Chapter 18 – Time-dependent perturbation theory

$$\hat{H}(t) = \hat{H}^0 + \hat{H}'(t)$$ Stationary system gets perturbed by a time-dependent perturbation

Solve $i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$ perturbatively.

Typical question: If system is initially in energy eigenstate $|i^0\rangle$ of $\hat{H}^0$, what is the probability of finding it in some (other) eigenstate $|f^0\rangle$ at a later time?

Without $\hat{H}'(t)$, this probability would be

$$P_{i\to f}(t) = |\langle f^0| e^{-iH^0 t/\hbar}|i^0\rangle|^2 = |e^{-iE_i^0 t/\hbar}\langle f^0|i^0\rangle|^2 = \delta_{if}$$

i.e. the system stays in the initial eigenstate forever.

Under the influence of $\hat{H}'(t)$, this changes to

$$P_{i\to f}(t) = \left|\langle f^0| e^{-\frac{i}{\hbar}\int_{t_0}^{t}\hat{H}(t')dt'}|i^0\rangle\right|^2$$

This is in general hard to work out (see later for a systematic approach); so we will first try 1st-order perturbation theory.

In the absence of $\hat{H}'(t)$, the states evolve as

$$|\psi(t)\rangle = \sum_n c_n(0)\, e^{-i/\hbar\, E_n^0 t}|n^0\rangle \qquad \text{if } |\psi(0)\rangle = \sum_n c_n(0)|n^0\rangle$$

If we turn on $\hat{H}'(t)$, this will change to

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-\frac{i}{\hbar}E_n^\circ t} |n^\circ\rangle$$

The Schrödinger equation reads

$$0 = \left(i\hbar\frac{d}{dt} - \hat{H}^\circ - \hat{H}'(t)\right)|\psi(t)\rangle = \sum_n \left(i\hbar\dot{c}_n(t) + (\cancel{E_n^\circ} - \cancel{E_n^\circ} - \hat{H}'(t))c_n(t)\right)e^{-\frac{i}{\hbar}E_n^\circ t}|n^\circ\rangle$$

$$= \sum_n \left(i\hbar\dot{c}_n - \hat{H}'(t)c_n\right)e^{-\frac{i}{\hbar}E_n^\circ t}|n^\circ\rangle$$

Project with $\langle f^\circ| e^{i/\hbar E_f^\circ t}$:

$$\Rightarrow \boxed{\begin{array}{l} i\hbar\dot{c}_f(t) = \sum_n \langle f^\circ|\hat{H}'(t)|n^\circ\rangle e^{i\omega_{fn}t} c_n(t) \\ \quad \text{with} \quad \omega_{fn} = (E_f^\circ - E_n^\circ)/\hbar \end{array}} \quad (*)$$

If initially the particle is in eigenstate $|i^\circ\rangle$,

$$c_n(0) = \delta_{ni}$$

then to <u>zeroth order</u> in $\hat{H}'$, $\dot{c}_f = 0 \Rightarrow c_f(t) = \delta_{fi}$

<u>To first order</u> in $\hat{H}'$, we use the zeroth order result $c_n(t) = c_n(0) = \delta_{ni}$ on the right hand side:

$$i\hbar\dot{c}_f(t) = \sum_n \langle f^\circ|\hat{H}'(t)|n^\circ\rangle e^{i\omega_{fn}t} \underbrace{c_n(0)}_{\delta_{ni}}$$

$$\Rightarrow \boxed{\dot{c}_f(t) = -\frac{i}{\hbar}\langle f^\circ|\hat{H}'(t)|i^\circ\rangle e^{i\omega_{fi}t}} \quad 1^{st}\text{-order pert. thy.}$$

$$\Rightarrow \boxed{c_f(t) = \delta_{fi} - \frac{i}{\hbar}\int_0^t \langle f^\circ|\hat{H}'(t')|i^\circ\rangle e^{i\omega_{fi}t'}dt'} \quad (**)$$

We can generate higher order approximations by iteration, i.e. feeding this $c_f^{(1)}(t)$ back into the r.h.s. of (*) and solving again. But there is a more compact scheme for achieving the same thing, so let's wait until we learn that instead.

