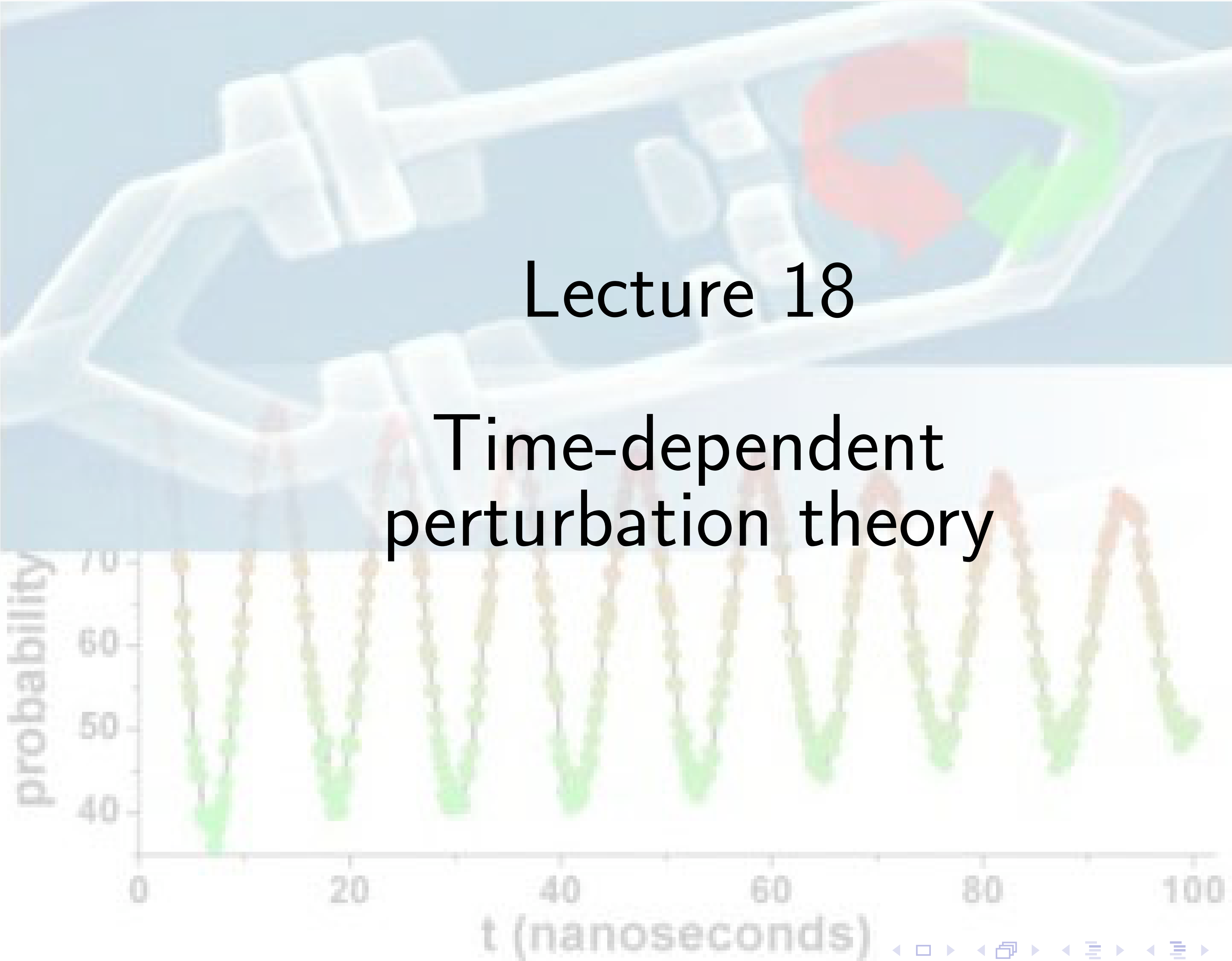

Lecture 18

Time-dependent perturbation theory

Time-dependent perturbation theory

- So far, we have focused on quantum mechanics of systems described by Hamiltonians that are *time-independent*.
- In such cases, time dependence of wavefunction developed through time-evolution operator, $\hat{U} = e^{-i\hat{H}t/\hbar}$, i.e. for $\hat{H}|n\rangle = E_n|n\rangle$,

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} \underbrace{|\psi(0)\rangle}_{\sum_n c_n(0)|n\rangle} = \sum_n e^{-iE_nt/\hbar} c_n(0)|n\rangle$$

- Although suitable for closed quantum systems, formalism fails to describe interaction with an external environment, e.g. EM field.
- In such cases, more convenient to describe "induced" interactions of small isolated system, $\hat{H}_0$, through time-dependent interaction $V(t)$.
- In this lecture, we will develop a formalism to treat such time-dependent perturbations.

