Semi-Classical Theory of Radiative Transitions

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Atomic Structure (recap)

Time-dependent Schroedinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi$$

Stationary solution: $\psi(r,t) = \varphi e^{iEt/\hbar}$, where

$$H\varphi = E\varphi$$

is time-independent Schroedinger equation.

For hydrogen atom, neglecting spin, relativistic effects, nuclear effects, the Hamiltonian is

$$H = \frac{|\mathbf{p}|^2}{2m_e} - e\phi,$$

where the momentum $\mathbf{p} = i\hbar\nabla$ is an operator and $\phi(r) = e/r$.

Solution for hydrogen atom in terms of eigenfunctions (complete orthonormal base):

$$\varphi(r,\theta,\phi) = \frac{R(n,l)}{r} Y_{l,m}(\theta,\phi)$$

Where spherical harmonics obey the eigenvalue problem,

$$L^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m}, \quad (1)$$

$$L_z Y_{l,m} = m\hbar Y_{l,m}, \quad (2)$$

and the radial function obeys the differential equation

$$\frac{d^2 R_{n,l}}{dr^2} + \left\{ \frac{2m_e}{\hbar^2} \left[E_n - \frac{e}{r} \right] - \frac{l(l+1)}{r^2} \right\} R_{n,l} = 0.$$

where $E_n = -e^2/2n^2$, with $n = l+1, l+2, l+3, ...$.

Non-relativistic limit of EM Hamiltonian

For hydrogen atom: $m_e v^2/2 \sim e^2/2a_0$ where $a_0 = \hbar^2/m_e e^2$. Thus, velocity $v/c \sim e^2/\hbar c \equiv \alpha = 1/137$ is NR.
The NR Hamiltonian of single particle in EM fied is:

$$H = \frac{1}{2m_e} \left| \mathbf{p} + \frac{e}{c}\mathbf{A} \right|^2 - e\phi,$$

where $m_e \dot{\mathbf{x}} = \mathbf{p} + (e/c)\mathbf{A}$ is the particle momentum and $\mathbf{A}$ and ϕ are the EM vector and scalar potentials.

In Coulomb gauge ($\nabla \cdot \mathbf{A} = \phi_{EM} = 0$) can be shown that $\mathbf{A}$ represent

EM in vacuum (*i.e.*, $\Box \mathbf{A} = 0$) and ϕ represent the static potential of atom.

Thus, Hamiltonian can be separated in $H = H_{st} + H_{int}$, with $H_{int} = H_1 + H_2$ where

$$H_1 \equiv \frac{e}{2m_e c}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) = \frac{e}{m_e c}\mathbf{A} \cdot \mathbf{p},$$

(note that in Coulomb gauge $[\mathbf{A}, \mathbf{p}] = 0$), and

$$H_2 \equiv \frac{e^2}{2m_e c^2}\mathbf{A} \cdot \mathbf{A} \ \ \text{(two photon processes)}.$$

Can show that $H_2 \ll H_1 \ll H_{st}$, with

$$H_2/H_1 \sim H_1/H_{st} \sim (n_{ph} a_0^3)^{1/2} \ll 1$$

Because $\Box \mathbf{A} = 0$ we can write:

$$\mathbf{A} = \sum_{\mathbf{k},\alpha} \left[\mathbf{e}_\alpha(\hat{\mathbf{k}}) a_\alpha(\mathbf{k}) e^{i(\mathbf{k}\cdot\mathbf{x} - \omega t)} + c.c. \right]$$

From Parsival theorem we have

$$H_{rad} = \frac{1}{8\pi} \int_V dx^3 \ (|\mathbf{E}|^2 + |\mathbf{B}|^2) = \frac{2V}{8\pi} \sum_{\mathbf{k},\alpha} (|\mathbf{E}_\alpha(\mathbf{k})|^2 + |\mathbf{B}_\alpha(\mathbf{k})|^2)$$

In Coulomb gauge we have $\mathbf{E} = -(\partial A/\partial t)/c$, $\mathbf{B} = \nabla \times \mathbf{A}$. Thus, $\mathbf{E}_\alpha = ika_\alpha \mathbf{e}_\alpha$, $\mathbf{B}_\alpha = ika_\alpha (\hat{\mathbf{k}} \times \mathbf{e}_\alpha)$ and

$$H_{rad} = \frac{V}{2\pi} \sum_{\mathbf{k},\alpha} k^2 |a_\alpha(\mathbf{k})|^2$$

