Chap 1. Time-dependent Quantum Theory

Hamiltonian : $H = H_0 + V(q,t)$

$$\left[\begin{array}{l} H_0 \text{ (time-independent) :} \\ \qquad H_0\phi_n(q) = E_n\phi_n(q) \\ \Rightarrow \text{ steady-state : } \phi_n(q)e^{-iE_nt/\hbar} \end{array}\right]$$

Schrodinger Eq (time-dependent) : $i\hbar\dfrac{\partial}{\partial t}\psi(q,t) = H\psi(q,t)$ (1)

Expand $\psi(q,t)$ by $\{\phi_n\}$ (= complete orthonormal set)

$$\psi(q,t) = \sum_n c_n(t)\phi_n(q)e^{-iE_nt/\hbar}$$

Enter into (1) and $\langle\phi_k|\times$ (and use orthogonality $\langle\phi_k|\phi_n\rangle = \delta_{kn}$)

$$\frac{d}{dt}c_k(t) = -\frac{i}{\hbar}\sum_n e^{i\omega_{kn}t}V_{kn}(t)c_n(t) \tag{2}$$

$$\left[\begin{array}{c} V_{kn}(t) = \int \phi_k(q)^* V(q,t)\phi_n(q)dq = \langle k|V(t)|n\rangle \\ \omega_{kn} = (E_k - E_n)/\hbar \text{ : transition energy } (n \leftrightarrow k) \end{array}\right]$$

• Illustration : 2-level system

$$\frac{d}{dt}\begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix} = -\frac{i}{\hbar}\begin{bmatrix} V_{11}(t) & e^{-i\omega_{12}t}V_{12}(t) \\ e^{+i\omega_{12}t}V_{21}(t) & V_{22}(t) \end{bmatrix}\begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix}$$

Simplifying assumptions

- $V_{11} = V_{22} = 0$ (V = interaction among different states)
- $V_{12}(t) = V_{21}(t) = v$ (const.)
- $\omega_{12} = 0$ (or $E_1 = E_2$)

Then

$$\frac{d}{dt}c_1 = -\frac{i}{\hbar}vc_2, \quad \frac{d}{dt}c_2 = -\frac{i}{\hbar}vc_1$$

With $c_1(0) = 1$ and $c_2(0) = 0$,

$$c_1 + c_2 = e^{-ivt/\hbar}, \quad c_1 - c_2 = e^{+ivt/\hbar}$$

$$\Rightarrow c_1 = \cos(vt/\hbar), \quad c_2 = i\sin(vt/\hbar)$$

Oscillation period $\propto v^{-1}$

i.e., larger interaction (v) $\Leftrightarrow$ faster resonance

Perturbative expansion

Back to (2). Matrix form :

$$\frac{d}{dt}\mathbf{c}(t) = -\frac{i}{\hbar}\mathbf{W}(t)\cdot\mathbf{c}(t) \qquad ([\mathbf{W}(t)]_{kn} = e^{i\omega_{kn}t}V_{kn}(t))$$

Integrate (formally) :

$$\mathbf{c}(t) = \mathbf{c}(0) - \frac{i}{\hbar}\int_0^t \mathbf{W}(\tau)\cdot\mathbf{c}(\tau)d\tau$$

Sequential expansion :

$$\begin{aligned}\mathbf{c}(t) = \quad & \mathbf{c}(0) - \frac{i}{\hbar}\int_0^t \mathbf{W}(\tau)\cdot\mathbf{c}(0)d\tau + \left(\frac{-i}{\hbar}\right)^2\int_0^t d\tau\int_0^\tau d\tau'\mathbf{W}(\tau)\cdot\mathbf{W}(\tau')\cdot\mathbf{c}(0)\\ & + \left(\frac{-i}{\hbar}\right)^3\int_0^t d\tau\int_0^\tau d\tau'\int_0^{\tau'} d\tau''\mathbf{W}(\tau)\cdot\mathbf{W}(\tau')\cdot\mathbf{W}(\tau'')\cdot\mathbf{c}(0)\\ & + \cdots\end{aligned}$$

First-order perturbation [SR 4.3.1]

$$\mathbf{c}^{(1)}(t) = \mathbf{c}(0) - \frac{i}{\hbar}\int_0^t d\tau \mathbf{W}(\tau)\cdot\mathbf{c}(0)$$

Assume : $c_n(0) = \delta_{nm}$ (initiate from $|m\rangle$ at $t = 0$)

Other state(s) $|k\rangle$ ($\neq |m\rangle$) at time t :

$$c_k^{(1)}(t) = -\frac{i}{\hbar}\int_0^t d\tau \sum_n W_{kn}(\tau)c_n(0) = -\frac{i}{\hbar}\int_0^t d\tau W_{km}(\tau)$$