Applications

(1) Consider 1-d oscillator with

$$\hat{H}'(t) = -e\mathcal{E}\hat{X}e^{-t^2/\tau^2}$$

and assume that at $t=-\infty$ the particle is in the ground state $|0\rangle$. We can then use (**) (with initial time $t_i=0$ replaced by $t_i=-\infty$) to get for $n\neq 0$

$$c_n(\infty) = -\frac{i}{\hbar}\int_{-\infty}^{\infty}\langle n|-e\mathcal{E}\hat{X}|0\rangle e^{i(n\omega)t}e^{-t^2/\tau^2}dt$$

Using $\hat{X} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^+)$ we see that we get a non-zero result only for $n=1$ $(\hat{a}^+|0\rangle = |1\rangle,\ \hat{a}|0\rangle = 0)$:

$$c_n(\infty) = \delta_{n1}\, c_1(\infty)$$

$$c_1(\infty) = \frac{ie\mathcal{E}}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_{-\infty}^{\infty}dt\, e^{i\omega t}e^{-t^2/\tau^2}$$

$$= \frac{ie\mathcal{E}}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\sqrt{\pi\tau^2}\, e^{-\omega^2\tau^2/4}$$

and thus

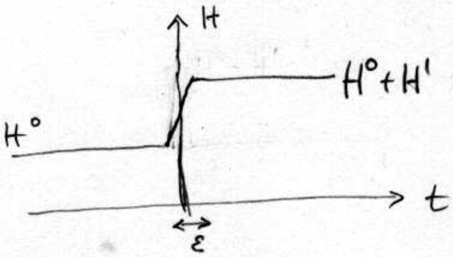
$$\boxed{P_{0\to 1} = |c_1(\infty)|^2 = \frac{e^2\mathcal{E}^2\pi\tau^2}{2m\hbar\omega}e^{-\omega^2\tau^2/2}}$$

So at first order in $\hat{H}'$ we get only excitation of the first excited state, with probability $\sim \mathcal{E}^2$ which decreases to zero as $\tau \to 0$ (pulse) or $\tau \to \infty$ (adiabatic perturbation).

Qualitatively similar result for $\hat{H}' \sim \dfrac{1}{1+(t/\tau)^2}$ (Exercise 18.2.1, p.476)

(2) Sudden perturbation

What happens when the Hamiltonian changes abruptly over a small time interval ε? Schematically,



As long as $\hat{H}'$ is finite, we can simply integrate the time dependent Schrödinger equation:

$$|\psi(\tfrac{\varepsilon}{2})\rangle - |\psi(-\tfrac{\varepsilon}{2})\rangle = |\psi_{after}\rangle - |\psi_{before}\rangle = -\frac{i}{\hbar}\int_{-\varepsilon/2}^{\varepsilon/2} \hat{H}(t)\,|\psi(t)\rangle\, dt$$

In the limit $\varepsilon \to 0$ we get

$$|\psi_{after}\rangle = |\psi_{before}\rangle$$

This agrees with the first-order result obtained above in the limit $\tau \to 0$.

Example Consider 1s electron bound by nucleus of charge Z that undergoes β-decay by emitting a relativistic ($E \gtrsim m_e c^2$) electron,

$$ {}_{Z}A^{N} \rightarrow {}_{Z+1}A^{N-1} + e^- + \bar{\nu}_e $$

The time for the emitted electron to get out of the $n=1$ shell is

$$ c\tau \simeq \frac{a_0}{Z} $$

whereas the characteristic time for the 1s electron is

$$ T \simeq \frac{\text{size of } n=1 \text{ shell}}{\text{velocity of 1s electron}} \simeq \frac{a_0}{Z} \Big/ (Z\alpha)c = \frac{a_0}{Z^2 \alpha c} $$

such that

$$ \frac{\tau}{T} = Z\alpha $$

For small Z we can thus use the sudden approximation and conclude that the 1s electron is in exactly the same state before and after the β-decay.

