

Chapter 6 Perturbation theory

6.1 Time-independent nondegenerate perturbation theory

(i) no perturbation system, $\hat{H}^{(0)}$, is given (to find solutions of $\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}'$)

$$\hat{H}^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad ; \quad \hat{H}^{(0)} : \text{Hamiltonian of basic state}$$

$$E_n^{(0)} : \text{eigenvalues of } \hat{H}^{(0)}$$

$$\psi_n^{(0)} : \text{orthonormal eigenfunctions of } \hat{H}^{(0)}$$

$$; \quad \langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{nm}$$

(ii) Rayleigh-Schrödinger perturbation theory

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}' \quad \dots\dots\dots(6.1) \quad ; \quad \hat{H} : \text{a general Hamiltonian}$$

$$\hat{H}' : \text{perturbation}$$

$$\lambda : \text{a small number}$$

general solution ψ_n, E_n of $\hat{H} \psi_n = E_n \psi_n \quad \dots\dots\dots(6.2)$ are expand by

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \quad \dots\dots\dots(6.3)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad \dots\dots\dots(6.4)$$

$E_n^{(i)}, \psi_n^{(i)} : \text{ith-order corrections to } E_n, \psi_n ;$

substitute equation (6.1), (6.3), (6.4) into (6.2)

$$\begin{aligned} \rightarrow & (\hat{H}^{(0)} + \lambda \hat{H}')(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) \\ & = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) \end{aligned}$$

$$\begin{aligned} \rightarrow & \hat{H}^{(0)} \psi_n^{(0)} + \lambda(\hat{H}^{(0)} \psi_n^{(1)} + \hat{H}' \psi_n^{(0)}) + \lambda^2(\hat{H}^{(0)} \psi_n^{(2)} + \hat{H}' \psi_n^{(1)}) + \dots \\ & = E_n^{(0)} \psi_n^{(0)} + \lambda(E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}) + \lambda^2(E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}) + \dots \end{aligned}$$

$$\rightarrow \begin{cases} \hat{H}^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad , (E_n^{(0)} , \psi_n^{(0)} \text{ are known firstly}) \\ \hat{H}^{(0)} \psi_n^{(1)} + \hat{H}' \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)} \quad \dots\dots (6.5) \\ \hat{H}^{(0)} \psi_n^{(2)} + \hat{H}' \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)} \quad \dots\dots (6.6) \\ \vdots \end{cases}$$

➤ First-order theory

(i) first-order correction to the energy

From equation (6.5)

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

take inner product with $\psi_n^{(0)}$

$$\rightarrow \langle \psi_n^{(0)} | \hat{H}^{(0)} \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | \hat{H}' \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle}_1$$

$\hat{H}^{(0)}$ is Hermitian :

$$\langle \psi_n^{(0)} | \hat{H}^{(0)} \psi_n^{(1)} \rangle = \langle \hat{H}^{(0)} \psi_n^{(0)} | \psi_n^{(1)} \rangle = \langle E_n^{(0)} \psi_n^{(0)} | \psi_n^{(1)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle$$

$$\rightarrow \boxed{E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' \psi_n^{(0)} \rangle = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle} \quad \text{the first-order correction to the energy}$$

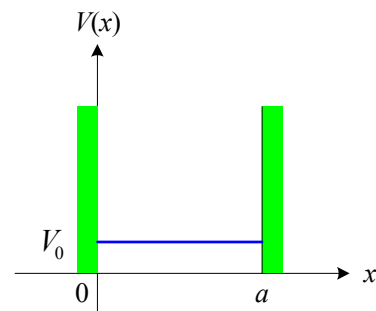
example 1

for the infinite square well

$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

perturb the system by a constant perturbation

$$\hat{H}' = V_0$$

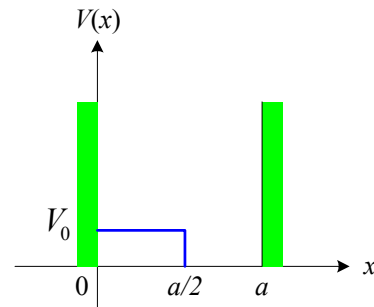


$$\rightarrow E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' \psi_n^{(0)} \rangle = \langle \psi_n^{(0)} | V_0 | \psi_n^{(0)} \rangle = V_0 \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = V_0$$

example 2

If the perturbation extends halfway across the well

$$\begin{aligned}
 \rightarrow E_n^{(1)} &= \langle \psi_n^{(0)} | \hat{H}' \psi_n^{(0)} \rangle \\
 &= \int_0^{a/2} V_0 |\psi_n^{(0)}|^2 dx \\
 &= \frac{2V_0}{a} \int_0^{a/2} \sin^2\left(\frac{n\pi}{a}x\right) dx \\
 &= \frac{V_0}{2}
 \end{aligned}$$



(ii) first-order correction to the wave function $\psi_n^{(1)}$

$$\text{from } \hat{H}^{(0)} \psi_n^{(1)} + \hat{H}' \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$$

$$\rightarrow (\hat{H}^{(0)} - E_n^{(0)}) \psi_n^{(1)} = (E_n^{(1)} - \hat{H}') \psi_n^{(0)} \dots\dots\dots(6.7)$$

The orthonormal eigenfunctions $\psi_m^{(0)}$ are assumed to form a complete set .

