LEC 7

Semi-classical theory of radiative transitions

Why non-relativistic QM?

Consider Bohr hydrogen atom and compute v of e^-

$$a_0 = \frac{\hbar^2}{m_e e^2} = \text{Bohr radius}$$

kinetic energy $\frac{m_e v^2}{2} = \frac{e^2}{2a_0} \Rightarrow$

$$\frac{v}{c} = \frac{e^2}{\hbar c} \equiv \alpha \approx \frac{1}{137}$$

fine structure const.

Corrections enter at $\left(\frac{v}{c}\right)^2$ so

$$\left(\frac{v}{c}\right)^2 \ll 1$$

No need for QED

Also, transition energies involve photons w/ $\hbar\omega = \frac{e^2}{2a_0}$ or

$$k = \frac{\omega}{c} = \left(\frac{\alpha}{2}\right) a_0^{-1} \text{ or}$$

$$k a_0 = \frac{\alpha}{2} \ll 1$$

which implies that a multipole expansion for the EM field should hold

For heavy atoms the above become

$\frac{v}{c} \sim Z\alpha$, and $k a_0 \sim Z\alpha$

Thus for moderate Z we can ignore QED & use multipole expansions low orders

In other words $k a_0 \lesssim 1 \Rightarrow$

$\frac{a_0}{\lambda} << 1 \Rightarrow$ The E-field of the radiation does not change much over the scale of the atom (i.e. pretty constant)

Time-dependent pert. theory

Consider atom with Hamiltonian H_0 eigenstates Φ_K with energy E_K.

We treat its interaction with the EM field as a (classical) perturbation with EM Hamiltonian H_1.

Unperturbed atom:

$$H^0 \varphi_K = E_K \varphi_K$$

Total wavefunction expanded in the complete basis Φ_K

$$\psi(t) = \sum_K a_K(t)\, \underbrace{\varphi_K e^{-iE_K t/\hbar}}$$

~~[illegible]~~ unperturbed Eigenstates

Now

$$H = H^0 + H'$$

time dependent

Consider the transition between two states i & f.

The trans. prob. from $i \to f$ per unit time is

$$W_{fi} = \frac{4\pi^2}{\hbar T} \left| H'_{fi}(\omega_{fi}) \right|^2$$

where

$$H'_{fi}(\omega) = \frac{1}{2\pi} \int_0^T H'_{fi}(t') e^{i\omega t'} dt'$$

perturbation occurred over $t \in [0, T]$

Fourier Transform of H'_{fi}, with

$$H'_{fi}(t) = \int \phi_f^* H' \phi_i \, d^3x = \langle \varphi_f | H' | \varphi_i \rangle$$

matrix elements of H' in the ϕ_K basis

and $\omega_{fi} = \dfrac{E_f - E_i}{\hbar}$

What is H'?

$$H' = \underbrace{A(t)\, e^{i\bar{k}\cdot\bar{x}}}_{\text{plane wave}} \, \vec{e}_\alpha(\hat{k}) \cdot \bar{p} \left(\frac{-e}{mc}\right)$$

its polarization

momentum of ~~atom~~ electron

$$H' = -\frac{e}{mc} \vec{A}\cdot\vec{p}$$

We assum $A(t)$ vanishes outside of $t \in [0, T]$

Dipole Approx.

$$e^{i\bar{k}\cdot\bar{x}} = 1 + i\cdot\bar{k}\cdot\bar{x} + \ldots +$$

But, $\bar{k}\cdot\bar{x} \sim k a_0 << 1$

Thus, keeping lowest order

$$e^{i\bar{k}\cdot\bar{x}} \simeq 1 \quad \text{(dipole)}$$

Therefor $H'_{fi} \propto \bar{e}_a \langle \varphi_f | p | \varphi_i \rangle$

Using commutation relation

$$\cancel{\quad} \bar{x}\cdot\bar{p}^2 - \bar{p}^2\bar{x} = 2i\hbar\bar{p}$$

and $H^0 = \frac{1}{2m_e}\bar{p}^2 + V(\bar{x})$ $\Rightarrow$

~~$i\hbar\bar{p} = \bar{p}^2(\bar{x}\cdot H \ldots)$~~

$$\bar{p}^2 = 2m_e H^0 - V(x)$$

thus $(\vec{x}\cdot H^0 - H^0\bar{x})\,\cancel{2}m_e = \cancel{2}i\hbar\bar{p}$ $\cdot(-i)$ $\Rightarrow$

