Supplementary information III

Time-Dependent Perturbation Theory

Time-Dependent Perturbation Theory

- We have seen that problems with no exact solution can often be approximately solved by separating the Hamiltonian into

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

  and approximating the full energies and wave functions using the matrix elements of $\hat{H}'$ in the basis of $\hat{H}_0$ eigenstates, assuming $\hat{H}'$ is independent of time.
- What if $\hat{H}'$ is time-dependent? For example, $\hat{H}' \sim \cos(\omega t)$, etc.?
  - We can construct a *time-dependent* perturbation theory to describe this situation.
  - Suppose that the time-independent portion $\hat{H}_0$ has known eigenstates $|\phi_n^{(0)}\rangle$ and energies $E_n^{(0)}$.
  - Suppose further that the time-dependent perturbation $\hat{H}'(t)$ is turned on at time $t = 0$.

Time-Dependent Coefficients of the State

- At time $t = 0$ the state of the system is

$$|\psi(0)\rangle = \sum_n |\phi_n^{(0)}\rangle \langle\phi_n^{(0)}|\psi(0)\rangle = \sum_n c_n(t=0)\, |\phi_n^{(0)}\rangle$$

- At some later time t, the **exact** state of the system is

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n^{(0)}t/\hbar}\, |\phi_n^{(0)}\rangle$$

- $c_n(t)$ contains all time dependence due to the perturbation. If $\hat{H}' = 0$, $c_n(t) = c_n(t=0)$ is time independent.
- The probability that the system will be in state n at time t is given by $P_n(t) = |c_n(t)|^2$.

Time-Dependent Coefficients of the State cont'ed

- The exact state $|\psi\rangle$ is a solution of

$$\hat{H}\,|\psi(t)\rangle = (\hat{H}_0 + \lambda \hat{H}')\,|\psi(t)\rangle = i\hbar \frac{d}{dt}\,|\psi(t)\rangle$$

- Substituting we obtain

$$\sum_n c_n(t) e^{-iE_n^{(0)} t/\hbar} E_n^{(0)}\,|\phi_n^{(0)}\rangle + \lambda \sum_n c_n(t) e^{-iE_n^{(0)} t/\hbar} \hat{H}'\,|\phi_n^{(0)}\rangle =$$
$$i\hbar \sum_n \dot{c}_n(t) e^{-iE_n^{(0)} t/\hbar}\,|\phi_n^{(0)}\rangle + \sum_n c_n(t) E_n^{(0)} e^{-iE_n^{(0)} t/\hbar}\,|\phi_n^{(0)}\rangle$$

where $\dot{c}_n(t) = \frac{d}{dt} c_n(t)$.

Time-Dependent Coefficients of the State cont'ed

- Taking the inner product with $\langle \phi_f^{(0)}|$, we find

$$\lambda \sum_n c_n(t) e^{-iE_n^{(0)} t/\hbar} \langle \phi_f^{(0)} | \hat{H}' | \phi_n^{(0)} \rangle = i\hbar \dot{c}_f(t) e^{-iE_f^{(0)} t/\hbar}$$

- This implies

$$i\hbar \dot{c}_f(t) = \lambda \sum_n c_n(t) e^{-i(E_n^{(0)} - E_f^{(0)})t/\hbar} H'_{fn}$$

where $H'_{fn} = \langle \phi_f^{(0)} | \hat{H}'(t) | \phi_n^{(0)} \rangle$.

Expanding in Powers of λ

As before, let's expand $c_f(t) = c_f^{(0)} + \lambda c_f^{(1)} + \lambda^2 c_f^{(2)} + \ldots$ in powers of the perturbation.
We substitute into above and equate equal powers of λ to obtain the coupled equations

$$\begin{aligned} i\hbar \dot{c}_f^{(0)} &= 0 \\ i\hbar \dot{c}_f^{(1)} &= \sum_n e^{-i\omega_{nf}t} H'_{fn} c_n^{(0)} \\ i\hbar \dot{c}_f^{(2)} &= \sum_n e^{-i\omega_{nf}t} H'_{fn} c_n^{(1)} \\ &\vdots \end{aligned}$$

where $\omega_{nf} = (E_n^{(0)} - E_f^{(0)})/\hbar$.

