VII Time dependent phenomena

VII.1 Time dependence of state

Simple for eigenstates of time-independent Hamiltonian

$$|E,t\rangle = e^{-\frac{iEt}{\hbar}} |E,0\rangle$$

Any state can be represented using energy eigenstates

$$|\psi(0)\rangle = \sum_n c_n |E_n\rangle \longrightarrow |\psi(t)\rangle = \sum_n c_n e^{-\frac{iE_n t}{\hbar}} |E_n\rangle$$

Formally by time development operator $U(t,t_0) = e^{-i\hat{H}(t-t_0)/\hbar}$

- U unitary, probability conserved

Example: 2 states $|E_1\rangle$ & $|E_2\rangle$

initially $\frac{1}{\sqrt{2}}(|E_1\rangle + |E_2\rangle) \rightarrow \frac{1}{\sqrt{2}}\left(e^{-\frac{iE_1 t}{\hbar}} |E_1\rangle + e^{-\frac{iE_2 t}{\hbar}} |E_2\rangle\right)$

$$= e^{-i\bar{E}t/\hbar} \frac{1}{\sqrt{2}}\left(e^{-\frac{i\Delta E t}{2\hbar}} |E_1\rangle + e^{\frac{i\Delta E t}{2\hbar}} |E_2\rangle\right) \qquad \bar{E} = \frac{1}{2}(E_1+E_2), \quad \Delta E = E_1 - E_2$$

$$= e^{-i\bar{E}t/\hbar}\left[\cos\frac{\Delta E t}{2\hbar} \cdot \frac{1}{\sqrt{2}}(|E_1\rangle + |E_2\rangle) - i \sin\frac{\Delta E t}{2\hbar} \cdot \frac{1}{\sqrt{2}}(|E_1\rangle - |E_2\rangle)\right]$$

Spin-$\frac{1}{2}$ particle in magnetic field $\bar{B} \Uparrow \hat{z}$

$$H = -\bar{\mu}\cdot\bar{B} = -\mu B \sigma_z$$

if initially $|+\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$, oscillates between $|+\rangle_x$ and $|-\rangle_x$, with some $|\pm\rangle_y$ in between.

Frequency $\frac{\Delta E}{2\hbar} = \frac{2\mu B}{2\hbar} = \mu B/\hbar$

Another example would be neutral kaons K^0, $\bar{K}^0$

- produced in strong interactions
- time development under total H including weak interaction, eigenstates $|K_L\rangle = \frac{1}{\sqrt{2}}(|K^0\rangle + |\bar{K}^0\rangle)$, $|K_S\rangle = \frac{1}{\sqrt{2}}(|K^0\rangle - |\bar{K}^0\rangle)$

Neutrino oscillations also work like this.

Time-dependent potential gives additional time dependence to states:

$$H = \underset{\text{time indep}}{H_0} + V(t) \qquad \text{e.g. atom in radiation field}$$

Expanded in eigenstates of H_0, coefficients depend on time

$$|\psi(t)\rangle = \sum_n c_n(t)\, e^{-iE_n t/\hbar} |E_n\rangle$$

Substitute in Schrödinger eq:

$$i\hbar \sum_n \dot{c}_n(t) e^{-iE_n t/\hbar} |E_n\rangle + \cancel{\sum_n c_n(t) E_n e^{-iE_n t/\hbar}} |E_n\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} (\cancel{E_n} + V(t)) |E_n\rangle$$

$$\langle E_m| \quad \Leftrightarrow \quad i\hbar \sum_n \dot{c}_n |E_n\rangle e^{-iE_n t/\hbar} = \sum_n c_n V(t) |E_n\rangle e^{-iE_n t/\hbar}$$

$$\Leftrightarrow \quad i\hbar \dot{c}_m(t) = \sum_n c_n(t) \langle m|V(t)|n\rangle e^{i(E_m - E_n)t/\hbar}$$

$$= \sum_n V_{mn}(t)\, e^{i\omega_{mn} t}\, c_n(t)$$

Set of differential equations for $c_n(t)$

- initial condition
$$c_n(t_0) = \langle E_n|\psi(t_0)\rangle e^{iE_n t_0/\hbar}$$
- if $V(t)$ weak, starting point for perturbation expansion