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Time-dependent perturbation theory: outline

- Time-dependent potentials: general formalism
- Time-dependent perturbation theory
- "Sudden" perturbation
- Harmonic perturbations: Fermi's Golden Rule

Time-dependent potentials: general formalism

- Consider Hamiltonian $\hat{H}(t) = \hat{H}_0 + V(t)$, where all time dependence enters through the potential $V(t)$.
- So far, we have focused on **Schrödinger representation**, where dynamics specified by time-dependent wavefunction,

$$i\hbar\partial_t|\psi(t)\rangle_{\mathrm{S}} = \hat{H}|\psi(t)\rangle_{\mathrm{S}}$$

- However, to develop time-dependent perturbation theory for $\hat{H}(t) = \hat{H}_0 + V(t)$, it is convenient to turn to a new representation known as the **Interaction representation**:

$$|\psi(t)\rangle_{\mathrm{I}} = e^{i\hat{H}_0 t/\hbar}|\psi(t)\rangle_{\mathrm{S}}, \qquad |\psi(0)\rangle_{\mathrm{I}} = |\psi(0)\rangle_{\mathrm{S}}$$

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- In the interaction representation, wavefunction obeys the following equation of motion:

$$\begin{aligned} i\hbar\partial_t|\psi(t)\rangle_{\mathrm{I}} &= e^{i\hat{H}_0 t/\hbar}(i\hbar\partial_t - \hat{H}_0)|\psi(t)\rangle_{\mathrm{S}} \\ &= e^{i\hat{H}_0 t/\hbar}(\hat{H} - \hat{H}_0)|\psi(t)\rangle_{\mathrm{S}} \\ &= \underbrace{e^{i\hat{H}_0 t/\hbar}V(t)e^{-i\hat{H}_0 t/\hbar}}_{V_{\mathrm{I}}(t)}|\psi(t)\rangle_{\mathrm{I}} \end{aligned}$$

We therefore have that

$$\boxed{i\hbar\partial_t|\psi(t)\rangle_{\mathrm{I}} = V_{\mathrm{I}}(t)|\psi(t)\rangle_{\mathrm{I}}, \qquad V_{\mathrm{I}}(t) = e^{i\hat{H}_0 t/\hbar}V(t)e^{-i\hat{H}_0 t/\hbar}}$$

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- Then, if we form eigenfunction expansion, $|\psi(t)\rangle_{\rm I} = \sum_n c_n(t)|n\rangle$, where $\hat{H}_0|n\rangle = E_n|n\rangle$,

$$i\hbar\partial_t \sum_n c_n(t)|n\rangle = e^{i\hat{H}_0 t/\hbar}V(t)e^{-i\hat{H}_0 t/\hbar}\sum_n c_n(t)|n\rangle$$

$$i\hbar\sum_n \dot{c}_n(t)|n\rangle = \sum_n c_n(t)e^{i\hat{H}_0 t/\hbar}V(t)\underbrace{e^{-i\hat{H}_0 t/\hbar}|n\rangle}_{e^{-iE_n t/\hbar}|n\rangle}$$

- If we now contract with a general state $|m\rangle$

$$\sum_n \dot{c}_n(t)\underbrace{\langle m|n\rangle}_{\delta_{mn}} = \sum_n c_n(t)\underbrace{\langle m|e^{i\hat{H}_0 t/\hbar}}_{\langle m|e^{iE_m t/\hbar}}V(t)e^{-iE_n t/\hbar}|n\rangle$$

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

Time-dependent potentials: general formalism

$$\boxed{i\hbar\partial_t|\psi(t)\rangle_{\rm I} = V_{\rm I}(t)|\psi(t)\rangle_{\rm I}, \qquad V_{\rm I}(t) = e^{i\hat{H}_0 t/\hbar}V(t)e^{-i\hat{H}_0 t/\hbar}}$$

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Time-dependent potentials: general formalism

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- So, in summary, if we expand wavefunction $|\psi(t)\rangle_{\rm I} = \sum_n c_n(t)|n\rangle$, where $\hat{H}_0|n\rangle = E_n|n\rangle$, the Schrödinger equation,

$$i\hbar\partial_t|\psi(t)\rangle_{\rm I} = V_{\rm I}(t)|\psi(t)\rangle_{\rm I} \quad \text{with} \quad V_{\rm I}(t) = e^{i\hat{H}_0 t/\hbar}V(t)e^{-i\hat{H}_0 t/\hbar}$$

translates to the relation,

$$\boxed{i\hbar\dot{c}_m(t) = \sum_n V_{mn}(t)e^{i\omega_{mn}t}c_n(t)}$$

where $V_{mn}(t) = \langle m|V(t)|m\rangle$ and $\omega_{mn} = \frac{1}{\hbar}(E_m - E_n) = -\omega_{nm}$.