Thus $\psi_n^{(1)}$ can be expanded in terms of the set $\psi_m^{(0)}$

$$\psi_n^{(1)} = \sum_m c_m^{(n)} \psi_m^{(0)} = c_n^{(n)} \psi_n^{(0)} + \sum_{m \neq n} c_m^{(n)} \psi_m^{(0)}$$

$$\text{where } \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = \sum_m c_m^{(n)} \langle \psi_m^{(0)} | \psi_m^{(0)} \rangle$$

$$\rightarrow c_m^{(n)} = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$$

$\psi_n^{(0)}$ are free solutions of equation (6.7) and can be dropped from $\psi_n^{(1)}$

$$\rightarrow c_n^{(n)} = 0 \quad \rightarrow \psi_n^{(1)} = \sum_{m \neq n} c_m^{(n)} \psi_m^{(0)} \dots\dots\dots(6.8)$$

substitute equation (6.8) into equation (6.7)

$$\rightarrow \hat{H}^{(0)} \sum_{m \neq n} c_m^{(n)} \psi_m^{(0)} - \sum_{m \neq n} E_n^{(0)} c_m^{(n)} \psi_m^{(0)} = (E_n^{(1)} - \hat{H}') \psi_n^{(0)}$$

$$\rightarrow \sum_{m \neq n} E_m^{(0)} c_m^{(n)} \psi_m^{(0)} - \sum_{m \neq n} E_n^{(0)} c_m^{(n)} \psi_m^{(0)} = (E_n^{(1)} - \hat{H}') \psi_n^{(0)}$$

$$\rightarrow \sum_{m \neq n} (E_m^{(0)} - E_n^{(0)}) c_m^{(n)} \psi_m^{(0)} = (E_n^{(1)} - \hat{H}') \psi_n^{(0)}$$

take inner product with $\psi_l^{(0)}$

$$\rightarrow \sum_{m \neq n} (E_m^{(0)} - E_n^{(0)}) c_m^{(n)} \delta_{lm} = E_n^{(1)} \delta_{ln} - \langle \psi_l^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \dots (6.9)$$

If $l = n$, $\delta_{ln} = 1$ $E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$

If $l \neq n$, only when $l = m$, the left side of equation (6.9)

remains only one term : $(E_m^{(0)} - E_n^{(0)}) c_m^{(n)}$ and $\delta_{ln} = 0$

$$\rightarrow (E_m^{(0)} - E_n^{(0)}) c_m^{(n)} = -\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

$$\rightarrow c_m^{(n)} = \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

so $\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$ (6.10) the first-order correction to the wave function

Nondegeneratation condition :

The above perturbation method apply only to non-degenerate eigenvalue $E_n^{(0)}$ of the unperturbed system .

Namely different unperturbed states corresponding to different energies .

$$E_n^{(0)} - E_m^{(0)} \neq 0 \text{ in general}$$

➤ Second-order solution of E_n

from equation (6.6) $\hat{H}^{(0)} \psi_n^{(2)} + \hat{H}' \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$

take inner product with $\psi_n^{(0)}$

$$\begin{aligned} \langle \psi_n^{(0)} | \hat{H}^{(0)} \psi_n^{(2)} + \hat{H}' \psi_n^{(1)} \rangle &= E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle \\ \langle \psi_n^{(0)} | \hat{H}' \psi_n^{(1)} \rangle &= E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \sum_{m \neq n} c_m^{(n)} \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle \end{aligned}$$

$$\langle \psi_n^{(0)} | \hat{H}^{(0)} \psi_n^{(2)} \rangle = \langle \hat{H}^{(0)} \psi_n^{(0)} | \psi_n^{(2)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle$$

$$\rightarrow E_n^{(2)} = \langle \psi_n^{(0)} | \hat{H}' \psi_n^{(1)} \rangle$$

$$= \sum_{n \neq m} c_m^{(n)} \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle$$

$$= \sum_{n \neq m} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle$$

$$E_n^{(2)} = \sum_{n \neq m} \frac{|\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

6.2 Time-independent degenerate perturbation theory

If some distinct states share the same energy, equation (6.10) fails

➤ Twofold degeneracy

Suppose $\psi_a^{(0)}, \psi_b^{(0)}$ share the same energy

$$\hat{H}^{(0)} \psi_a^{(0)} = E^{(0)} \psi_a^{(0)}, \quad \hat{H}^{(0)} \psi_b^{(0)} = E^{(0)} \psi_b^{(0)}, \quad \langle \psi_a^{(0)} | \psi_b^{(0)} \rangle = 0$$

It is noted that $\psi^{(0)} = \alpha \psi_a^{(0)} + \beta \psi_b^{(0)}$ is also an eigenstate of $\hat{H}^{(0)}$

$$\hat{H}^{(0)} \psi^{(0)} = E^{(0)} \psi^{(0)}$$

While the perturbation will break the degeneracy: as increase λ , the common unperturbed energy $E^{(0)}$ splits into two.