Note also: if $V_{mn}(t)$ oscillates with frequency $-\omega_{mn}$, c_m grows without limit: <u>resonance</u>

VII.2 Pictures of quantum mechanics

Previously: Schrödinger eq.
→ time dependence into states
Operators corresponding to observables time independent
"Schrödinger picture"

Consider now unitary transformation of time dependent states (let $t_0 = 0$)

$$e^{iHt/\hbar}|\psi(t)\rangle = e^{iHt/\hbar}U(t,0)|\psi(0)\rangle = |\psi(0)\rangle \equiv |\psi_H\rangle$$

⇒ State time independent.
Also operators must transform!

$$e^{iHt/\hbar}\hat{A}\,|\psi(t)\rangle = \underbrace{e^{iHt/\hbar}\hat{A}\,e^{-iHt/\hbar}}_{\substack{\hat{A}'(t) \equiv \hat{A}_H(t) \\ \text{time dependent}}} \cdot \underbrace{e^{iHt/\hbar}|\psi(t)\rangle}_{|\psi_H\rangle}$$

$\hat{A}_S = \hat{A} \neq \hat{A}_H$ unless $[\hat{A}, \hat{H}] = 0$

Heisenberg picture: states time independent
operators (and eigenstates) time dep.

Closer to classical (?): operators (⇔ observables) time dependent

Equation of motion for operators

$$i\hbar \frac{d}{dt}\hat{A}_H(t) = i\hbar\frac{d}{dt}\left[e^{i\hat{H}t/\hbar}\hat{A}_S\,e^{-i\hat{H}t/\hbar}\right]$$

$$= -\hat{H}\,e^{i\hat{H}t/\hbar}\hat{A}_S\,e^{-i\hat{H}t/\hbar} + e^{i\hat{H}t/\hbar}\hat{A}_S\,e^{-i\hat{H}t/\hbar}\,\hat{H}$$

$$= \underline{[\hat{A}_H(t), \hat{H}]} \qquad \text{Heisenberg eq. of motion}$$

Compare with Poisson bracket classically:

$$\frac{dA}{dt} = [A, H]_{class}$$

- matrix elements & expectation values unchanged
- same-time operator commutation as before

$\Rightarrow$ same physics

Intermediate: Dirac or interaction picture

Suppose H can be divided

$$\hat{H} = \hat{H}_0 + \hat{V}$$ with $\hat{H}_0$ time independent, $\hat{V}$ may depend on time.

starting point for time dependent perturbation theory

Define $|\psi_I(t)\rangle = e^{iH_0 t/\hbar}|\psi_S(t)\rangle$ take away time dep from H_0

and
$$\hat{A}_I(t) = e^{iH_0 t/\hbar}\hat{A}_S e^{-iH_0 t/\hbar}$$

Eq. of motion for states:

$$i\hbar \frac{d}{dt}|\psi_I(t)\rangle = e^{\frac{i}{\hbar}H_0 t}(-H_0)|\psi_S(t)\rangle + e^{\frac{i}{\hbar}H_0 t} H |\psi_S(t)\rangle$$
$$= e^{\frac{i}{\hbar}H_0 t}\underbrace{(H-H_0)}_{V_S} e^{-\frac{i}{\hbar}H_0 t} e^{\frac{i}{\hbar}H_0 t}|\psi_S(t)\rangle$$
$$= \hat{V}_I(t)|\psi_I(t)\rangle$$

Time development of states from $\hat{V}_I(t)$ (~ Schröding

Operator eom:
$$i\hbar\frac{d\hat{A}_I(t)}{dt} = i\hbar\frac{d}{dt}\left(e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{A}_S e^{-\frac{i}{\hbar}\hat{H}_0 t}\right) = [\hat{A}_I(t), \hat{H}_0]$$