Of course, this state is an eigenstate of $\vec{H}^0$, the Coulomb Hamiltonian with charge Z, and not an eigenstate of the charge $Z+1$ ion. However, we can compute the probability for finding the electron in any eigenstate of the new ion by simply computing the overlap between the $(Z, n=1)$ and the $(Z+1, n)$ eigenstates:

$$P_{nlm}(Z+1) = |\langle nlm; Z+1 | 100; Z\rangle|^2 = \delta_{l0}\,\delta_{m0}\,|\langle n00; Z+1 | 100; Z\rangle|^2$$

since $\int d\Omega\, Y^*_{lm} Y_{00} = \delta_{l0}\delta_{m0}$

For example (exercise 18.2.4, p.478), in the radioactive decay of tritium,

$${}_1H^3 \longrightarrow {}_2He^3 + e^- + \bar{\nu} \quad , \quad T_{e^-} = 16\,\text{keV}$$

the emitted electron has velocity $\frac{v}{c} = \sqrt{\frac{2T_e}{m_e c^2}} = 0.25$ and

thus $\frac{\tau}{T} \simeq \frac{a_0/0.25c}{a_0/(\alpha c)} = 4\alpha = 0.03 \ll 1$; we can use the sudden approximation, with error of at most a few %.

The probability that the emerging $(He^3)^+$ ion is in its ground state is

$$P_{100}(He^3) = |\langle 100, He | 100, H\rangle|^2$$

(the states depend only on Z, not on the nuclear mass which is $\approx \infty$ in both cases)

$$= \left[\int d\Omega \int_0^\infty \sqrt{\frac{1}{\pi a_0^3}}\, e^{-r/a_0} \sqrt{\frac{2^3}{\pi a_0^3}}\, e^{-2r/a_0}\, r^2 dr\right]^2$$

$$= \left(\frac{4\pi\sqrt{8}}{\pi a_0^3}\right)^2 \left(\int_0^\infty r^2 dr\, e^{-3r/a_0}\right)^2 = 2^7 \left(\int_0^\infty \xi^2 d\xi\, e^{-3\xi}\right)^2$$

$$= 2^7 \cdot \left(\frac{2!}{3^3}\right)^2 = \frac{2^9}{3^6} = 70\%.$$

Only s-states of the $(He^3)^+$ ion have non-zero probability (due to the angular distribution of $|\psi_{after}\rangle$ being $\sim Y_{00}$).

(3) Adiabatic perturbation

In the other extreme we can study what happens if $\hat{H}(t)$ changes very slowly from $\hat{H}(0)$ to $\hat{H}(\tau)$ at time τ.

If the system is initially in an eigenstate $|n(0)\rangle$ of $\hat{H}(0)$, where will it be at time τ?

Adiabatic Theorem: If $\hat{H}(t)$ changes "slowly enough," then $|\psi(\tau)\rangle = |n(\tau)\rangle$ = corresponding eigenstate of $\hat{H}(\tau)$

We will skip over the precise definition of "slowly enough" and the proof of the theorem, and rather use an example to illustrate it:

Consider a particle in a box of length $L(0)$ initially which expands slowly to length $L(\tau)$. Let us introduce as the characteristic time T for the particle

$$T \sim \frac{1}{\omega_{min}} \qquad \text{where} \quad \hbar\omega_{min} = \min\left[E_f^0 - E_i^0\right],$$

i.e. the smallest transition frequency between box eigenstates. Here $E_n^0 = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\cdot n^2$, so $E_f^0 - E_i^0 = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(n_f^2 - n_i^2)$,

so parametrically

$$T \sim \frac{mL^2}{\hbar} \qquad \text{(we ignore factors of order 1)}$$

For the adiabatic theorem to hold, we need $\tau \gg T$ or $\boxed{\omega_{min}\tau \gg 1}$

Example: harmonic oscillator subject to perturbation

$$\hat{H}'(t) = -e\mathcal{E}\hat{X}\,e^{-t^2/\tau^2}$$

We saw before that $P_{0\to 1}(\infty) \sim \tau^2 e^{-\omega^2\tau^2/2}$

Here ω is the transition frequency between harmonic oscillator eigenstates (it's the same between all neighboring states). We see that $P_{0\to 1}$ vanishes exponentially

for $\quad \omega\tau \gg 1 \quad$ or $\quad \tau \gg \frac{1}{\omega} = \frac{1}{\omega_{min}}$ ✓