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}' \quad \text{and} \quad E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

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

substitute into $\hat{H}\psi = E\psi$

$$\hat{H}^{(0)}\psi^{(0)} + \lambda(\hat{H}'\psi^{(0)} + \hat{H}^{(0)}\psi^{(1)}) + \dots = E^{(0)}\psi^{(0)} + \lambda(E^{(1)}\psi^{(0)} + E^{(0)}\psi^{(1)}) + \dots$$

at order λ : $\hat{H}'\psi^{(0)} + \hat{H}^{(0)}\psi^{(1)} = E^{(1)}\psi^{(0)} + E^{(0)}\psi^{(1)}$

(i) take inner product with $\psi_a^{(0)}$

$$\langle \psi_a^{(0)} | \hat{H}'\psi^{(0)} \rangle + \langle \psi_a^{(0)} | \hat{H}^{(0)}\psi^{(1)} \rangle = E^{(1)}\langle \psi_a^{(0)} | \psi^{(0)} \rangle + E^{(0)}\langle \psi_a^{(0)} | \psi^{(1)} \rangle$$

and $\langle \psi_a^{(0)} | \hat{H}^{(0)}\psi^{(1)} \rangle = E^{(0)}\langle \psi_a^{(0)} | \psi^{(1)} \rangle$

$$\langle \psi_a^{(0)} | \hat{H}'\psi^{(0)} \rangle = E^{(1)}\langle \psi_a^{(0)} | \psi^{(0)} \rangle$$

$$\langle \psi_a^{(0)} | \hat{H}'(\alpha\psi_a^{(0)} + \beta\psi_b^{(0)}) \rangle = E^{(1)}\langle \psi_a^{(0)} | (\alpha\psi_a^{(0)} + \beta\psi_b^{(0)}) \rangle$$

$$\alpha\langle \psi_a^{(0)} | \hat{H}' | \psi_a^{(0)} \rangle + \beta\langle \psi_a^{(0)} | \hat{H}' | \psi_b^{(0)} \rangle = \alpha E^{(1)}$$

let $W_{ij} = \langle \psi_i^{(0)} | \hat{H}' | \psi_j^{(0)} \rangle$

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^{(1)} \dots\dots\dots(6.11)$$

(ii) similarly take inner product with $\psi_b^{(0)}$

$$\alpha W_{ba} + \beta W_{bb} = \beta E^{(1)} \dots\dots\dots(6.12)$$

from equation (6.11) , (6.12)

$$\begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E^{(1)} \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

$$E_{\pm}^{(1)} = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]$$

is the fundamental result of degenerate perturbation theory

if $W_{ab} = W_{ba} = 0$ then $E_+^{(1)} = W_{aa} = \langle \psi_a^{(0)} | \hat{H}' | \psi_a^{(0)} \rangle$

$$E_-^{(1)} = W_{bb} = \langle \psi_b^{(0)} | \hat{H}' | \psi_b^{(0)} \rangle$$

the same as we obtained using the Nondegenerate perturbation theory

Theorem

Let A be a Hermitian operator that commutes with $\hat{H}'$

If $\psi_a^{(0)}, \psi_b^{(0)}$ are eigenfunctions of A with distinct eigenvalues

$$A\psi_a^{(0)} = \mu\psi_a^{(0)}, A\psi_b^{(0)} = \nu\psi_b^{(0)}; \mu \neq \nu$$

then $W_{ab} = 0$ and $\psi_a^{(0)}, \psi_b^{(0)}$ are good states to use in perturbation theory

proof :

$$\begin{aligned} [A, \hat{H}'] &= 0 \quad \Rightarrow \quad \langle \psi_a^{(0)} | [A, \hat{H}'] | \psi_b^{(0)} \rangle = 0 \\ &\Rightarrow \quad \langle \psi_a^{(0)} | A\hat{H}'\psi_b^{(0)} \rangle - \langle \psi_a^{(0)} | \hat{H}'A\psi_b^{(0)} \rangle \\ &= \langle A\psi_a^{(0)} | \hat{H}'\psi_b^{(0)} \rangle - \langle \psi_a^{(0)} | \hat{H}'\nu\psi_b^{(0)} \rangle \\ &= \langle \mu\psi_a^{(0)} | \hat{H}'\psi_b^{(0)} \rangle - \langle \psi_a^{(0)} | \hat{H}'\nu\psi_b^{(0)} \rangle \\ &= (\mu - \nu) \langle \psi_a^{(0)} | \hat{H}'\psi_b^{(0)} \rangle \\ &= (\mu - \nu)W_{ab} = 0 \\ &\Rightarrow \quad W_{ab} = 0 \end{aligned}$$