Time development of operators from $\hat{H}_0$ (~ Heisenberg)

VII.3 Time dependent perturbation theory

Let the initial state at $t=t_0$ be $|\varphi_i\rangle$ and integrate the eq. of motion:

$$|\psi_I(t)\rangle = |\varphi_i\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} V_I(t')\,|\psi_I(t')\rangle\, dt'$$

$$\approx \underbrace{|\varphi_i\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt_1\, V_I(t_1)|\varphi_i\rangle}_{\text{First order time development}} + \underbrace{\left(\frac{1}{i\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2\, V_I(t_1)V_I(t_2)|\varphi_i\rangle}_{\text{second order}} + \dots$$

$$= \sum_{n=0}^{\infty}\left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n\, V_I(t_1)\cdots V_I(t_n)\,|\varphi_i\rangle$$

Probability amplitude of state $|\varphi_f\rangle$ at time t

$$c_{fi}(t) = \langle\varphi_f|\psi_I(t)\rangle \approx \langle\varphi_f|\varphi_i\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt_1\, \langle\varphi_f|\hat{V}_I(t_1)|\varphi_i\rangle$$

In most applications $|\varphi_i\rangle$, $|\varphi_f\rangle$ eigenstates of H_0 (atomic transitions, interaction pulse, ...)

$$\Rightarrow c_{fi} \approx \delta_{fi} + \frac{1}{i\hbar}\int_{t_0}^{t} dt_1\, \underbrace{\langle\varphi_f|\hat{V}_S(t_1)|\varphi_i\rangle}_{\substack{\text{matrix element of } V_S \text{ between} \\ \text{original \& final states}}}\, e^{\frac{i}{\hbar}(E_f - E_i)t_1}$$

Development from H_0 only phase; transitions between states if $[\hat{V}_S, \hat{H}_0] \neq 0$

In the special case of time independent potential:

$$c_{fi} = -\frac{i}{\hbar}\int_0^t dt_1\, V_{fi}\, e^{\frac{i}{\hbar}(E_f - E_i)t} = \frac{V_{fi}}{E_f - E_i}\left(1 - e^{\frac{i}{\hbar}(E_f - E_i)t}\right)$$

$$= \frac{V_{fi}}{E_f - E_i}\, e^{\frac{i}{2\hbar}(E_f - E_i)t}\left(-2i\,\sin(E_f - E_i)\frac{t}{2\hbar}\right) \qquad \omega_{fi} = \frac{E_f - E_i}{\hbar}$$

$$\Rightarrow P_{fi} = \frac{4|V_{fi}|^2 \sin^2\frac{(E_f - E_i)t}{2\hbar}}{(E_f - E_i)^2} = \frac{|V_{fi}|^2}{\hbar^2}\,\frac{\sin^2\frac{\omega_{fi}t}{2}}{(\omega_{fi}/2)^2}$$

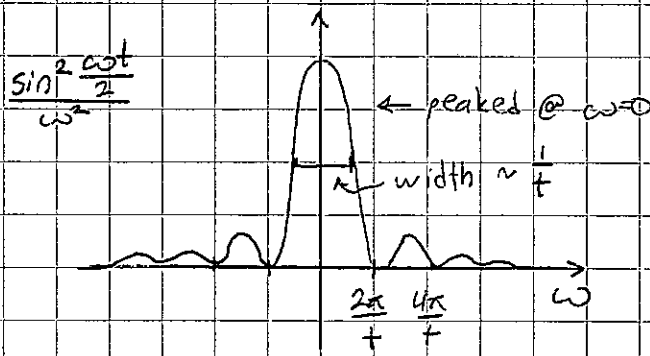
$$\xrightarrow[t\to\infty]{} \frac{2\pi t}{\hbar^2}|V_{fi}|^2\,\delta(\omega_{fi}) = \frac{2\pi t}{\hbar}|V_{fi}|^2\,\delta(E_f - E_i)$$