First Order in λ

- We are mostly interested in the case where the system starts off at $t = 0$ in a definite eigenstate $|\phi_i^{(0)}\rangle$ of $\hat{H}_0$, i.e., $c_f(t = 0) = \delta_{fi}$.
- For the first order term, we can integrate $i\hbar\dot{c}_f^{(1)} = e^{-i\omega_{if}t} H'_{fi}$:

$$c_f^{(1)}(t) = c_f^{(1)}(t = 0) - \frac{i}{\hbar} \int_0^t e^{-i\omega_{if}t'} H'_{fi}(t')dt'$$

- Then, up to first order in the interaction λ (which we now set equal to 1),

$$c_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_0^t e^{-i\omega_{if}t'} H'_{fi}(t')dt'$$

Probability of Transitions

- If $\hat{H}'$ can be factorized into time-independent and -dependent parts $\hat{H}' = \hat{V}(\vec{r})\mathcal{F}(t)$ (which is usually the case), then for $f \neq i$

$$c_f(t) = -\frac{i}{\hbar} V_{fi} \int_0^t e^{-i\omega_{if}t'} \mathcal{F}(t')dt'$$

- The probability of starting in state i and being observed in state f to first order is

$$P_{if} = |c_f|^2 = \frac{|V_{fi}|^2}{\hbar^2} \left| \int_0^t e^{-i\omega_{if}t'} \mathcal{F}(t')dt' \right|^2$$

  - Conventionally we write $V_{fi} = \langle \phi_f^{(0)} | \hat{V} | \phi_i^{(0)} \rangle$ as $\langle$final state$|$interaction$|$initial state$\rangle$

Harmonic Perturbations

Consider the case

$$\hat{H}'(\vec{r},t) = \begin{cases} 0 & \text{for } t < 0 \\ 2\hat{V}(\vec{r})\cos(\omega t) & \text{for } t \geq 0 \end{cases}$$

Then, to first order,

$$\begin{aligned} c_f(t) &= \delta_{fi} - \frac{i}{\hbar} V_{fi} \int_0^t e^{-i\omega_{if}t'}(e^{i\omega t'} + e^{-i\omega t'})dt' \\ &= \delta_{fi} - \frac{1}{\hbar} V_{fi} \left[\frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} + \frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega} \right] \end{aligned}$$

where $\omega_{fi} = (E_f^{(0)} - E_i^{(0)})/\hbar$.

Harmonic Perturbations cont'ed

If $f \neq i$ we can rewrite this as

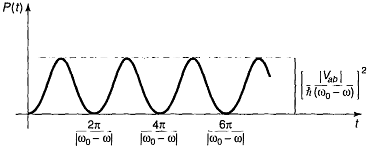
$$c_f(t) = -\frac{2i}{\hbar} V_{fi} \left[\frac{e^{i(\omega_{fi}-\omega)t/2}}{\omega_{fi}-\omega} \sin\left[(\omega_{fi}-\omega)t/2\right] \right.$$
$$\left. + \frac{e^{i(\omega_{fi}+\omega)t/2}}{\omega_{fi}+\omega} \sin\left[(\omega_{fi}+\omega)t/2\right] \right]$$

There are two important scenarios where the driving frequency comes into resonance with the energy difference:

- $\omega \approx \omega_{fi}$. Then the first term in brackets dominates, $E_f^{(0)} > E_i^{(0)}$, and the system is excited by the perturbation to a higher energy state. This corresponds to **absorption**.
- $\omega \approx -\omega_{fi}$. Then the second term in brackets dominates, $E_i^{(0)} > E_f^{(0)}$, and the system loses energy to the perturbing field. This corresponds to **stimulated emission**.