Example: Dynamics of a driven two-level system

$$\boxed{i\hbar\dot{c}_m(t) = \sum_n V_{mn}(t)e^{i\omega_{mn}t}c_n(t)}$$

- Consider an atom with just two available atomic levels, $|1\rangle$ and $|2\rangle$, with energies E_1 and E_2. In the eigenbasis, the time-independent Hamiltonian can be written as

$$\hat{H}_0 = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2| \equiv \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

Note that the two-level atom mirrors a spin $1/2$ system.

- If the system is driven by an electric field, $\mathcal{E}(\mathbf{r}, t) = \mathcal{E}_0(\mathbf{r})\cos(\omega t)$, and the states have different parity, close to resonance, $|\omega - \omega_{21}| \ll \omega_{21}$, the effective interaction potential is given by

$$V(t) \simeq \delta e^{i\omega t}|1\rangle\langle 2| + \delta e^{-i\omega t}|2\rangle\langle 1| \equiv \delta \begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix}$$

where the matrix element, $\delta = \langle 1|\mathcal{E}|2\rangle$ is presumed real.

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$$\hat{H}_0 + V(t) = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} + \delta \begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix}$$

- The electric field therefore induces transitions between the states.
- If we expand the "spinor-like" wavefunction in eigenstates of $\hat{H}_0$, i.e. $|\psi(t)\rangle_{\mathrm{I}} = c_1(t)|1\rangle + c_2(t)|2\rangle$, the equation

$$\boxed{i\hbar \dot{c}_m(t) = \sum_n V_{mn}(t) e^{i\omega_{mn}t} c_n(t)}$$

translates to the quantum dynamics

$$i\hbar\partial_t \mathbf{c} = \delta \begin{pmatrix} 0 & e^{i(\omega-\omega_{21})t} \\ e^{-i(\omega-\omega_{21})t} & 0 \end{pmatrix} \mathbf{c}(t), \qquad \omega_{21} = \frac{1}{\hbar}(E_2 - E_1)$$

where $\mathbf{c}(t) = (c_1(t)\ c_2(t))$.

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from which we obtain an equation for c_2,

$$\ddot{c}_2(t) + -i(\omega - \omega_{21})\dot{c}_2(t) + \left(\frac{\delta}{\hbar}\right)^2 c_2(t) = 0$$

- With the initial conditions, $c_1(0) = 1$ and $c_2(0) = 0$, i.e. particle starts in state $|1\rangle$, we obtain the solution,

$$\boxed{c_2(t) = e^{-i(\omega-\omega_{21})t/2} \sin(\Omega t)}$$

where $\Omega = ((\delta/\hbar)^2 + (\omega - \omega_{21})^2/4)^{1/2}$ is known as **Rabi frequency**.

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$$\boxed{c_2(t) = Ae^{-i(\omega-\omega_{21})t/2}\sin(\Omega t), \qquad \Omega = \left(\left(\frac{\delta}{\hbar}\right)^2 + \left(\frac{\omega-\omega_{21}}{2}\right)^2\right)^{1/2}}$$

- Together with $c_1(t) = \frac{i\hbar}{\delta}e^{i(\omega-\omega_{21})t}\dot{c}_2$, we obtain the normalization, $A = \frac{\delta}{\sqrt{\delta+\hbar^2(\omega-\omega_{21}^2/4}}$ and

$$\boxed{|c_2(t)|^2 = \frac{\delta^2}{\delta^2+\hbar^2(\omega-\omega_{21})^2/4}\sin^2\Omega t, \quad |c_1(t)|^2 = 1-|c_2(t)|^2}$$

- Periodic solution describes transfer of probability between states 1 and 2. Maximum probability of occupying state 2 is Lorentzian,

$$|c_2(t)|^2_{\max} = \frac{\delta^2}{\delta^2+\hbar^2(\omega-\omega_{21})^2/4},$$