(4) Recovering time-independent perturbation theory from time-dependent perturbation theory

Consider $\quad \hat{H}(t) = \hat{H}^0 + e^{t/\tau}\hat{H}' \quad , \quad -\infty < t \leq 0$

(increases from $\hat{H}^0$ at $t=-\infty$ to $\hat{H}^0 + \hat{H}' = \hat{H}$ "now", i.e. at $t=0$). For $\tau \to \infty$, the rise of the exponential is slow, and the adiabatic theorem holds: an eigenstate $|n^0\rangle$ at $t=-\infty$ evolves into the corresponding state $|n\rangle$ of $\hat{H} = \hat{H}^0 + \hat{H}'$ at $t=0$. So if we work out this state $|n\rangle$ in time-dependent perturbation theory at a given order in $\hat{H}'$, the adiabatic theorem tells us that for $\tau \to \infty$ this should agree with the time-independent perturbative formula for the state $|n\rangle$ at the same order in $\hat{H}'$. Let's check this:

1st-order time-dependent perturbation theory gives

$$\langle m^0 | n' \rangle = C^{(1)}_{mn}(0) = -\frac{i}{\hbar}\int_{-\infty}^{0} dt\, \langle m^0|\hat{H}'|n^0\rangle e^{t/\tau} e^{i\omega_{mn}t}$$

$$= -\frac{i}{\hbar}\,\frac{\langle m^0|\hat{H}'|n^0\rangle}{1/\tau + i\omega_{mn}} \xrightarrow[\tau\to\infty]{} \frac{\langle m^0|\hat{H}'|n^0\rangle}{E_n^0 - E_m^0} \quad \checkmark$$

This is the familiar result from 1st-order time-independent perturbation theory.

(5) Time-dependent perturbation theory for time-independent perturbations – continuum transitions

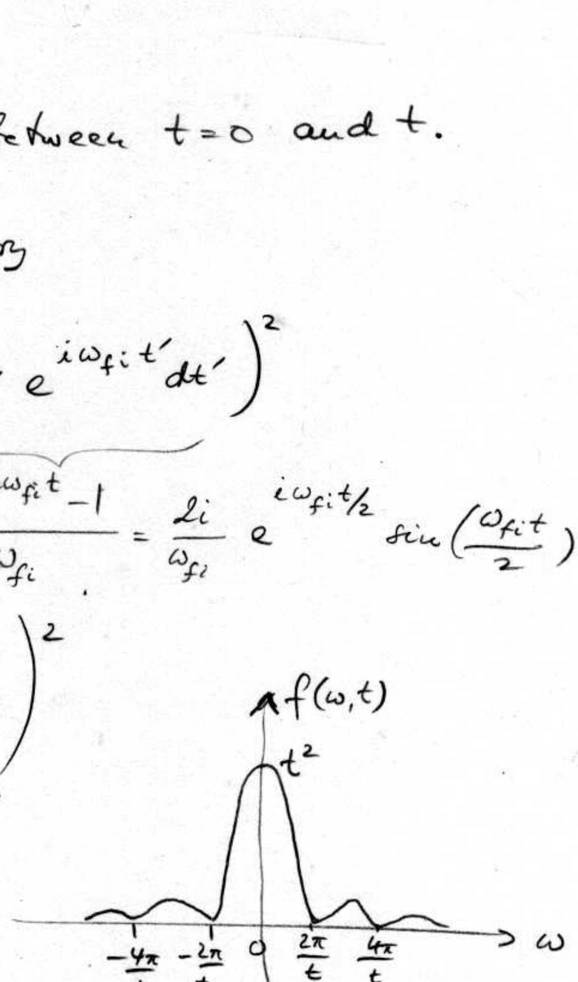
$$\hat{H} = \hat{H}^0 + \hat{H}'$$

Compute evolution of $|\psi(t)\rangle$ between $t=0$ and t.