Transition probability $|m\rangle \rightarrow |k\rangle$

$$P_k^{(1)}(t) = |c_k^{(1)}(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t d\tau V_{km}(\tau)e^{i\omega_{km}\tau}\right|^2$$

- Example 1 : [SR 4.3.2] Excitation of diatomic molecule by collision of atom

- Example 2 : [SR 4.5.1] Time-independent interaction

Assume : V_{km} = const. (time independent)

Then

$$c_k^{(1)}(t) = -V_{km}\frac{e^{i\omega_{km}} - 1}{\hbar\omega_{km}}$$

$$\Rightarrow P_k^{(1)}(t) = |V_{km}|^2 \frac{\sin^2(\omega_{km}t/2)}{(\hbar\omega_{km}/2)^2}$$

$P_k^{(1)}(t)$ along E_k : Peak at E_m, width $\sim 2\pi\hbar/t$, height $\sim (t/\hbar)^2$

width $\propto 1/t \sim$ Short time $\Leftrightarrow$ large energy uncertainty

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Second-order perturbation

$$\mathbf{c}^{(2)}(t) = \mathbf{c}^{(1)}(t) + \left(\frac{-i}{\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau' \mathbf{W}(\tau) \cdot \mathbf{W}(\tau') \cdot \mathbf{c}(0)$$

Assume : $c_n(0) = \delta_{nm}$ (as before)

$$[\mathbf{W}(\tau) \cdot \mathbf{W}(\tau') \cdot \mathbf{c}(0)]_k = \sum_n \sum_l W_{kn}(\tau) W_{nl}(\tau') c_l(0) = \sum_n W_{kn}(\tau) W_{nm}(\tau')$$

$$\Rightarrow c_k^{(2)}(t) = c_k^{(1)}(t) + \left(\frac{-i}{\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau' \sum_n V_{kn}(\tau) V_{nm}(\tau') e^{i\omega_{kn}\tau} e^{i\omega_{nm}\tau'}$$

Transition $|m\rangle \to |k\rangle$ via intermediate states $|n\rangle$

[Examples : • Raman scattering
• Bridge-mediated electron transfers]

Important when 1st-order (direct) transitions are forbidden $V_{km} = 0$

Schrodinger vs Interaction Pictures

Schrodinger picture : $i\hbar \frac{\partial}{\partial t}|\psi_S(t)\rangle = H(t)|\psi_S(t)\rangle$

Integrate : $|\psi_S(t)\rangle = |\psi_S(0)\rangle - \frac{i}{\hbar}\int_0^t d\tau H(\tau)|\psi_S(\tau)\rangle$

Sequential expansion : (omit subscript S)

$$
\begin{aligned}
|\psi(t)\rangle = |\psi(0)\rangle \quad & -\frac{i}{\hbar}\int_0^t d\tau H(\tau)|\psi(0)\rangle \\
& + \left(\frac{-i}{\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau' H(\tau)H(\tau')|\psi(0)\rangle \\
& + \cdots
\end{aligned}
$$

BUT dealing with the operators $H(t)$ is rather tedious

$\Rightarrow$ *Interaction picture* is often more convenient $\quad [H = H_0 + V]$

Interaction picture

Definition : $|\psi_I(t)\rangle \equiv e^{iH_0 t/\hbar}|\psi_S(t)\rangle$

Eq of motion : $$\frac{\partial}{\partial t}|\psi_I(t)\rangle = -\frac{i}{\hbar}V_I(t)|\psi_I(t)\rangle$$

$$(\; V_I(t) \equiv e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} \;)$$

$$\left[\begin{array}{ll} \frac{\partial}{\partial t}|\psi_I\rangle & = \frac{i}{\hbar}H_0 e^{iH_0 t/\hbar}|\psi_S\rangle + e^{iH_0 t/\hbar}\frac{\partial}{\partial t}|\psi_S\rangle \\ & = -\frac{i}{\hbar}e^{iH_0 t/\hbar}V|\psi_S\rangle = -\frac{i}{\hbar}e^{iH_0 t/\hbar}Ve^{-iH_0 t/\hbar}|\psi_I\rangle \end{array} \right]$$

Sequential expansion :

$$\begin{aligned} |\psi_I(t)\rangle = |\psi_I(0)\rangle \quad & -\frac{i}{\hbar}\int_0^t d\tau V_I(\tau)|\psi_I(0)\rangle \\ & + \left(\frac{-i}{\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau' V_I(\tau)V_I(\tau')|\psi_I(0)\rangle + \cdots \end{aligned}$$