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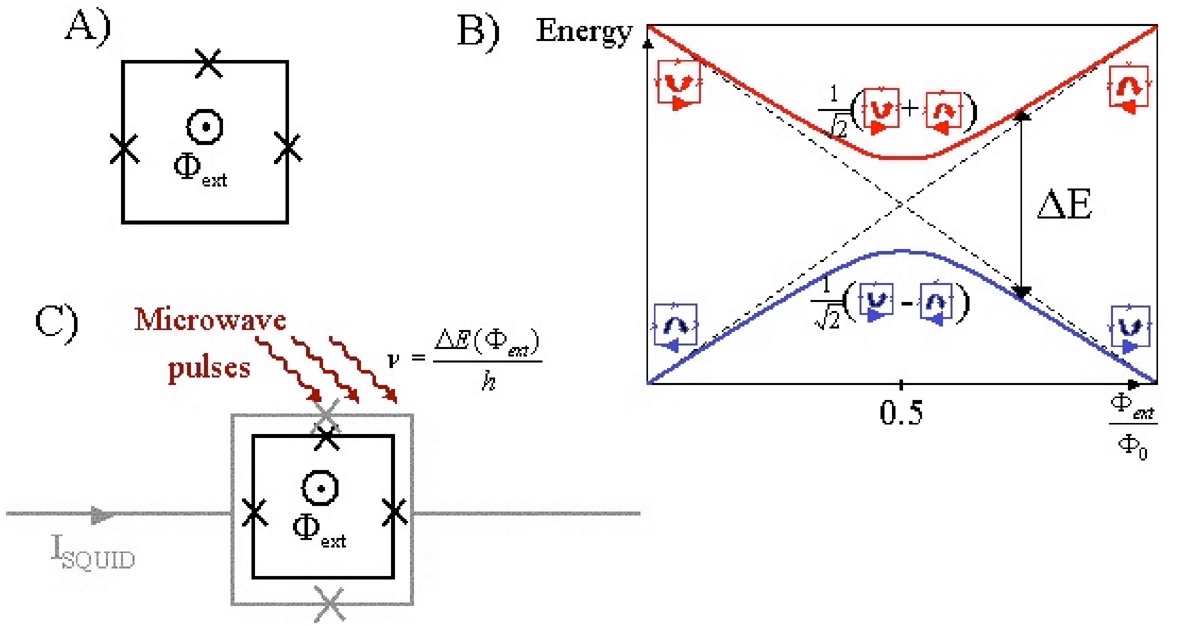
Rabi oscillations: persistent current qubit

- It is different to prepare and analyse ideal atomic two-level system.
- However, circuits made of superconducting loops provide access to "two-level" systems. These have been of great interest since they (may yet) provide a platform to develop qubit operation and quantum logic circuits.



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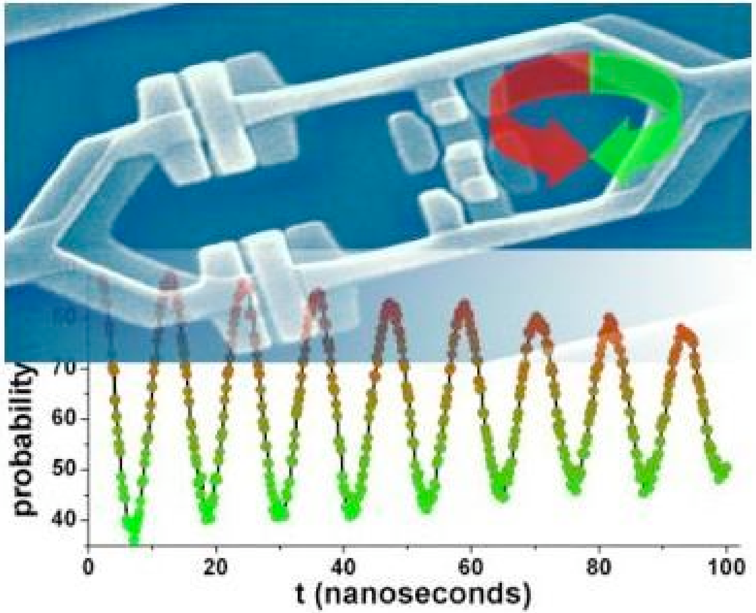

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Time-dependent perturbation theory

- For a general time-dependent Hamiltonian, $\hat{H} = \hat{H}_0 + V(t)$, an analytical solution is usually infeasible.
- However, as for the time-independent Schrödinger equation, we can develop to a perturbative expansion (in powers of interaction):

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where $\hat{H}_0|n\rangle = E_n|n\rangle$, $c_n^{(m)} \sim O(V^m)$, and $c_n^{(0)}$ represents some (time-independent) initial state of the system.