Absorption of the Perturbing Field

Let's consider the absorption case first where $E_f^{(0)} > E_i^{(0)}$, ω is positive, and the first term dominates in the expression for $c_f(t)$.
Then the probability of a "transition" from state i to f is



$$P_{if} = |c_f(t)|^2 = \frac{4|V_{fi}|^2}{\hbar^2(\omega_{fi}-\omega)^2}\sin^2\left[\frac{(\omega_{fi}-\omega)t}{2}\right]$$

Transitions via Absorption and Stimulated Emission

- A very similar argument for stimulated emission may be made, so the probability of transitions from state i to state f in general is

$$P_{if} = \frac{4|V_{fi}|^2}{\hbar^2(\omega_{fi} \mp \omega)^2} \sin^2 \left[\frac{(\omega_{fi} \mp \omega)t}{2} \right]$$

  where the minus signs correspond to absorption and the plus signs to stimulated emission.
- Note that the probability of absorption/emission is “reversible” in the sense that the behavior is symmetric in time.
- If two *discrete* states $|i\rangle$ and $|f\rangle$ are resonantly coupled by a harmonic, then the system oscillates between these states in time.

Time-Energy "Uncertainty Relation"

- Note that at finite times

$$P_{if} = \frac{4|V_{fi}|^2}{\hbar^2(\omega_{fi} \mp \omega)^2} \sin^2\left[\frac{(\omega_{fi} \mp \omega)t}{2}\right]$$

- Within the time interval Δt, states within the energy range $\hbar|\omega_{fi} \mp \omega| \sim \dfrac{2\pi\hbar}{\Delta t}$ are likely to be excited by the perturbation.
- Therefore after a given time Δt the spread in the energies likely to be observed is approximately $\Delta t \Delta E \sim \hbar$.
- This is akin to an energy-time "uncertainty relation." An analysis studying the temporal evolution of expectation values can yield $\Delta E \Delta t \geq \hbar/2$.

Transitions within a Continuous Spectrum

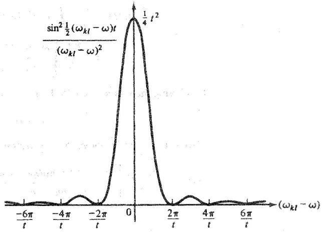
- What if instead of having discrete states $|f\rangle$, there is a continuum of final states $|f\rangle$ available, such that the excited states are labeled by index f and lie within a continuous *band* of energies E_f?
- In such a case, rather than the probability that the system will transition to a particular discrete eigenstate $|f\rangle$, it is more meaningful to consider the probability that we find the system within a group of final states $\{|f\rangle\}$ whose energies fall within a range 2Δ around E_f.
- The probability is

$$P_{if} = \int_{f\in\{E_f\pm\Delta\}} |\langle f|\psi(t)\rangle|^2 df$$

$$= \int_{f\in\{E_f\pm\Delta\}} \frac{4|V_{fi}|^2}{\hbar^2(\omega_{fi}\mp\omega)^2}\sin^2\left[\frac{(\omega_{fi}\mp\omega)t}{2}\right] df$$

The Long Time Limit

- Consider the behavior of the time dependence as $t \to \infty$ (the long time limit). In practice this corresponds to $t \gg \dfrac{1}{\omega_{fi} \mp \omega}$.



- It can be shown that

$$\delta(\omega) = \frac{2}{\pi} \lim_{t\to\infty} \frac{\sin^2(\omega t/2)}{\omega^2 t}$$

For large times this allows us to write

$$\lim_{t\to\infty} P_{if} = \lim_{t\to\infty} \int_{f\in\{E_f \pm \Delta\}} \frac{4|V_{fi}|^2}{\hbar^2(\omega_{fi} \mp \omega)^2} \sin^2\left[\frac{(\omega_{fi} \mp \omega)t}{2}\right] df$$

$$= \frac{2\pi t}{\hbar^2} \int |V_{fi}|^2 \delta(\omega_f - \omega_i \mp \omega) df$$

Continuous Transition Rates: The Fermi Golden Rule

- Often we are interested in the rate of transitions R_{if} rather than the total probability. This allows us to write

$$R_{if} = \frac{dP_{if}}{dt}$$
$$= \frac{2\pi}{\hbar} \int |V_{fi}|^2 \delta(E_f - E_i \mp \hbar\omega) df$$

where we change the argument of the delta function from frequency to energy by using $\frac{1}{\hbar}\delta(x) = \delta(\hbar x)$.