In terms of photon occupation number:

$$H_{rad} = \sum_{\mathbf{k},\alpha} \hbar\omega \mathcal{N}_\alpha(\mathbf{k}), \rightarrow |a_\alpha(\mathbf{k})| = c \left[\frac{h\mathcal{N}_\alpha(k)}{V\omega} \right]$$

Thus,

$$H_1 = \sum [H_\alpha^{abs} e^{-i\omega t} + H_\alpha^{em} e^{i\omega t}]$$

where

$$H_\alpha^{abs} = \frac{e}{m_e} \left[\frac{h}{V\omega} \mathcal{N}_\alpha(\mathbf{k}) \right]^{1/2} e^{i\mathbf{k}\cdot\mathbf{x}} \mathbf{e}_\alpha(\hat{\mathbf{k}}) \cdot \mathbf{p}, \quad (3)$$

$$H_\alpha^{am} = \frac{e}{m_e} \left\{ \frac{h}{V\omega} [1 + \mathcal{N}_\alpha(\mathbf{k})] \right\}^{1/2} e^{-i\mathbf{k}\cdot\mathbf{x}} \mathbf{e}_\alpha(\hat{\mathbf{k}}) \cdot \mathbf{p}, \quad (4)$$

(5)

Note, we added 1 to 2nd eq. to account for spontaneous emission processes. Our semi-classic treatment in which the EM field is not quantized. a and $a^\dagger$ should be operators (creation/annihilation operators) that do not commute: $[a, a^\dagger] = hc/\omega V$. This gives rise to spontaneous emission term.

Perturbation theory

We may expand the perturbed wave function ψ as follows:

$$\psi(x,t) = \sum_j c_j(t)\varphi_j(x)e^{-iE_jt/\hbar}$$

because H_0 is Hermitian operator and φ_j satisfying $H_0\varphi_j = E_j\varphi_j$ forms a complete orthonormal basis for representing any wave function for the atomic system.
Thus, eliminating the zero-th order terms we have

$$H_1\psi = \sum_j c_j H_1 \varphi_j e^{-iE_jt/\hbar} = i\hbar \sum_j \dot{c}_j \varphi_j e^{-iE_jt/\hbar} =$$

Now we can multiply by $\langle\varphi_f| = \varphi_f^* e^{iE_ft/\hbar}$

$$\sum_j e^{i\omega_{fj}t} c_j(t)\langle\varphi_f|H_1|\varphi_j\rangle = i\hbar\dot{c}_f(t) \text{ where } \omega_{fi} \equiv (E_f - E_j)/\hbar.$$

Absorption transition probability

Because at $t = 0$ we have $c_j = \delta_{ji}$ to zero-th order we can drop all terms $j \neq i$ in the summation:

$$\begin{aligned} c_f(t) &= -i\hbar^{-1} \int_0^t < \varphi_f | H_1 | \varphi_i > e^{i\omega_{fi} t'} dt' \\ &= -\hbar^{-1} < \varphi_f | H_\alpha^{abs} | \varphi_i > \left[\frac{e^{i(\omega_{fi} - \omega)t} - 1}{(\omega_{fi} - \omega)} \right] \end{aligned}$$

Thus, going to the continuous limit and using $dk^3 = c^{-3}\omega^2 d\omega d\Omega$, the transition probability $P_{if} = \sum_{\mathbf{k},\alpha} |c_f|^2$ is

$$P_{if} = \frac{V}{(2\pi)^2} \int \frac{d^3k}{\hbar^2} |\langle \varphi_f | H_\alpha^{abs} | \varphi_i \rangle|^2 \frac{\sin^2[(\omega - \omega_{fi})t/2]}{[(\omega - \omega_{fi})/2]^2} \propto t \mathcal{N}_\alpha \langle \varphi_f | e^{i\mathbf{k}\cdot\mathbf{x}} \mathbf{e}_\alpha \cdot \mathbf{p} | \varphi_i \rangle$$

Thus, the transition rate probability is $dP_{if}/dt \sim const(t)$.