- As with the Schrödinger representation, in the interaction representation, $|\psi(t)\rangle_{\rm I}$ related to inital state $|\psi(t_0)\rangle_{\rm I}$, at time t_0, through a **time-evolution operator**,

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$$\boxed{|\psi(t)\rangle_{\mathrm{I}} = \hat{U}_{\mathrm{I}}(t, t_0)|\psi(t_0)\rangle_{\mathrm{I}}}$$

- Substituted into Schrödinger equation $i\hbar\partial_t|\psi(t)\rangle_{\mathrm{I}} = V_{\mathrm{I}}(t)|\psi(t)\rangle_{\mathrm{I}}$,

$$i\hbar\partial_t \hat{U}_{\mathrm{I}}(t, t_0)|\psi(t_0)\rangle_{\mathrm{I}} = V_{\mathrm{I}}(t)\hat{U}_{\mathrm{I}}(t, t_0)|\psi(t_0)\rangle_{\mathrm{I}}$$

- Since this is true for any initial state $|\psi(t_0)\rangle_{\mathrm{I}}$, we must have

$$\boxed{i\hbar\partial_t \hat{U}_{\mathrm{I}}(t, t_0) = V_{\mathrm{I}}(t)\hat{U}_{\mathrm{I}}(t, t_0)}$$

  with the boundary condition $U_{\mathrm{I}}(t_0, t_0) = \mathbb{I}$.

- Integrating t_0 to t, $i\hbar\int_{t_0}^{t} dt'\, \partial_{t'}\hat{U}_{\mathrm{I}}(t', t_0) = i\hbar(\hat{U}_{\mathrm{I}}(t, t_0) - \mathbb{I})$, i.e.

$$\boxed{\hat{U}_{\mathrm{I}}(t, t_0) = \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_{\mathrm{I}}(t')\hat{U}_{\mathrm{I}}(t', t_0)}$$

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- If we substitute $\hat{U}_{\mathrm{I}}(t',t_0)$ on right hand side,

$$\begin{aligned}\hat{U}_{\mathrm{I}}(t,t_0) = \mathbb{I} &- \frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_{\mathrm{I}}(t') \\ &+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt'\, V_{\mathrm{I}}(t') \int_{t_0}^{t'} dt''\, V_{\mathrm{I}}(t'')\hat{U}_{\mathrm{I}}(t'',t_0)\end{aligned}$$

- Iterating this procedure,

$$\boxed{\hat{U}_{\mathrm{I}}(t,t_0) = \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n\, V_{\mathrm{I}}(t_1)V_{\mathrm{I}}(t_2)\cdots V_{\mathrm{I}}(t_n)}$$

where term $n=0$ translates to $\mathbb{I}$.

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$$\begin{aligned}\hat{U}_{\mathrm{I}}(t,t_0) &= \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_{\mathrm{I}}(t') \\ &\quad + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt'\, V_{\mathrm{I}}(t') \int_{t_0}^{t'} dt''\, V_{\mathrm{I}}(t'')\hat{U}_{\mathrm{I}}(t'',t_0)\end{aligned}$$

- Iterating this procedure,

$$\boxed{\hat{U}_{\mathrm{I}}(t,t_0) = \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n\, V_{\mathrm{I}}(t_1)V_{\mathrm{I}}(t_2)\cdots V_{\mathrm{I}}(t_n)}$$

where term $n = 0$ translates to $\mathbb{I}$.

Time-dependent perturbation theory

$$\boxed{\hat{U}_{\rm I}(t,t_0) = \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n V_{\rm I}(t_1) V_{\rm I}(t_2)\cdots V_{\rm I}(t_n)}$$

- **Remark:** Since operators $V_{\rm I}(t)$ appear as a time-ordered sequence, with

  $$t_0 \leq t_n \leq t_{n-1} \leq \cdots t_1 \leq t$$

  this expression is sometimes written as

  $$\hat{U}_{\rm I}(t,t_0) = {\rm T}\left[e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' V_{\rm I}(t')}\right]$$

  where "T" denotes the time-ordering operator and is understood as the identity above.
- Note that, for V independent of t, $\hat{U}_{\rm I}(t,t_0) = e^{-\frac{i}{\hbar}Vt}$ reminiscent of the usual time-evolution operator for time-independent $\hat{H}$.