$$\bar{p} = i\frac{m_e}{\hbar}(H^0\bar{x} - \bar{x}H_0)$$

Hence

$$\langle\varphi_f|\bar{p}|\varphi_i\rangle = i\, m_e\omega_{fi}\frac{1}{e}\langle\varphi_f|e\bar{x}|\varphi_i\rangle$$

and $\bar{d} \equiv -e\bar{x}$ ← electric dipole operator

$$\langle\varphi_f|\bar{p}|\varphi_i\rangle = -i\frac{m_e\omega_{fi}}{e}\langle\varphi_f|\bar{d}|\varphi_i\rangle$$

Thus $H'_{fi} = -\frac{e}{m_e c} A(t)\cdot\bar{e}_\alpha \langle\varphi_f|p|\varphi_i\rangle$

$$= i\,\underline{\omega_{fi}}\,\langle\varphi_f|\bar{d}|\varphi_i\rangle A(t)\cdot\vec{e}_\alpha$$

$$\Rightarrow \quad H'_{fi}(\omega) = \frac{i\omega_{fi}}{\cancel{}} A(\omega_{fi})\, \hat{e}_a \langle \varphi_f | \vec{d} | \varphi_i \rangle$$

Therefore, the transition rate is

$$W_{fi} = \frac{4\pi^2}{\hbar^2 T} \left| H'_{fi}(\omega_{fi}) \right|^2$$

$$\cancel{H'_{fi}(\omega) = \frac{1}{2\pi} \int_0^T \varphi_f^* \left(-\frac{e}{mc}\right) \vec{A}\cdot\vec{p}\, d^3x\, \varphi_i}$$

$$W_{fi} = \frac{4\pi^2}{\hbar^2 T c^2}\, \omega_{fi}^2\, A^2(\omega_{fi})\, |d_{fi}|^2$$

For monochromatic light

$$\frac{dE}{dA\,d\omega\,dt} = J(\omega) = \frac{\omega^2}{cT} |A(\omega)|^2$$

See Eqs. 10.14
10.15
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in R&L

$$W_{fi} = \frac{4\pi^2}{\hbar^2 c} \underbrace{\frac{\omega_{fi}^2}{cT} A^2(\omega_{fi})}_{J(\omega_{fi})} \cdot |d_{fi}|^2 \Rightarrow$$

$$\boxed{W_{fi} = \frac{4\pi^2}{\hbar c} |d_{fi}|^2 J(\omega_{fi})}$$

For unpolarized incoming radiation

$$\langle \varphi_f | \bar{e}_\alpha \cdot \bar{d} | \varphi_i \rangle = \frac{1}{3} |d_{fi}|^2$$

So, the average transition rate is

$$W_{fi} = \frac{4\pi^2}{3c\hbar^2} |d_{fi}|^2 \frac{\omega_{fi}^2}{cT} |\bar{A}(\omega_{fi})|^2$$

If you see $\langle W_{fi} \rangle$ it means angle average over incoming plane wave polarizations.

Connecting to Einstein Coef.