In first order perturbation theory

$$P^{(1)}_{i\to f}(t) = \frac{|\langle f^0|\hat{H}'|i^0\rangle|^2}{\hbar^2}\Bigg(\underbrace{\int_0^t dt'\, e^{i\omega_{fi}t'} dt'}_{\frac{e^{i\omega_{fi}t}-1}{\omega_{fi}} = \frac{2i}{\omega_{fi}} e^{i\omega_{fi}t/2}\sin\left(\frac{\omega_{fi}t}{2}\right)}\Bigg)^2$$

$$= \frac{|H'_{fi}|^2}{\hbar^2}\underbrace{\left(\frac{\sin\frac{\omega_{fi}t}{2}}{\frac{\omega_{fi}t}{2}}\cdot t\right)^2}_{f(\omega,t)}$$



As $t\to\infty$, $f(\omega,t) \longrightarrow \sim\delta(\omega)$,
i.e. the system remains in state i.

Assume that the state $|i\rangle$ is embedded in a (quasi-) continuum of neighboring states,

E_i°

with density of states $\rho(E_f^\circ) = \frac{dN}{dE}(E_f^\circ)$ (= number of states per energy interval dE_f around E_f°).

Then the transition probability for transitions into any of the states in interval ΔE_f is

$$\Delta P^{(1)}_{i\to\Delta E_f}(t) = \int_{\Delta E_f} dE_f^\circ \, P^{(t)}_{i\to f} \, \rho(E_f^\circ).$$

Since for sufficiently large t $P_{i\to f}(t)$ is highly peaked around $\omega_{fi}=0$, we can for

$$\Delta E_f > \frac{2\pi\hbar}{t}$$

replace the integration limits by $E_f^\circ = \pm\infty$:

$$\Delta P^{(1)}_{i\to\Delta E_f}(t) \xrightarrow[t>\frac{2\pi\hbar}{\Delta E_f}]{} \int_{-\infty}^{\infty} dE_f^\circ \, \frac{|H'_{fi}|^2}{\hbar^2} \left(\frac{\sin\frac{\omega_{fi}t}{2}}{\frac{\omega_{fi}t}{2}}\right)^2 t^2 \rho(E_f^\circ)$$

$$\underset{\substack{\text{(saddle}\\\text{point}\\\text{integration)}}}{\approx} \frac{|H'_{fi}|^2}{\hbar^2}\rho(E_f^\circ) \int_{-\infty}^{\infty} d(\hbar\omega_{fi}t) \left(\frac{\sin\frac{\omega_{fi}t}{2}}{\frac{\omega_{fi}t}{2}}\right)^2 t$$

$$\xi = \frac{\omega_{fi}t}{2} \qquad = \frac{|H'_{fi}|^2}{\hbar}\rho(E_f^\circ)\, t \underbrace{\int_{-\infty}^{\infty} d\xi \, \frac{\sin^2(\xi)}{\xi^2}}_{\pi} = \frac{2\pi}{\hbar}|H'_{fi}|^2 \rho(E_f^\circ)\, t$$

So we find for the transition probability into states near E_i° in first order

$$\boxed{\Delta P^{(1)}_{i\to\Delta E_f} = \frac{2\pi}{\hbar}\left|\langle f^\circ|\hat{H}'|i^\circ\rangle\right|^2 \rho(E_f^\circ)\, t \qquad (E_f^\circ \approx E_i^\circ)}$$

This means that for continuum states the expression at the bottom of p. 63 can be written as

$$\boxed{P^{(1)}_{i\to f}(t) = \frac{2\pi}{\hbar}\left|\langle f^\circ|\hat{H}'|i^\circ\rangle\right|^2 \cdot t\ \delta(E_i^\circ - E_f^\circ)}$$

The transition rate $\dfrac{dP_{i\to f}}{dt} = \dfrac{2\pi}{\hbar}\langle f^\circ|\hat{H}'|i^\circ\rangle\,\delta(E_i^\circ - E_f^\circ)$

is constant in time.

(Of course, this violates the conservation of probability at large times, for too large times 1st-order p.t. breaks down in this expression.)