For n -fold degeneracy (High order degeneracy):

we look for the eigenvalue of the $n \times n$ W -matrix

$$W_{ij} = \langle \psi_i^{(0)} | \hat{H}' | \psi_j^{(0)} \rangle$$

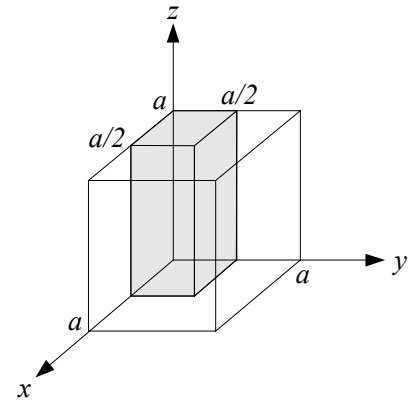
example

three-dimensional infinite cubical well

$$V(x, y, z) = \begin{cases} 0, & 0 < x < a, 0 < y < a, 0 < z < a \\ \infty, & \text{otherwise} \end{cases}$$

The perturbation :

$$H' = \begin{cases} V_0, & 0 < x < a/2, 0 < y < a/2 \\ 0, & \text{otherwise} \end{cases}$$



from $-\frac{\hbar^2}{2m} \nabla^2 \psi + V(x, y, z) \psi = E \psi$

$$= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + V(x, y, z) \psi = E \psi$$

$$= (E_x + E_y + E_z) \psi$$

let $\psi(x, y, z) = \psi_x(x) \psi_y(y) \psi_z(z)$

see $-\frac{\hbar^2}{2m} \frac{d^2 \psi_x}{dx^2} + V(x, y, z) \psi_x = E_x \psi_x$

inside the well $-\frac{\hbar^2}{2m} \frac{d^2 \psi_x}{dx^2} = E_x \psi_x \rightarrow \psi_{n_x}^{(0)} = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a} x\right)$

$$E_{n_x}^{(0)} = \frac{n_x^2 \pi^2 \hbar^2}{2ma^2}$$

similarly $\psi_{n_y}^{(0)} = \sqrt{\frac{2}{a}} \sin\left(\frac{n_y \pi}{a} y\right) \quad \psi_{n_z}^{(0)} = \sqrt{\frac{2}{a}} \sin\left(\frac{n_z \pi}{a} z\right)$

$$\psi_{n_x n_y n_z}^{(0)} = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right)$$

the corresponding allowed energies :

$$E_n^{(0)} = E_{n_x n_y n_z}^{(0)} = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

(i) the ground state is nondegenerate

$$E_0^{(0)} = E_{111}^{(0)} = \frac{3\pi^2 \hbar^2}{2ma^2} \quad , \quad \psi_{111}^{(0)} = \left(\frac{2}{a}\right)^{3/2} \left(\sin \frac{\pi}{a} x\right) \left(\sin \frac{\pi}{a} y\right) \left(\sin \frac{\pi}{a} z\right)$$

thus the first-order correction to the ground state energy is

$$\begin{aligned} E_0^{(1)} &= \langle \psi_{111}^{(0)} | \hat{H}' | \psi_{111}^{(0)} \rangle \\ &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a} x\right) dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a} y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a} z\right) dz \\ &= \frac{1}{4} V_0 \end{aligned}$$

(ii) the first excited state is triply degenerate

$$\text{let } \psi_a^{(0)} \equiv \psi_{112}^{(0)} \quad , \quad \psi_b^{(0)} \equiv \psi_{121}^{(0)} \quad , \quad \psi_c^{(0)} \equiv \psi_{211}^{(0)}$$

$$\text{have the same energy } E_1^{(0)} = \frac{3\pi^2 \hbar^2}{ma^2} \quad (E_{211}^{(0)} = E_{121}^{(0)} = E_{112}^{(0)})$$

thus the first-order correction to the first excited state must find W -matrix

the matrix elements :

$$W_{aa} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a} x\right) dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a} y\right) dy \int_0^a \sin^2\left(\frac{2\pi}{a} z\right) dz = \frac{1}{4} V_0$$

$$\text{similarly } W_{bb} = W_{cc} = \frac{1}{4} V_0$$

$$\text{and } W_{ab} = W_{ba} = W_{ac} = W_{ca} = 0 \quad , \quad W_{bc} = W_{cb} = \frac{16}{9\pi^2 V_0}$$

$$\Rightarrow W = \begin{bmatrix} \frac{V_0}{4} & 0 & 0 \\ 0 & \frac{V_0}{4} & \frac{V_0}{4} k \\ 0 & \frac{V_0}{4} k & \frac{V_0}{4} \end{bmatrix} \quad \text{where } k = \left(\frac{8}{3\pi}\right)^2$$

let eigenvalues of W is ω

then the characteristic equation is :

$$\left(\frac{V_0}{4} - \omega\right)^3 - \left(\frac{V_0}{4}k\right)^2 \left(\frac{V_0}{4} - \omega\right) = 0$$

$$\rightarrow \omega_1 = \frac{V_0}{4} \quad , \quad \omega_2 = \frac{V_0}{4}(1+k) \quad , \quad \omega_3 = \frac{V_0}{4}(1-k)$$