In W_{fi} the part $\frac{\omega_{fi}^2}{cT} |\bar{A}(\omega_{fi})|^2 = \frac{dE}{dA\,d\omega\,dt}$

unidirectional intensities

$$J_\nu = \frac{1}{4\pi} \mathcal{J}(\nu) = \frac{1}{2 \cdot 4\pi} 2\pi \mathcal{J}(\omega) = \frac{\mathcal{J}(\omega)}{2}$$

But $W_{eu} = B_{eu} J_\nu$

lower upper

$$\text{Thus} \quad B_{eu} = \frac{W_{eu}}{J_\nu} = \frac{2W_{eu}}{\mathcal{J}(\omega)} = \frac{8\pi^2 |d_{eu}|^2}{3c\hbar^2}$$

~~since $|d_{u\ell}|^2 = |d_{\ell u}|^2$~~

Hence $B_{\ell u} = \cancel{B} \dfrac{8\pi^2 |d_{\ell u}|^2}{3c\hbar^2}$

~~Similarly for stimulated~~ emis S p104

~~Alter~~ From the Einstein relations for non-degenerate levels

$$B_{\ell u} = B_{u\ell}$$

$$A_{u\ell} = \frac{2h\nu_{u\ell}^3}{c^2} B_{\ell u}$$

$$= \frac{32\pi^3 \nu_{u\ell}^3}{3c^3\hbar} |d_{u\ell}|^2 = \frac{64\pi^4 \nu_{u\ell}^3}{3c^3 h} |d|^2$$

Of course $|d_{u\ell}|^2 = |d_{\ell u}|^2$

<u>Notes</u>

1) If levels are degenerate, the transition rates average over the initial states, and sum over the final states

$$A_{u\ell} = \frac{64\pi^4 \nu_{u\ell}^3}{3c^3 h} \frac{1}{g_u} \sum |d_{u\ell}|^2$$

2) Common to define the oscilator strength f_{lu} as

$$B_{lu} = \frac{4\pi^2 e^2}{h\nu_{ul} m_e c} f_{lu}$$

where
$$f_{lu} = \frac{2m_e}{3\hbar^2 g_l e^2} (E_u - E_l) \sum |d_{lu}|^2$$

The only difference between an emission oscillator strength and an absorption — " — " is

$$\frac{1}{g_u} \rightarrow \frac{1}{g_l} \quad \text{and} \quad \nu_{ul} = -\nu_{lu}$$

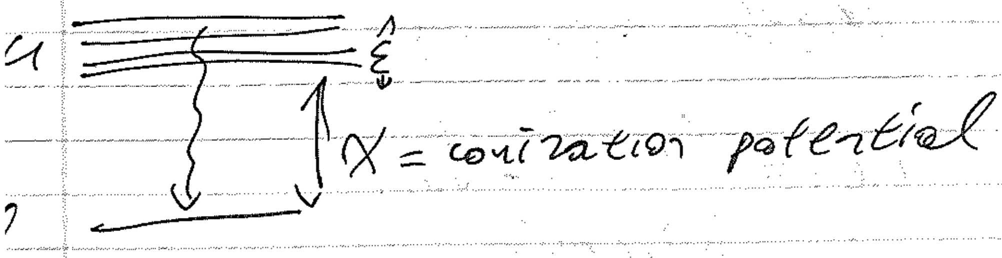
This way
$$\boxed{g_l f_{lu} = -g_u f_{ul}}$$

n the Einstein relations

3) Continuum osc. strength

If the upper state lies in a continuum (bound-free), not meaningful to define trans. probability to a single state, but define per freq. range

$$I = I_0 + I_1$$



$$h\nu = \chi + \varepsilon,$$

Cont. osc. strength $\quad f_c = \int_{\nu_0}^{\infty} \frac{df}{d\nu}\, d\nu$

Where $h\nu_0 = \chi$

Oscillator strengths are either directly computed or determined experimentally!

~~Lecture~~

Selection Rules

Last time we derived

$$W_{fi} = \frac{4\pi^2}{3c\hbar^2} \frac{\omega_{fi}^2}{cT} |A(\omega_{fi})|^2 |d_{fi}|^2$$

Selection rules refer to magnitude of $|d_{fi}|^2 = \langle \psi_f | \vec{d} | \psi_i \rangle$. If $|d_{fi}|^2$ is nonzero transition is allowed. If it is 0, transition is forbidden.