The range of validity is

$$\frac{2\pi\hbar}{\Delta E_f} < t \ll \tau_i$$

where τ_i is the lifetime (or decay time) of the state $|i^\circ\rangle$

$$\left(\tau_i \sim \frac{1}{|H'_{fi}|^2}\right).$$

Example Auto-ionization of He in the (22) state

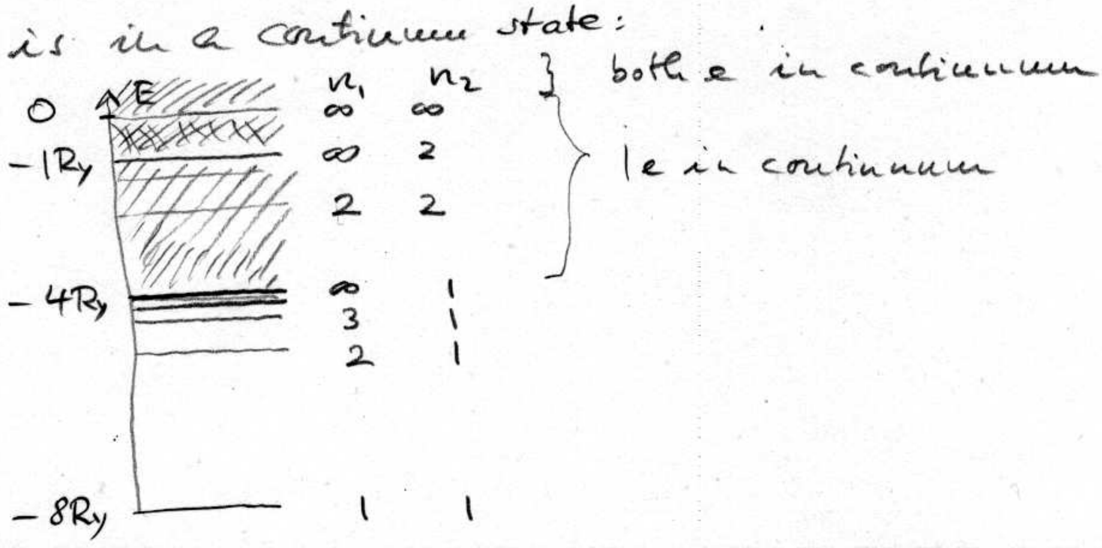
$$\hat{H} = \underbrace{\frac{\hat{\vec{p}}_1^{\,2}}{2m} + \frac{\hat{\vec{p}}_2^{\,2}}{2m} - \frac{2e^2}{\hat{r}_1} - \frac{2e^2}{\hat{r}_2}}_{\hat{H}^0} + \underbrace{\frac{e^2}{|\hat{\vec{r}}_1 - \hat{\vec{r}}_2|}}_{\hat{H}'}$$

Consider the case where initially both electrons (spin triplet) are in the hydrogenic 2s state. This corresponds to the unperturbed energy eigenvalue

$$E_i^0 = -2 \cdot \frac{m(2e)^2 e^2}{2\hbar^2 n^2} \underset{n=2}{=} -2\,R_y$$

which lies 6 Ry above the unperturbed He ground state $E_0^0 = -2 \cdot 4R_y = -8\,R_y$.

This excitation energy of +6 Ry is enough to fully ionize one of the two electrons (which requires only 4 Ry), with 2Ry of kinetic energy to spare. So the (2s, 2s) state is energetically degenerate with a continuum of 2-particle states where 1 electron is in the 1s and the other electron is in a continuum state:



So, without any coupling to the electromagnetic radiation field (i.e. without emission of photons), the (2s, 2s) state can decay into the (energetically degenerate) (1s, continuum) state — "radiationless auto-ionization" or Auger effect.

To compute the decay rate of the (2s, 2s) state due to auto-ionization, we use perturbation theory.