Time-dependent perturbation theory

$$\boxed{\hat{U}_{\mathrm{I}}(t,t_0) = \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n V_{\mathrm{I}}(t_1)V_{\mathrm{I}}(t_2)\cdots V_{\mathrm{I}}(t_n)}$$

- If a system is prepared in an initial state, $|i\rangle$ at time $t = t_0$, at a subsequent time, t, the system will be in a final state, $\hat{U}_{\mathrm{I}}(t,t_0)|i\rangle$. Using the resolution of identity, $\sum_n |n\rangle\langle n| = \mathbb{I}$, we therefore have

$$\hat{U}_{\mathrm{I}}(t,t_0)|i\rangle = \sum_n |n\rangle \overbrace{\langle n|\hat{U}_{\mathrm{I}}(t,t_0)|i\rangle}^{c_n(t)}$$

- From relation above, the coefficients in the expansion given by

$$c_n(t) = \delta_{ni} - \frac{i}{\hbar}\int_{t_0}^{t} dt' \langle n|V_{\mathrm{I}}(t')|i\rangle$$
$$- \frac{1}{\hbar^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \langle n|V_{\mathrm{I}}(t')V_{\mathrm{I}}(t'')|i\rangle + \cdots$$

Time-dependent perturbation theory

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- Recalling the definition, $V_{\mathrm{I}}(t) = e^{i\hat{H}_0 t/\hbar}V(t)e^{-i\hat{H}_0 t/\hbar}$, the matrix elements entering the coefficients are then given by

$$\langle n|V_{\mathrm{I}}(t)|m\rangle = \langle n|e^{i\hat{H}_0 t/\hbar}V(t)e^{-i\hat{H}_0 t/\hbar}|m\rangle$$
$$= \underbrace{\langle n|V(t)|m\rangle}_{V_{nm}} \underbrace{\exp\left[\frac{i}{\hbar}(E_n - E_m)\right]}_{e^{i\omega_{nm}t}}$$

where $V_{nm}(t) = \langle n|V(t)|m\rangle$ denote matrix elements between the basis states of $\hat{H}_0$ on the perturbation, and $\omega_{nm} = (E_n - E_m)/\hbar$.

Time-dependent perturbation theory

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- Therefore, using the relation, $\langle n|V_{\mathrm{I}}(t)|m\rangle = \langle n|V(t)|m\rangle e^{i\omega_{nm}t}$,

$$\boxed{\begin{aligned} c_n^{(1)}(t) &= -\frac{i}{\hbar}\int_{t_0}^{t} dt'\, e^{i\omega_{ni}t'} V_{ni}(t') \\ c_n^{(2)}(t) &= -\frac{1}{\hbar^2}\sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, e^{i\omega_{nm}t' + i\omega_{mi}t''} V_{nm}(t') V_{mi}(t'') \end{aligned}}$$

- As a result, we obtain **transition probability** $|i\rangle \to |n \neq i\rangle$,

$$P_{i\to n}(t) = |c_n(t)|^2 = |c_n^{(1)} + c_n^{(2)} + \cdots|^2$$

Example: Kicked oscillator

- Suppose quantum harmonic oscillator, $\hat{H} = \hbar\omega(a^\dagger a + 1/2)$, prepared in ground state $|0\rangle$ at time $t = -\infty$. If it is perturbed by weak (transient) electric field,

$$V(t) = -e\mathcal{E}x\, e^{-t^2/\tau^2}$$

what is probability of finding it in first excited state, $|1\rangle$, at $t = +\infty$?

- Working to first order in V, $P_{0\to 1} \simeq |c_1^{(1)}|^2$ where

$$c_1^{(1)}(t) = -\frac{i}{\hbar}\int_{t_0}^{t} dt'\, e^{i\omega_{10}t'}\, V_{10}(t')$$

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- Using the ladder operator formalism, with $|1\rangle = a^\dagger|0\rangle$ and

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger), \qquad \langle 1|x|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle 0|a(a+a^\dagger)|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}$$

- With $\displaystyle\int_{t_0=-\infty}^{t\to\infty} dt'\, e^{i\omega t'} e^{-t'^2/\tau^2} = \sqrt{\pi}\tau \exp\left[-\frac{1}{4}\omega^2\tau^2\right]$,

$$c_1^{(1)}(t\to\infty) = ie\mathcal{E}\tau\sqrt{\frac{\pi}{2m\hbar\omega}}e^{-\omega^2\tau^2/4}$$

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Note that $P_{0\to 1}$ is maximal for $\tau \sim 1/\omega$.