The eigenvalues $\omega_1, \omega_2, \omega_3$ are the correction to energies

Thus the first-order correction for the excited state to energy is

$$E_1 = E_1^{(0)} + \lambda E_1^{(1)} = \begin{cases} E_1^{(0)} + \lambda \omega_1 = E_1^{(0)} + \lambda \frac{V_0}{4} \\ E_1^{(0)} + \lambda \omega_2 = E_1^{(0)} + \lambda \frac{V_0}{4}(1+k) \\ E_1^{(0)} + \lambda \omega_3 = E_1^{(0)} + \lambda \frac{V_0}{4}(1-k) \end{cases}$$

➤ The fine structure of hydrogen

fine structure due to $\begin{cases} \text{relativistic correction} \\ \text{spin - orbit coupling correction} \end{cases}$

fine structure constant $\alpha \equiv \frac{e^2}{4\pi \epsilon_0 \hbar c}$

(i) the relativistic correction

relativistic formula for kinetic energy :

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2$$

relativistic formula for momentum :

$$p = \frac{mv}{\sqrt{1-(v/c)^2}}$$

$$\rightarrow p^2 c^2 + m^2 c^4 = \frac{m^2 v^2 c^2 + m^2 c^4 [1 - (v/c)^2]}{1 - (v/c)^2} = \frac{m^2 c^4}{1 - (v/c)^2} = (T + mc^2)^2$$

Instead of velocity, the relativistic $\hat{T}$ and $\hat{p}$ is

$$\begin{aligned}
 \rightarrow T &= \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \\
 &= mc^2 \left[\sqrt{1 + \left(\frac{p}{mc} \right)^2} - 1 \right] = mc^2 \left[1 + \frac{1}{2} \left(\frac{p}{mc} \right)^2 - \frac{1}{8} \left(\frac{p}{mc} \right)^4 + \dots - 1 \right] \\
 &= \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots
 \end{aligned}$$

lowest order relativistic $H'_r = -\frac{\hat{p}^4}{8m^3 c^2}$

$$E_r^{(1)} = \langle H'_r \rangle = -\frac{\langle \psi | \hat{p}^4 | \psi \rangle}{8m^3 c^2} = -\frac{\langle \hat{p}^2 \psi | \hat{p}^2 \psi \rangle}{8m^3 c^2}$$

Now the Schrödinger equation to the unperturbed state is

$$\hat{p}^2 \psi = 2m(E - V)\psi$$

$$\rightarrow E_r^{(1)} = -\frac{\langle (E - V)^2 \rangle}{2mc^2} = -\frac{[E^2 - 2E\langle V \rangle + \langle V^2 \rangle]}{2mc^2}$$

for hydrogen : $V(r) = -\frac{e^2}{4\pi \epsilon_0 r}$

$$\rightarrow E_r^{(1)} = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi \epsilon_0} \right) \langle 1/r \rangle + \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 \langle 1/r^2 \rangle \right]$$

$$\langle 1/r \rangle = \int \psi_{nlm}^* (1/r) \psi_{nlm} d\mathbf{r} = \frac{1}{n^2 a}$$

$$\langle 1/r^2 \rangle = \int \psi_{nlm}^* (1/r^2) \psi_{nlm} d\mathbf{r} = \frac{1}{(l+1/2)n^3 a^2}$$

where $\psi_{nlm} = \sqrt{\left(\frac{2}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{r}{na}} \left(\frac{2r}{na} \right)^l L_{n-l-1}^{2l+1}(2r/na) Y_l^m(\theta, \phi)$,

a is the Bohr radius

$$\rightarrow E_r^{(1)} = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi \epsilon_0} \right) \frac{1}{n^2 a} + \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 \frac{1}{(l+1/2)n^3 a^2} \right]$$

substitute into $a = \frac{4\pi \epsilon_0 \hbar^2}{me^2}$

$$\rightarrow E_r^{(1)} = -\frac{E_n^2}{2mc^2} \left[\frac{4n}{l+1/2} - 3 \right], \quad \frac{E_n}{mc^2} \approx 2 \times 10^{-5}$$

the relativistic correction is smaller than E_n

(ii) Spin-orbit coupling correction

(a) Electron in a magnetic field

A spinning charged particle constitutes a magnetic dipole.