We need

$$\langle f^0 | \hat{H}' | i^0 \rangle = \iint d^3r_1 \, d^3r_2 \, \psi^*_{1s}(\vec{r}_2) \psi_{\vec{k}s}(\vec{r}_1) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_{2s}(\vec{r}_1) \psi_{2s}(\vec{r}_2)$$

using

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = 4\pi \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \frac{1}{2l+1} \sum_{m=-l}^{l} Y^*_{lm}(\vartheta_1, \varphi_1) Y_{lm}(\vartheta_2, \varphi_2)$$

and the fact that $\psi_{1s}, \psi_{2s} \sim Y_{00} = \text{const.}$ we see that the integration over $d\Omega_2$ selects $l = m = 0$, so the final state continuum electron must also be in an s state.

If we approximate the continuum state as a spherical wave with energy $E_k = \frac{\hbar^2 k^2}{2m} = 2E_{2s} - E_{1s}$, we get for the Auger transition rate

$$W = \frac{dP_{s\to k}}{dt} = \frac{2\pi}{\hbar} e^4 \Big| (4\pi)^2 N \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2\, e^{-Zr_2/a_0} \frac{\sin(kr_1)}{kr_1} \cdot$$

product of 4
norm. factors
of ψ's

$$\cdot \frac{1}{r_>} \cdot e^{-Zr_1/2a_0}\left(1 - \frac{Zr_1}{2a_0}\right) e^{-Zr_2/2a_0}\left(1 - \frac{Zr_2}{2a_0}\right) \Big|^2 \rho_f(E_k)$$

where

$$N^2 \rho_f(E_k) = \frac{mk}{2^7 \pi^5 \hbar^2} \left(\frac{Z}{a_0}\right)^9 \qquad \left(\rho_f \sim \frac{4\pi p^2 dp}{dE} \sim p\right)$$

The result of the integration is

$$W = C \frac{me^4}{\hbar^3}$$ where $C \sim O(10^{-3})$ and $\frac{me^4}{\hbar^3} = 4\times 10^{16}\, s^{-1}$ is the "Bohr frequency".

The constant C is independent of Z.

(6) Periodic perturbations - Fermi's Golden Rule

Consider $\hat{H}'(t) = \hat{H}' e^{-i\omega t}$

(A real perturbation would go like $\sin(\omega t)$ or $\cos(\omega t)$ which can be expressed through $e^{\pm i\omega t}$)

Let's assume this perturbation starts at $t=0$ (e.g. by turning a light switch). Then

$$c_f^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \langle f^\circ | \hat{H}' | i^\circ \rangle e^{-i\omega t'} e^{i\omega_{fi} t'} dt'$$

$$= -\frac{i}{\hbar} \langle f^\circ | \hat{H}' | i^\circ \rangle \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i(\omega_{fi} - \omega)}$$

and

$$P_{i\to f}^{(1)}(t) = |c_f^{(1)}(t)|^2 = \frac{|\langle f^\circ | \hat{H}' | i^\circ \rangle|^2}{\hbar^2} \frac{\sin^2\left(\frac{(\omega_{fi}-\omega)t}{2}\right)}{\left(\frac{\omega_{fi}-\omega}{2} t\right)^2} t^2$$

This is the same result as for the time-independent perturbation, except for the shift $\omega_{fi} \to \omega_{fi} - \omega$.

This probability is narrowly peaked as a function of ω_{fi} around $\omega_{fi} = \omega$, with contributions only for

$$\left| \frac{(\omega_{fi} - \omega)t}{2} \right| \lesssim \pi$$

$$\Rightarrow \quad E_f^\circ - E_i^\circ = \hbar\omega \Big(1 \underbrace{\pm \frac{2\pi}{\omega t}}_{\Delta E_f/2}\Big)$$

This leads (in the same way as before) to

$$\boxed{w_{i\to f} = \frac{dP_{i\to f}}{dt} = \frac{2\pi}{\hbar} \left|\langle f^0|\hat{H}'|i^0\rangle\right|^2 \delta\left(E_f^0 - E_i^0 - \hbar\omega\right)}$$

Fermi's Golden Rule

We will apply this result to electromagnetic radiative transitions later in this chapter. As in the auto-ionization example, the δ-function gets in the end integrated over for one reason or another, and thus is not problematic.