Time independent potential causes transitions all the time with probability $\propto$ time, so relevant quantity would be transition rate (per time)

$$\boxed{W_{fi} = \frac{dP_{fi}}{dt} = \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i)}$$

Fermi golden rule

energy conservation when $t \to \infty$



Transitions into continuum:

Often transitions go into energy continuum, where each energy may correspond to many states

- radioactive decay
- atom de-excitation
- scattering

Assume energy interval $(E, E+dE)$ contains $\rho(E)\,dE$ possible final states. Then transition rate is (sum over all possible final states)

$$W_{fi} = \int dE_f \, \rho(E_f) \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i) = \underline{\underline{\frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_i)}}\Big|_{E_f = E_i}$$

The more possible final states, the larger transition rate and shorter life time of initial state,

$$\tau_i = \frac{1}{W_{fi}}$$

What is density of states $\varrho(E)$?
Depends on the potential, usually a good approximation would be plane waves (free) in a box of side L (see example at the end of sec VI.2),

$$\varrho(E) = C\,V\sqrt{E}\,, \quad C = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}, \quad V = L^3$$

If final state has spin degeneracy (spin s), $C \to (2s+1)C$

For only a limited set of directions, density of states per solid angle $d\Omega$

$$\varrho(E, d\Omega) = \frac{1}{16\pi^3}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}\,L^3\,d\Omega = \frac{mk}{\hbar^2}\left(\frac{L}{2\pi}\right)^3 d\Omega\,,$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

Another important time dependence: harmonic $\hat{V}(t)$:

$$\hat{V}_S(t) = \hat{K}e^{-i\omega t} + \hat{K}^{+}e^{i\omega t}$$

$\Rightarrow$ time integral in transition amplitude $\int_0^t e^{\frac{i}{\hbar}(E_f - E_i)t_1 \pm i\omega t_1}\,dt_1$ easy to do

$$\Rightarrow \langle \varphi_f|\hat{K}|\varphi_i\rangle \frac{1}{i\hbar} e^{\frac{i}{2}(\omega_{fi}-\omega)t}\,\frac{2\sin\frac{1}{2}(\omega_{fi}-\omega)t}{\omega_{fi}-\omega}$$

$$+ \langle \varphi_f|\hat{K}^{+}|\varphi_i\rangle \frac{1}{i\hbar} e^{\frac{i}{2}(\omega_{fi}+\omega)t}\,\frac{2\sin\frac{1}{2}(\omega_{fi}+\omega)t}{\omega_{fi}+\omega}$$

At large times the energy conserving δ function is $\delta(E_f - E_i \pm \hbar\omega)$. Cross term in $|C_{fi}|^2$ stays bounded as $t \to \infty$, and can be neglected.

Potential transfers energy to / from the system in quanta of energy $\hbar\omega$.

Golden rule $\Rightarrow$

$$W = \frac{2\pi}{\hbar}\, \rho(E_i + \hbar\omega)\, |\langle \varphi_f | \hat{K} | \varphi_i \rangle|^2 \Big|_{E_f = E_i + \hbar\omega}$$
$$+ \frac{2\pi}{\hbar}\, \rho(E_i - \hbar\omega)\, |\langle \varphi_f | \hat{K}^\dagger | \varphi_i \rangle|^2 \Big|_{E_f = E_i - \hbar\omega}$$

General time dependence: $V(t) = \int_{-\infty}^{\infty} d\omega\, \tilde{V}(\omega)\, e^{i\omega t}$

all frequencies, no energy conservation
(for V time indep., $\tilde{V}(\omega) \propto \delta(\omega) \Rightarrow \omega = 0$, E conserved)

VII.4 Charged particle in electromagn. field

Semiclassical theory:
- particles (electrons, atoms) QM
- EM field classical
  (field quantization: QM II)

Remember from electrodynamics: fields can be written using potentials $\varphi(\bar{r},t)$ & $\bar{A}(\bar{r},t)$

$$\bar{E} = -\nabla\varphi - \frac{\partial \bar{A}}{\partial t} \qquad \bar{B} = \nabla \times \bar{A}$$

