{(0)} \left\langle \psi_1^{(0)} \mid \psi^{(1)} \right\rangle}_{0} + E^{(1)} \left\langle \psi_1^{(0)} \mid \psi_1^{(0)} \right\rangle$$

$$\boxed{E^{(1)} = \left\langle \psi_1^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle \text{ first order correction}}$$

zero for many systems

$$H^{(0)}\psi^{(2)} + H^{(1)}\psi^{(1)} = E^{(0)}\psi^{(2)} + E^{(1)}\psi^{(1)} + E^{(2)}\psi_1^{(0)} \qquad \Big| \qquad \lambda^2$$

Multiply by $\psi_1^{(0)*}$ and $\int$

$$\underbrace{\left\langle \psi_1^{(0)} \middle| H^{(0)} \middle| \psi^{(2)} \right\rangle}_{0} + \left\langle \psi_1^{(0)} \middle| H^{(1)} \middle| \psi^{(1)} \right\rangle = \underbrace{E^{(0)} \left\langle \psi_1^{(0)} \mid \psi^{(2)} \right\rangle + E^{(1)} \left\langle \psi_1^{(0)} \mid \psi^{(1)} \right\rangle}_{0} + E^{(2)} \left\langle \psi_1^{(0)} \mid \psi_1^{(0)} \right\rangle$$

$$\boxed{E^{(2)} = \left\langle \psi_1^{(0)} \middle| H^{(1)} \middle| \psi^{(1)} \right\rangle}$$

So what is $\psi^{(1)}$?

Go back to

$$\left[H^{(0)} - E_1^{(0)} \right] \psi^{(1)} = \left[E^{(1)} - H^{(1)} \right] \psi_1^{(0)}$$

$$\psi^{(1)} = a\psi_2^{(0)}$$

Multiply by $\psi_2^{(0)*}$ and $\int$

$$\Rightarrow a = \frac{\left\langle \psi_2^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle}{E_1^{(0)} - E_2^{(0)}}$$

$$\psi^{(1)} = \frac{\left\langle \psi_2^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle \psi_2^{(0)}}{E_1^{(0)} - E_2^{(0)}}$$

$$E^{(2)} = \frac{\left| \left\langle \psi_1^{(0)} \middle| H^{(1)} \middle| \psi_2^{(0)} \right\rangle \right|^2}{E_1^{(0)} - E_2^{(0)}} = \frac{\left| H_{1\,2}^{(1)} \right|^2}{E_1^{(0)} - E_2^{(0)}}$$

We also know that we can treat this problem variationally

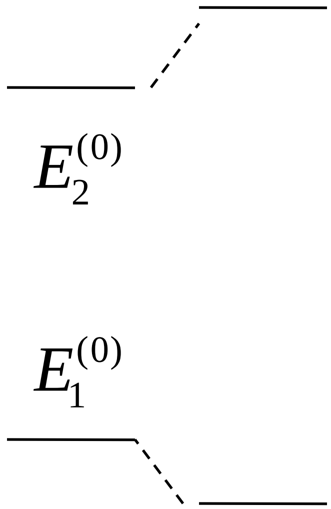
$$\psi = a_1\psi_1^{(0)} + a_2\psi_2^{(0)}$$

$$E_\pm = \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) \pm \frac{1}{2}\sqrt{\left(E_1^{(0)} - E_2^{(0)}\right)^2 + 4\varepsilon^2}$$

$$\varepsilon^2 = \left|H_{1\,2}^{(1)}\right|^2$$

$$E_+ \approx E_1^{(0)} - \frac{\varepsilon^2}{\Delta E^{(0)}}, \qquad \Delta E^{(0)} = E_2^{(0)} - E_1^{(0)}$$

$$E_- \approx E_2^{(0)} + \frac{\varepsilon^2}{\Delta E^{(0)}}$$



So, solving the problem exactly and doing a Taylor-series expansion gives the same result as *PT*

$$\psi_+ \approx \psi_1^{(0)} - \frac{H_{1\,2}^{(1)}}{\Delta E^{(0)}}\psi_2^{(0)} \qquad \psi_- \approx \psi_2^{(0)} + \frac{H_{1\,2}^{(1)}}{\Delta E^{(0)}}\psi_1^{(0)}$$

General expansion for PT

$$E_0^{(1)} = \left\langle 0 \middle| H^{(1)} \middle| 0 \right\rangle$$

$$\psi_0^{(1)} = \sum_{n\neq 0} a_n \psi_n^{(0)}$$

$$= \sum_k {}' \frac{H_{k0}^{(1)}}{E_0^{(0)} - E_k^{(0)}} \psi_k^{(0)}$$

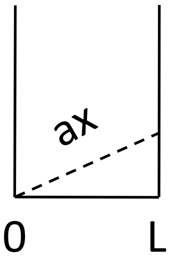
← Sum over all allowed mixed states

$$E_0^{(2)} = H_{00}^{(2)} + \sum_n {}' \frac{\left| H_{0n}^{(1)} \right|^2}{E_0^{(0)} - E_n^{(0)}}$$

↑

if there is an *H*

For many systems $E^{(1)} = 0$



Consider the particle in the box with a sloped bottom

$\left\langle n \middle| ax \middle| n \right\rangle = 0$ For all $\psi_n^{(0)}$

How do we use PT with ∞ sized basis sets

Often many integrals are 0

H atom in *1s* level – add electric field in *z* direction

only $\left\langle 1s \middle| z \middle| \psi_{np_z} \right\rangle \neq 0$

So would need $2p_{z'}$ $3p_{z'}$ etc.

Closure approximation

$$E_0^{(2)} = \sum_n {}' \frac{\left|H_{0n}^{(1)}\right|^2}{E_0^{(1)} - E_n^{(0)}} \approx \frac{1}{\Delta E} \sum {}' \left|H_{0n}^{(1)}\right|^2$$

↖ Average exc. energy

$$\sum_n {}' \left|H_{0n}^{(1)}\right|^2 = \sum_n \left|H_{0n}^{(1)}\right|^2 - \left|H_{00}^{(1)}\right|^2$$

$$= \left\langle 0 \middle| H^{(1)} H^{(1)} \middle| 0 \right\rangle - \left\langle 0 | H^{(1)} \middle| 0 \right\rangle^2 = \varepsilon^2$$

$$E_0^{(2)} \approx \frac{\varepsilon^2}{\Delta E}$$

Example 6.4 *H* atom in el. field in *z* direction

$$H^{(1)} = ez\varepsilon, \quad \varepsilon = \text{electric field}$$

Using the closure relation

$$E_0^{(2)} \approx \frac{e^2 \varepsilon^2 \left\langle r^2 \right\rangle}{3\Delta E}$$