(Compare with the previous page : $H(t) \rightarrow V_I(t)$)

Time-ordered Exponential

Assume : $|\psi_I(0)\rangle = |\phi_m\rangle \quad (= |m\rangle)$

Amplitudes of other states $|k\rangle \;\; (\neq |m\rangle)$ at time t :

$$\begin{aligned} c_k(t) &= \langle k|\psi_I(t)\rangle \\ &= \langle k|1 + \left(\frac{-i}{\hbar}\right)\int_0^t d\tau V_I(\tau) + \left(\frac{-i}{\hbar}\right)^2 \int_0^t d\tau \int_0^t d\tau' V_I(\tau)V_I(\tau') + \cdots |m\rangle \\ &\equiv \left\langle k \left| \exp_+ \left[\frac{-i}{\hbar}\int_0^t d\tau V_I(\tau)\right] \right| m \right\rangle \quad \text{(time} - \text{ordered exponential)} \end{aligned}$$

[can be also expressed (formally) via "Dyson time-ordering operator" P

$$PA(t_1)B(t_2) = \begin{cases} A(t_1)B(t_2) & (t_1 > t_2) \\ B(t_2)A(t_1) & (t_1 < t_2) \end{cases}$$

$$\exp_+ \left[\frac{-i}{\hbar}\int_0^t d\tau V_I(\tau)\right] = P\sum_{n=0}^{\infty}\left[\frac{-i}{\hbar}\int_0^t d\tau V_I(\tau)\right]^n = P\exp\left[\frac{-i}{\hbar}\int_0^t d\tau V_I(\tau)\right]$$

]

Fermi's golden rule

Assume : • time-independent V_{km}, • $c_k(0) = \delta_{km}$ (or $|\psi(0)\rangle = |m\rangle$)

$$\Rightarrow P_k^{(1)}(t) = |c_k^{(1)}(t)|^2 = |V_{km}|^2 \frac{\sin^2(\omega_{km}t/2)}{(\hbar\omega_{km}/2)^2}$$

(1st-order perturbation) [cf page 5]

Total probability of transition (from $|m\rangle$) : $P_T \equiv \sum_{k \neq m} P_k^{(1)}(t)$

$$= \sum_k |V_{km}|^2 \frac{\sin^2(\omega_{km}t/2)}{(\hbar\omega_{km}/2)^2} = \int dE \rho(E) |V_{*m}(E)|^2 \frac{\sin^2((E-E_m)t/2\hbar)}{((E-E_m)/2)^2}$$

$\rho(E) = \sum_k \delta(E - E_k)$: density of states

As $t \to \infty$: $P_T \to \int dE \rho(E) |V_{*m}(E)|^2 \frac{2\pi t}{\hbar} \delta(E - E_m) = \frac{2\pi t}{\hbar} \rho(E_m) |V_{*m}|^2$

Transition rate $w_T = \frac{2\pi}{\hbar} |V_{*m}|^2 \rho(E_m)$ $\cdots$ Fermi's golden-rule

- **State-to-state form**

$$t \to \infty : \; P_k^{(1)}(t) \to |V_{km}|^2 \frac{2\pi t}{\hbar} \delta(E_k - E_m)$$

State-to-state transition rate $w_{km} = \frac{2\pi}{\hbar} |V_{km}|^2 \delta(E_k - E_m)$

By summing over the final states, w_T is recovered

$$\sum_k w_{km} = \int dE_k \rho(E_k) w_{km} = \frac{2\pi}{\hbar} |V_{*m}| \rho(E_m) = w_T$$

[Note :

As $t \to \infty : \; \frac{\sin^2(\cdot)}{(\cdot)^2} \to \delta(E_k - E_m) \sim$ Energy conservation

Energy width (= uncertainty) $\to$ smaller

uncertainty principle ($E \leftrightarrow t$)]

- **Periodic interaction** : $V(t) = Ue^{\pm i\omega t}$

(e.g. semiclassical theory of light-matter interaction)

$$c_k^{(1)}(t) = \frac{i}{\hbar}\int_0^t d\tau V_{km}(\tau)e^{i\omega_{km}\tau} = \frac{i}{\hbar}\int_0^t d\tau U_{km}e^{i(\omega_{km}\pm\omega)\tau}$$

Use the previous results, replace $V_{km} \to U_{km}, \quad \omega_{km} \to \omega_{km} \pm \omega$

- Total transition rate

$$w_T = \frac{2\pi}{\hbar}|U_{km}|^2\rho(E_m \mp \hbar\omega)$$

- State-to-state form

$$w_{km} = \frac{2\pi}{\hbar}|U_{km}|^2\delta(E_k - E_m \pm \hbar\omega)$$