magnetic dipole moment : $\mu = \gamma \mathbf{S}$ γ is **gyromagnetic ratio**

when a magnetic dipole placed in a magnetic field $\mathbf{B}$

the energy $H = -\mu \cdot \mathbf{B} = -\gamma \mathbf{B} \cdot \mathbf{S}$

magnetic dipole moment of the electron

from classical electrodynamics

the magnetic dipole moment of the ring is

$$\mu = \frac{q \pi r^2}{T}, \quad T \text{ is the period}$$

the angular momentum is

$$L = \frac{2\pi m r^2}{T}$$

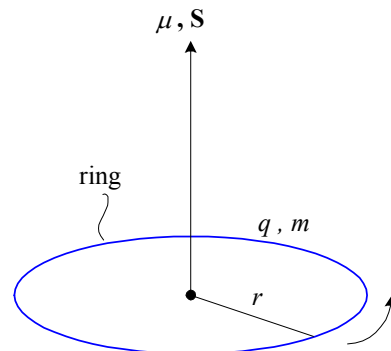
$$\rightarrow \mu = \frac{q}{2m} \mathbf{L}$$

for a spinning charged particle

the electron's magnetic dipole moment is $\mu = g \left(\frac{q}{2m} \right) \mathbf{S} = -g \frac{e}{2m_e} \mathbf{S}$

where g is a factor ($g = 2$)

so $\mu_e = -\frac{e}{m_e} \mathbf{S}$ for the electron



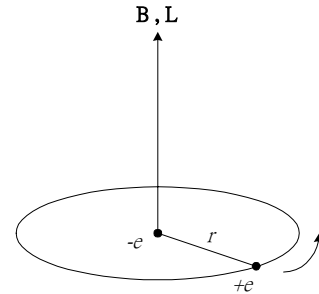
(b) orbit positive charge sets up a magnetic field $\mathbf{B}$, which exerts a torque on the electron, tending to align its magnetic moment along the direction of $\mathbf{B}$

from the Biot-Savart law ,
the magnetic field of the proton is

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2r} \frac{e}{T} \quad T \text{ is the period of the orbit}$$

and $L = rmv = \frac{2\pi mr^2}{T}$

$$\begin{aligned} \Rightarrow \mathbf{B} &= \frac{\mu_0}{2r} \frac{e}{T} = \frac{\mu_0}{2r} \frac{e}{2\pi mr^2} \mathbf{L} \\ &= \frac{\mu_0 e}{4\pi mr^3} \mathbf{L} \\ &= \frac{e}{4\pi \epsilon_0 mc^2 r^3} \mathbf{L} , \end{aligned}$$



where $c = \frac{1}{\sqrt{\epsilon_0 \mu_0}}$

(c) The spin-orbit interaction

from (a) , (b)

$$\begin{aligned} H &= -\boldsymbol{\mu}_e \cdot \mathbf{B} = -\left(-\frac{e}{m_e}\right) \mathbf{S} \cdot \frac{e}{4\pi \epsilon_0 m_e c^2 r^3} \mathbf{L} \\ &= \frac{e^2}{4\pi \epsilon_0 m_e^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \quad \text{.....for an inertial system} \end{aligned}$$

for the electron orbits around the nucleus ,

$$H'_{so} = \left(\frac{e^2}{8\pi \epsilon_0} \right) \frac{1}{m_e^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \quad \text{.....is the spin-orbit interaction}$$

(d) find the $\mathbf{S} \cdot \mathbf{L}$

for the spin-orbit coupling , the Hamiltonian no longer commutes with $\mathbf{L}$ and $\mathbf{S}$

$$H'_{so} \text{ commute with } L^2, S^2$$

total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ are conserved

$$J^2 = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S}$$

$$\Rightarrow \mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

$$(\mathbf{L} \cdot \mathbf{S})\psi = \frac{1}{2}(J^2 - L^2 - S^2)\psi = \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]\psi$$

$$(e) \quad E_{SO}^{(1)} = \langle H'_{SO} \rangle = \left\langle \left(\frac{e^2}{8\pi \epsilon_0} \right) \frac{1}{m_e^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \right\rangle$$

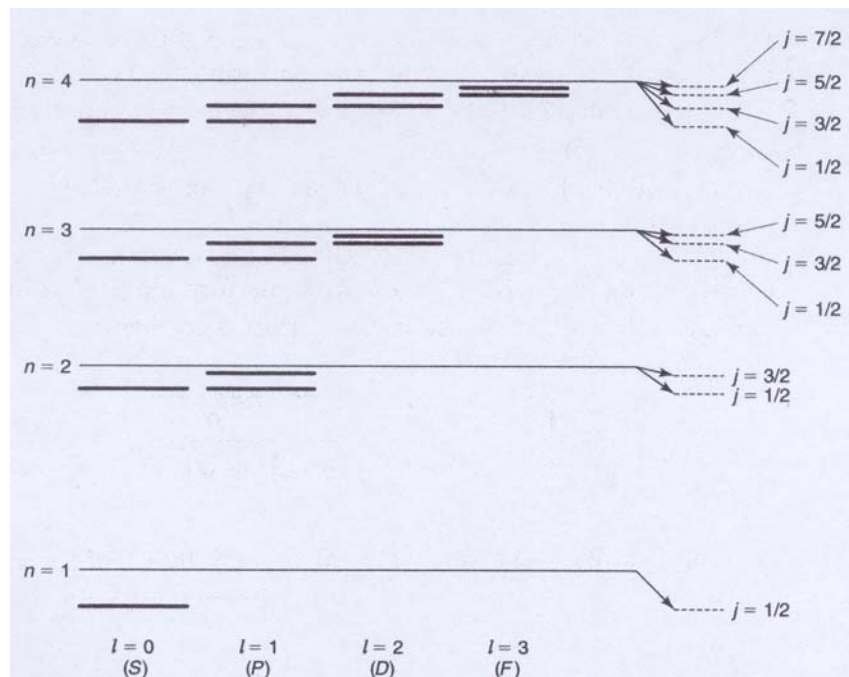
$$= \left(\frac{e^2}{8\pi \epsilon_0} \right) \frac{1}{m_e^2 c^2} \left\langle \frac{1}{r^3} \right\rangle \langle \mathbf{S} \cdot \mathbf{L} \rangle$$