Dipole Approximation

Approximate $e^{i\mathbf{k}\cdot\mathbf{x}} = 1 + \mathbf{k}\cdot\mathbf{x} + ... \sim 1$ thus

$$< \varphi_f | e^{i\mathbf{k}\cdot\mathbf{x}} \mathbf{e}_\alpha \cdot \mathbf{p} | \varphi_i > \sim \mathbf{e}_\alpha \cdot < \varphi_f | \mathbf{p} | \varphi_i >$$

It is useful to express the momentum operator as the commutator

$$[H_0, \mathbf{x}] \equiv H_0 \mathbf{x} - \mathbf{x} H_0 = -\frac{\hbar^2}{2m_e}(\nabla^2 \mathbf{x} - \mathbf{x}\nabla^2) = -\frac{\hbar^2}{m_e}\nabla = -\frac{i\hbar}{m_e}\mathbf{p}$$

Thus,

$$< \varphi_f | \mathbf{p} | \varphi_i > = i m_e \omega_{fi} \mathbf{X}_{fi}, \text{ where } \mathbf{X}_{fi} \equiv < \varphi_f | \mathbf{x} | \varphi_i >$$

Bound-bound absorption cross section

Finally, from the transition probability rate we derive the cross section σ_ν for a flux of photons $c\mathcal{N}$ integrated over phase-space elements:

$$\frac{dP_{if}}{dt} = \frac{4\pi e^2 \omega_{fi}^3}{3hc^3}\mathcal{N}(\omega_{fi})|\mathbf{X}_{fi}|^2 = \frac{1}{(2\pi)^3}\int_0^\infty \sigma_\nu c\mathcal{N}(\omega) d^3k.$$

Thus, $\sigma_\nu = \frac{4\pi^2}{3}\alpha|\mathbf{X}_{fi}|^2\omega\delta(\omega - \omega_{fi})$, where α is the fine structure constant. In terms of the classical cross section for bound-bound transitions we have:

$$\sigma_\nu = \frac{\pi e^2}{m_e c} f_{12}\phi_{12}(\nu),$$

where the oscillator strength in terms of the matrix elements is:

$$f_{12} = \frac{2m_e(\omega_{21}|\mathbf{X_{21}}|)^2}{3\hbar\omega_{21}} \sim 1.$$

(ratio of kinetic energy of electron to the emitted photon energy).

Relativistic Electromagnetic Hamiltonian

Relativistic Hamiltonian with EM field:

$$H = [(c\mathbf{p} - e\mathbf{A})^2 + m^2c^4]^{1/2} + e\phi$$

Relativistic hard to separate due to square root. Two approaches:
1) Klein-Gordon (without electromagnetic potentials for simplicity)
square operators in Schroedinger eq before applying to ψ:
$H^2\psi = \hbar\partial^2\psi/\partial t^2$

$$\left[\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right) - \left(\frac{mc}{\hbar}\right)^2\right]\psi = 0$$

Operator is d'Alambertian where the second term is the Compton wavenumber of particle of mass m.
The solution represent the equation for scalar field ψ in QFT. Scalar field represent a gauge boson of mass m and spin $s = 0$. Photon is a massless boson of spin $s = 1$.

Dirac approach

Rewrite relativistic equation as linear in $\mathbf{p}$:

$$H = \mathbf{a} \cdot \mathbf{P}c + bmc^2 + e\phi \equiv [(c^2\mathbf{P}^2 + m^2c^4]^{1/2} + e\phi$$

where $\mathbf{P} = \mathbf{p} - e/c\mathbf{A}$ is the relativistic particle momentum.
The coefficient $\mathbf{a}$ and b need to be 4×4 matrices to satisfy the equation.
The solution gives rise to concepts of spin and anti-matter. For particle at rest in vacuum there are 2 possible eigenvalues of energy:

$$E = \pm m_e c^2.$$

What represent a negative rest mass energy? Dirac interpretation of anti-particle: a hole in “sea” of negative rest-mass energy particles (not quite rigorous).
Feynman interpretation of anti-particle: positive rest-mass energy but moving backward in time (more rigorous interpretation).