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“Sudden” perturbation – quantum quench

- Suppose there is a switch from $\hat{H}_0$ to $\hat{H}'_0$ in a time shorter than any other characteristic scale – perturbation theory is irrelevant:

- If system is initially in eigenstate $|n\rangle$ of $\hat{H}_0$, time evolution after switch will just follow that of $\hat{H}'_0$,

  i.e. simply expand initial state as a sum over eigenstates of $\hat{H}'_0$,

$$|n\rangle = \sum_{n'} |n'\rangle\langle n'|n\rangle, \qquad |n(t)\rangle = \sum_{n'} e^{-iE_{n'}t/\hbar}|n'\rangle\langle n'|n\rangle$$

- “Non-trivial” part of the problem lies in establishing that the change is sudden enough.

- This is achieved by estimating the actual time taken for the Hamiltonian to change, and the periods of motion associated with the state $|n\rangle$ and with its transitions to neighbouring states.

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Harmonic perturbations: Fermi's Golden Rule

- Consider system prepared in initial state $|\mathrm{i}\rangle$ and perturbed by a periodic harmonic potential $V(t) = Ve^{-i\omega t}$ which is abruptly switched on at time $t = 0$.

  e.g. atom perturbed by an external oscillating electric field.

- What is the probability that, at some later time t, the system is in state $|\mathrm{f}\rangle$?

- To first order in perturbation theory,

$$\boxed{c_{\mathrm{f}}^{(1)}(t) = -\frac{i}{\hbar}\int_{t_0}^{t} dt'\, e^{i\omega_{\mathrm{fi}}t'} V_{\mathrm{fi}}(t')}$$

- i.e. probability of effecting transition after a time t,

$$P_{\mathrm{i}\to\mathrm{f}}(t) \simeq |c_{\mathrm{f}}^{(1)}(t)|^2 = \left| -\frac{i}{\hbar}\langle \mathrm{f}|V|\mathrm{i}\rangle e^{i(\omega_{\mathrm{fi}}-\omega)t/2} \frac{\sin((\omega_{\mathrm{fi}}-\omega)t/2)}{(\omega_{\mathrm{fi}}-\omega)/2} \right|^2$$

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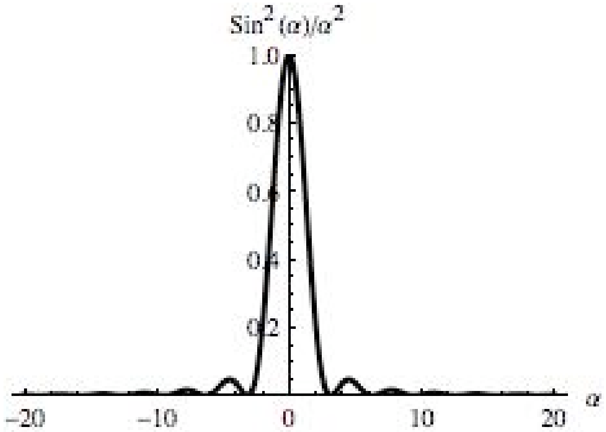

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- For large t, $\displaystyle\lim_{t\to\infty}\frac{1}{t}\left(\frac{\sin(\alpha t)}{\alpha}\right)^2 = \pi\delta(\alpha) = 2\pi\delta(2\alpha)$
- **Fermi's Golden rule:** transition rate,

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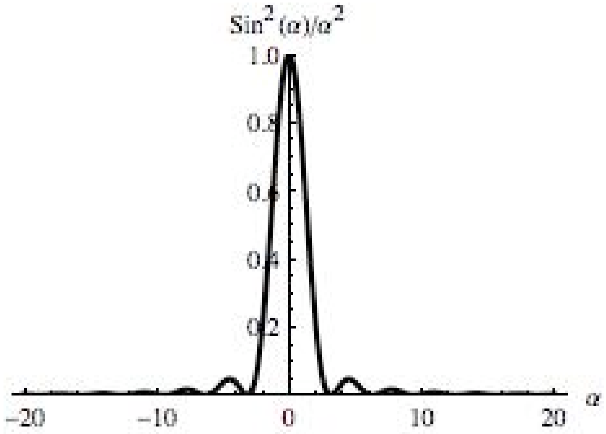
Harmonic perturbations: Fermi's Golden Rule



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$$\boxed{R_{\mathrm{i}\to\mathrm{f}}(t) = \frac{2\pi}{\hbar^2}|\langle \mathrm{f}|V|\mathrm{i}\rangle|^2\delta(\omega_{\mathrm{fi}} - \omega)}$$

- This result shows that, for a transition to occur, to satisfy energy conservation we must have:

  (a) final states exist over a continuous energy range to match $\Delta E = \hbar\omega$ for fixed perturbation frequency ω, or

  (b) perturbation must cover sufficiently wide spectrum of frequency so that a discrete transition with $\Delta E = \hbar\omega$ is possible.