$$\begin{aligned} \text{where } \langle \mathbf{S} \cdot \mathbf{L} \rangle &= \int \psi^* \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)] \psi d\mathbf{r} \\ &= \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)] \\ \left\langle \frac{1}{r^3} \right\rangle &= \frac{1}{l(l+1/2)(l+1)n^3 a^3} \end{aligned}$$

$$\text{so } E_{SO}^{(1)} = \left(\frac{e^2}{8\pi \epsilon_0} \right) \frac{1}{m_e^2 c^2} \frac{(\hbar^2 / 2) [j(j+1) - l(l+1) - s(s+1)]}{l(l+1/2)(l+1)n^3 a^3}$$

$$\text{where } a = \frac{4\pi \epsilon_0 \hbar^2}{m_e e^2}$$

$$E_{fs}^{(1)} = E_r^{(1)} + E_{SO}^{(1)}$$



Energy levels for the fine structure of hydrogen

6.3 The variational principle

Theorem

The ground-state energy E_g for a system described by the Hamiltonian $\hat{H}$

$$E_g \leq \langle \psi | \hat{H} | \psi \rangle \equiv \langle \hat{H} \rangle$$

for any normalized wave function ψ

proof :

the unknown eigenfunctions of $\hat{H}$ form a complete set ,
express ψ as a linear combination of them

$$\psi = \sum_n c_n \psi_n, \text{ with } \hat{H} \psi_n = E_n \psi_n$$

$$\langle \psi | \psi \rangle = 1 = \langle \sum_m c_m \psi_m | \sum_n c_n \psi_n \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2$$

$$\langle \hat{H} \rangle = \langle \psi | \hat{H} \psi \rangle = \langle \sum_m c_m \psi_m | \hat{H} \sum_n c_n \psi_n \rangle$$

$$= \sum_m \sum_n c_m^* c_n E_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2 E_n$$

the ground-state energy E_g is the smallest eigenvalue,

$$\Rightarrow E_g \leq E_n$$

$$\Rightarrow E_g \leq \sum_n |c_n|^2 E_n = \langle \hat{H} \rangle$$

example

for the one-dimensional harmonic oscillator :

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2$$

use a “ trial “ wave function : $\psi(x) = A e^{-bx^2}$

normalize $\psi(x)$:

$$|A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx = |A|^2 \sqrt{\frac{\pi}{2b}} = 1 \quad \rightarrow \quad A = \left(\frac{2b}{\pi}\right)^{1/4}$$

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= |A|^2 \left[\int_{-\infty}^{\infty} e^{-bx^2} \left(-\frac{\hbar^2}{2m} \right) \frac{d^2}{dx^2} e^{-bx^2} dx + \frac{1}{2} m \omega^2 \int_{-\infty}^{\infty} x^2 e^{-2bx^2} dx \right] \\ &= |A|^2 \left[-\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} (4b^2 x^2 - 2b) e^{-2bx^2} dx + \frac{1}{2} m \omega^2 \int_{-\infty}^{\infty} x^2 e^{-2bx^2} dx \right] \\ &= |A|^2 \left[-\frac{\hbar^2}{2m} \left(4b^2 \sqrt{\frac{\pi}{32b^3}} - 2b \sqrt{\frac{\pi}{2b}} \right) + \frac{1}{2} m \omega^2 \sqrt{\frac{\pi}{2b}} \right] \\ &= \frac{b\hbar^2}{2m} + \frac{m\omega^2}{8b} \end{aligned}$$

minimize $\langle \hat{H} \rangle$ with respect to b

$$\frac{d}{db} \langle \hat{H} \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \quad \rightarrow \quad b = \frac{m\omega}{2\hbar}$$

$$\text{so } \langle \hat{H} \rangle_{\min} = \frac{1}{2} \hbar \omega$$

In this case it is the precise form of the actual ground state $E_g = \langle \hat{H} \rangle_{\min}$

6.4 The WKB approximation

WKB method is a technique for obtaining approximate solutions to the time-independent Schrödinger equation in one dimension

It is particularly useful in calculating bound-state energies and tunneling rates through potential barriers.