Classical Hamiltonian which gives correct equation of motion $\left(\dot{\bar{p}} = q(\bar{E} + \bar{v} \times \bar{B}) \right)$ is

$$H = \frac{1}{2m}\left(\bar{p} - q\bar{A}(\bar{r},t)\right)^2 + q\,\varphi(\bar{r},t)$$

usual electric potential

minimal substitution: $\bar{p} \to \bar{p} - q\bar{A}$
$H \to H + q\varphi$

For spin-0 this would give the right QM Hamiltonian when $\bar{p}, \bar{r} \to \hat{\bar{p}}, \hat{\bar{r}}$ (no spin in class. mechanics)

In the case of spin-$\frac{1}{2}$-particles

$$\frac{\bar{p}^2}{2m} = \frac{(\bar{\sigma}\cdot\bar{p})^2}{2m} \qquad (\text{as } \bar{\sigma}\cdot\bar{a}\,\bar{\sigma}\cdot\bar{b} = \bar{a}\cdot\bar{b} + i\,\bar{a}\cdot\bar{b}\times\bar{\sigma})$$

$\Rightarrow$ minimal substitution

$$[\bar{\sigma}\cdot(\bar{p}-q\bar{A})]^2 = \sigma_i(p_i - qA_i)\,\sigma_j(p_j - qA_j)$$

$$= (\bar{p}-q\bar{A})^2 + i(\bar{p}-q\bar{A})\times(\bar{p}-q\bar{A})\cdot\bar{\sigma}$$

$$= (\bar{p}-q\bar{A})^2 - iq(\underbrace{\bar{p}\times\bar{A}}_{-i\hbar\nabla\times\bar{A}} + \bar{A}\times\bar{p})\cdot\bar{\sigma}$$

$$-i\hbar\nabla\times\bar{A} = -i\hbar(\nabla\times\bar{A}) + i\hbar\bar{A}\times\nabla = (\bar{p}\times\bar{A}) - \bar{A}\times\bar{p}$$

$$= (\bar{p}-q\bar{A})^2 - iq(-i\hbar\underbrace{\nabla\times\bar{A}}_{\bar{B}})\cdot\bar{\sigma} = (\bar{p}-q\bar{A})^2 - q\hbar\,\bar{\sigma}\cdot\bar{B}$$

$$\Leftrightarrow \quad H = \frac{1}{2m}(\bar{p}-q\bar{A})^2 - \frac{q\hbar}{2m}\bar{\sigma}\cdot\bar{B} + q\varphi$$

if $q=e$ & $m=m_e$, Bohr magneton μ_B

Pauli equation

$$\bar{\mu} = 2\mu_B\,\bar{S}$$

Assume EM radiation field as presented by plane wave potentials

$$\begin{cases} \bar{A}(\bar{r},t) = A_0\,\bar{\varepsilon}\,\sin(\bar{k}\cdot\bar{r}-\omega t) \\ \varphi(\bar{r},t) = 0 \end{cases}$$

Fields are then

$$\bar{E} = E_0\,\bar{\varepsilon}\cos(\bar{k}\cdot\bar{r}-\omega t), \quad E_0 = \omega A_0 \qquad \omega = c|\bar{k}|$$

$$\bar{B} = B_0\,\hat{k}\times\bar{\varepsilon}\cos(\bar{k}\cdot\bar{r}-\omega t), \quad B_0 = |\bar{k}|A_0$$

- propagating at speed of light
- polarization $\bar{E}\perp\bar{B}$
- $\bar{\varepsilon}\perp\bar{k} \Leftrightarrow$ Coulomb gauge $\nabla\cdot\bar{A} = 0$

Atom in this field: for electron $q = -e$

$$(\bar{p} + e\bar{A})^2 = \bar{p}^2 + e\,\bar{p}\cdot\bar{A} + e\bar{A}\cdot\bar{p} + e^2A^2$$
$$= \bar{p}^2 + 2e\,\bar{A}\cdot\bar{p} - i\hbar\underbrace{(\nabla\cdot\bar{A})}_{=0} + e^2A^2$$
in Coulomb gauge