- This equation is a version of the Fermi golden rule.
- Note that the delta function enforces conservation of energy during absorption/emission processes

$$E_{fi} = E_f^{(0)} - E_i^{(0)} = \pm\hbar\omega$$
$$E_{final} = E_{initial} \pm \hbar\omega$$

Fermi Golden Rule & Density of States

- We use the Fermi golden rule to determine the rate at which a system initially in an energy eigenstate $|i\rangle$ will jump into a continuous range of eigenstates via absorption or emission of an external harmonic field.
- Note that in the Fermi golden rule we are integrating over a range of final states $|f\rangle$ such that $E_f = E_i \pm \hbar\omega$. In general, if there are many states $|f\rangle$ with the same energy, V_{fi} may be a function of f and the integration over f must be performed explicitly.
- However, in many cases the matrix elements V_{fi} may be roughly constant as a function of f. In this case we are primarily interested in how many states have energy $E(f)$. We can define a function called the density of states (DOS) $g(E_f)$ such that $df = g(E_f)dE_f$ is the number of eigenstates in the interval $[E_f, E_f + dE_f]$.

DOS and Fermi Golden Rule Redux

- If the matrix element V_{fi} is indeed roughly constant, we find

$$
\begin{aligned}
R_{if} &\simeq \frac{2\pi|V_{fi}|^2}{\hbar}\int \delta(E_f - E_i \mp \hbar\omega)df \\
&= \frac{2\pi|V_{fi}|^2}{\hbar}\int \delta(E_f - E_i \mp \hbar\omega)g(E_f)dE_f \\
&= \frac{2\pi|V_{fi}|^2}{\hbar}g(E_i \pm \hbar\omega)
\end{aligned}
$$

- This form of the Fermi golden rule is frequently used in atomic physics and as a phenomenological tool for estimating transition rates. Note the rate of transitions is intuitively proportional to the strength of the perturbation $|V_{fi}|^2$ and the density of states for energies at which transitions can be made.

Comments on Time-Dependent Problems

- If we consider a purely monochromatic field ($\sim \cos(\omega t)$) applied to a system with discrete eigenstates, the transition probability P_{if} is time-reversible and typically oscillates in time.
- If we involve a continuous spectrum of states to which transitions are possible, to first order and in the long time limit, we should consider the transition rate R_{if} which is given by the Fermi golden rule.
- This rules imposes a form of energy conservation and can explain linear absorption and (stimulated) emission processes.
- Though not proven here, it can be shown that if transitions to a continuous spectrum of states are allowed, the probability that the system remains in its initial state after a time t is given by $P_i = \exp(-R_{if}t)$.

Comments on Fermi Golden Rule cont'ed

- This implies that Fermi golden rule-type transitions into a continuum are <u>not</u> time reversible, i.e., the probability that the system remains in the initial state will decrease continually with time and will not recover via oscillations in time.
- There is a qualitative difference between truly discrete monochromatic systems (time reversible with "recoverability" of the initial state) and systems where transitions to a continuum are possible (which lead to irreversible decay of the initial state).
- The Fermi golden rule is a very useful tool in physics and engineering to understand all kinds of linear effects.
  - Nonlinear processes (such as two-photon absorption, etc.) requires higher order perturbation terms (λ^2, etc).
  - The perturbative field $\hat{H}'$ we couple to is implicitly *semiclassical*. We need to consider a *quantum* field for spontaneous emission.
  - The dynamics of the system when the field is first "turned on" may be quite complex and require separate study.