The process of **WKB** method :

$$\text{From } -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi \quad \rightarrow \quad \frac{d^2 \psi}{dx^2} = -\frac{2m}{\hbar^2} (E - V(x)) \psi$$

$$\frac{d^2 \psi}{dx^2} = -\frac{p^2(x)}{\hbar^2} \psi \quad \dots\dots\dots (6.15) \quad , \text{ where } p(x) \equiv \sqrt{2m[E - V(x)]}$$

(i) Assume that $E > V(x)$

In general ψ is some complex function

express $\psi = A(x)e^{i\phi(x)}$

$$\text{find } \frac{d\psi}{dx} = \left(\frac{dA}{dx} + iA \frac{d\phi}{dx} \right) e^{i\phi(x)}$$

$$\text{and } \frac{d^2\psi}{dx^2} = \left[\frac{d^2A}{dx^2} + 2i \frac{dA}{dx} \frac{d\phi}{dx} + iA \frac{d^2\phi}{dx^2} - A \left(\frac{d\phi}{dx} \right)^2 \right] e^{i\phi(x)}$$

substitute into equation (6.16)

$$\rightarrow \left[\frac{d^2A}{dx^2} + 2i \frac{dA}{dx} \frac{d\phi}{dx} + iA \frac{d^2\phi}{dx^2} - A \left(\frac{d\phi}{dx} \right)^2 \right] = -\frac{p^2}{\hbar^2} A$$

$$\rightarrow \begin{cases} \frac{d^2A}{dx^2} - A \left(\frac{d\phi}{dx} \right)^2 = -\frac{p^2}{\hbar^2} A \\ 2 \frac{dA}{dx} \frac{d\phi}{dx} + A \frac{d^2\phi}{dx^2} = 0 \end{cases} \rightarrow \begin{cases} \frac{d^2A}{dx^2} = A \left[\left(\frac{d\phi}{dx} \right)^2 - \frac{p^2}{\hbar^2} \right] \dots\dots\dots(6.16) \\ \frac{d}{dx} \left(A^2 \frac{d\phi}{dx} \right) = 0 \dots\dots\dots(6.17) \end{cases}$$

from equation (6.17)

$$A^2 \frac{d\phi}{dx} = C^2 \quad \text{and} \quad A = \frac{C}{\sqrt{d\phi/dx}}$$

in equation (6.16), we assume A varies slowly so that $\frac{d^2A}{dx^2}$ is negligible

$$\frac{d^2A}{dx^2} \frac{1}{A} \text{ is much less than } \left(\frac{d\phi}{dx} \right)^2, p^2 / \hbar^2$$

$$\rightarrow \left(\frac{d\phi}{dx} \right)^2 = \frac{p^2}{\hbar^2} \rightarrow \frac{d\phi}{dx} = \pm \frac{p(x)}{\hbar}$$

$$\text{so } \phi(x) = \pm \frac{1}{\hbar} \int p(x) dx$$

$$\text{and } \boxed{\psi(x) \cong \frac{C}{\sqrt{p(x)}} e^{\pm \frac{i}{\hbar} \int p(x) dx}}$$

example

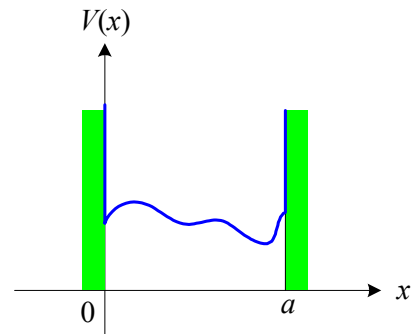
For the potential well with two vertical walls

$$V(x) = \begin{cases} \text{some specified function,} & 0 < x < a \\ \infty, & \text{otherwise} \end{cases}$$

boundary condition $\psi(0) = \psi(a) = 0$

Outside the well, $\psi(x) = 0$

Inside the well, assuming $E > V(x)$



$$\begin{aligned} \psi(x) &\cong \frac{1}{\sqrt{p(x)}} [C_+ e^{i\phi(x)} + C_- e^{-i\phi(x)}] \\ &\cong \frac{1}{\sqrt{p(x)}} [C_1 \sin \phi(x) + C_2 \cos \phi(x)] \end{aligned}$$

where $\phi(x) = \frac{1}{\hbar} \int_0^x p(x') dx'$, $\phi(0) = 0$

$$\psi(0) \cong \frac{1}{\sqrt{p(0)}} [C_1 \sin \phi(0) + C_2 \cos \phi(0)] = 0 \quad \rightarrow \quad C_2 = 0$$

$$\psi(a) \cong \frac{1}{\sqrt{p(a)}} C_1 \sin \phi(a) = 0 \quad \rightarrow \quad \phi(a) = n\pi, \quad n = 1, 2, 3, \dots$$

so $\int_0^a p(x) dx = n\pi \hbar$, this quantization condition is main result, it determine the approximate allowed energies

(ii) Assume that $E < V(x)$

the same as previous process

$$\psi(x) \cong \frac{C}{\sqrt{|p(x)|}} e^{\pm \frac{1}{\hbar} \int |p(x)| dx}$$