$\bar{r}$ is of atomic scale, $r \sim 10^{-10} - 10^{-2}$
For ~visible light $\lambda \sim 10^{-6}\,m \Rightarrow k = \frac{2\pi}{\lambda} \approx 10^{7}\,m^{-1}$

$$\Rightarrow \langle \bar{k}\cdot\bar{r}\rangle \sim 10^{-3} - 10^{-3}$$

Approximate $\bar{A}(\bar{r},t) \approx -A_0\,\bar{\varepsilon}\,\sin\omega t$

Magnetic interaction also small, as
$p \sim \hbar/r$ (Heisenberg uncertainty)

$$\Rightarrow \frac{\langle \hbar\,\bar{\sigma}\cdot\bar{B}\rangle}{\langle \bar{A}\cdot\bar{p}\rangle} \approx \frac{\hbar|k|A_0}{A_0\,\hbar/r} = kr \ll 1$$

$e^2A^2 \propto \alpha^2$, small unless large field

$$\Rightarrow \hat{H} \simeq \underbrace{\frac{p^2}{2m} + V_{bind}(r)}_{\hat{H}_0} \underbrace{- \frac{e}{m}A_0\,\bar{\varepsilon}\cdot\bar{p}\,\sin\omega t}_{\hat{V}_s(t)}$$

$\hat{V}_s(t)$ of harmonic form with $\hat{K} = \frac{ie}{2m}A_0\,\bar{\varepsilon}\cdot\bar{p}$

Golden rule gives transition rate

$$W = \frac{\pi e^2}{2\hbar m^2}A_0^2\Big[\underbrace{\rho(E_i+\hbar\omega)\,|\langle\varphi_f|\bar{\varepsilon}\cdot\bar{p}|\varphi_i\rangle|^2\Big|_{E_f=E_i+\hbar\omega}}_{\text{absorption}}$$
$$+ \underbrace{\rho(E_i-\hbar\omega)\,|\langle\varphi_f|\bar{\varepsilon}\cdot\bar{p}|\varphi_i\rangle|^2\Big|_{E_f=E_i-\hbar\omega}}_{\text{emission}}\Big]$$

Atom can take or give energy to/from the field in quanta $\hbar\omega$ (photon energy).
- proportional to $A_0^2 \Rightarrow$ need initially field

$\Rightarrow$ no spontaneous emission semiclassically

Matrix elements easier to compute through

$$\langle \varphi_f | \bar{p} | \varphi_i \rangle = \frac{1}{2i\hbar} \langle \varphi_f | [\bar{r}, \bar{p}^2] | \varphi_i \rangle$$

$$= \frac{m}{i\hbar} \langle \varphi_f | [\bar{r}, \frac{\bar{p}^2}{2m} + V_{bind}(\bar{r})] | \varphi_i \rangle$$

$$= \frac{m}{i\hbar} \langle \varphi_f | [\bar{r}, \hat{H}_0] | \varphi_i \rangle = \frac{im(E_f - E_i)}{\hbar} \langle \varphi_f | \bar{r} | \varphi_i \rangle$$

must be $E_f - E_i = \pm \hbar\omega$

$$\Rightarrow W = \frac{\pi\omega^2}{2\hbar} A_0^2 \Big[\rho(E_i + \hbar\omega) \, | \bar{\varepsilon} \cdot \langle \varphi_f | -e\bar{r} | \varphi_i \rangle |^2$$

$$+ \rho(E_i - \hbar\omega) \, | \bar{\varepsilon} \cdot \langle \varphi_f | -e\bar{r} | \varphi_i \rangle |^2 \Big]$$

Operator $\bar{d} = -e\bar{r}$ electric dipole momentum of the electron

$\Rightarrow$ known as dipole approximation, magnetic interaction neglected