- For any two discrete pair of states $|\mathrm{i}\rangle$ and $|\mathrm{f}\rangle$, since $|V_{\mathrm{fi}}|^2 = |V_{\mathrm{if}}|^2$, we have $P_{\mathrm{i}\to\mathrm{f}} = P_{\mathrm{f}\to\mathrm{i}}$

  statement of **detailed balance**.

Harmonic perturbations: second order transitions

- Although first order perturbation theory often sufficient, sometimes $\langle \mathrm{f}|V|\mathrm{i}\rangle = 0$ by symmetry (e.g. parity, selection rules, etc.). In such cases, transition may be accomplished by indirect route through other non-zero matrix elements.
- At second order of perturbation theory,

$$c_{\mathrm{f}}^{(2)}(t) = -\frac{1}{\hbar^2}\sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{i\omega_{\mathrm{f}m}t' + i\omega_{m\mathrm{i}}t''} V_{\mathrm{f}m}(t') V_{m\mathrm{i}}(t'')$$

- If harmonic potential perturbation is gradually switched on, $V(t) = e^{\varepsilon t}\, V e^{-i\omega t}$, $\varepsilon \to 0$, with the initial time $t_0 \to -\infty$,

$$c_{\mathrm{f}}^{(2)}(t) = -\frac{1}{\hbar^2}\sum_m \langle \mathrm{f}|V|m\rangle\langle m|V|\mathrm{i}\rangle$$

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Harmonic perturbations: second-order transitions

- From time integral,

$$c_n^{(2)} = -\frac{1}{\hbar^2} e^{i(\omega_{\mathrm{fi}}-2\omega)t} \frac{e^{2\varepsilon t}}{\omega_{\mathrm{fi}} - 2\omega - 2i\varepsilon} \sum_m \frac{\langle \mathrm{f}|V|m\rangle\langle m|V|\mathrm{i}\rangle}{\omega_{m\mathrm{i}} - \omega - i\varepsilon}$$

- Leads to transition rate ($\varepsilon \to 0$):

$$\boxed{\frac{d}{dt}|c_n^{(2)}(t)|^2 = \frac{2\pi}{\hbar^4} \left| \sum_m \frac{\langle \mathrm{f}|V|m\rangle\langle m|V|\mathrm{i}\rangle}{\omega_{m\mathrm{i}} - \omega - i\varepsilon} \right|^2 \delta(\omega_{\mathrm{fi}} - 2\omega)}$$

- This translates to a transition in which system gains energy $2\hbar\omega$ from harmonic perturbation, i.e. two "photons" are absorbed – Physically, first photon takes effects virtual transition to short-lived intermediate state with energy ω_m.

- If an atom in an arbitrary state is exposed to monochromatic light, other second order processes in which two photons are emitted, or one is absorbed and one emitted are also possible.

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Time-dependent perturbation theory: summary

- For a general time-dependent Hamiltonian, $\hat{H} = \hat{H}_0 + V(t)$, in which all time-dependence containing in potential $V(t)$, the wavefunction can be expressed in the interaction representation,

$$\boxed{|\psi(t)\rangle_{\mathrm{I}} = e^{i\hat{H}_0 t/\hbar}|\psi(t)\rangle_{\mathrm{S}}, \qquad |\psi(0)\rangle_{\mathrm{I}} = |\psi(0)\rangle_{\mathrm{S}}}$$

- In this representation, the time-dependent Schrödinger equation takes the form,

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$$\boxed{R_{\mathrm{i}\to\mathrm{f}}(t) = \lim_{t\to\infty}\frac{P_{\mathrm{i}\to\mathrm{f}}(t)}{t} = \frac{2\pi}{\hbar^2}|\langle \mathrm{f}|V|\mathrm{i}\rangle|^2\delta(\omega_{\mathrm{fi}} - \omega)}$$

Fermi's Golden rule.

- If this term vanishes by symmetry, transitions can be effected by second and higher order processes through intermediate states.
- In the next lecture, we will apply these ideas to the consideration of radiative transitions in atoms.

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