However, it is a forbidden *dipole* transition! Higher multipoles can still allow it!

So, Notes

① A transition prob. can be 0 in the dipole approx $e^{i\vec{k}\cdot\vec{r}} = 1 + \ldots$

but non-zero for higher multipoles (e.g. magnetic dipole, electric quadrupole etc.)

(2) Laporte's rule: there are no allowed transitions between states of the same parity. (again dipole transitions)

$$d_{fi} = e\int \psi_f^* \bar{r}\, \psi_i\, d^3x = 0$$

if f and i have the same parity ($\vec{r} \to \bar{r}$)

(3) Electron wave functions ψ consist of

$$\psi = R_{nl}(r)\, Y_{lm}(\theta,\varphi)\, |m_s\rangle$$

The matrix element $\langle \psi_f | \bar{r} | \psi_i \rangle$ turns out to be non-zero for

$$\Delta l = \pm 1$$
$$\Delta m = 0, \pm 1$$

(orbital ang. mom. numbers)

(4) General result even for higher multipole transitions

$J = 0 \to J = 0$ transition is forbidden

J = total ang. momentum

this is because photons carry away unit ang. momentum.

~~Transition rates~~
for H

Also for multi-electron atoms the total L, S, J must satisfy

$\Delta S = 0$
$\Delta L = 0, \pm 1$ (but $\Delta l = 0$ is not allowed)
$\Delta J = 0, \pm 1$ → except $J=0 \to J=0$

Transition rates

For H, He II, Li III etc. because $V(r)$ is Coulomb (for $1e^-$) and relatively easy

$|d_{fi}| \sim \int R_{nl} \, R_{n'l\pm1} \, r \, dr$

known (Laguerre pol.)

Ex. $n=1, n=2$ $\quad g_f = 0.8324$ → dipole osc. strength

$h\nu = 13.6 \left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$ eV

Bound-free transitions of hydrogen

Upper states lie in continuum — absorption in continuous range of frequencies. A.K.a photoionization.

The differential transition rate is

$$dW = W_{fi} \frac{dn}{dp\,d\Omega}\, dp\, d\Omega =$$

like a bound-bound transition probability

density of states (# of free e^- states available)

$$dW = \frac{4\pi^2}{m^2 c} \frac{I(\omega)}{\omega_{fi}^2} \left| \langle \psi_f | \bar{e}_\alpha \cdot \bar{d} | \psi_i \rangle \right|^2$$

$$= \frac{d\sigma}{d\Omega}\, d\Omega \frac{dN}{dA\,dt\,d\omega}\, d\omega$$

photon flux

as in EM $\quad \frac{dP}{d\Omega} = \frac{d\sigma}{d\Omega} \langle S \rangle$

energy flux (Poynting vector)

The previous eqn. is from bound state i to continuum state f.

1) Energy conservation

$$\hbar\omega = \frac{p^2}{2m} + \chi \rightarrow \text{ionization potential}$$

kinetic energy

$$\frac{d}{d\omega}(\hbar\omega) = \frac{d}{d\omega}\left(\frac{p^2}{2m} + \chi\right) \Rightarrow$$

$$\hbar\, d\omega = \frac{p}{m}\, dp$$

\# photons

2) Also $\dfrac{dN}{dA\,dt\,d\omega} = \dfrac{S(\omega)}{\hbar\omega}$

3) Density of states of e^- in volume V

$$\frac{dn}{dp\,d\Omega} = \frac{p^2 V}{h^3} = \frac{dN}{dp\,d\Omega} \quad \text{because}$$

$$dN = \frac{d^3p\, d^3x}{h^3} = \frac{p^2 dp\, d\Omega \cdot V}{h^3}$$

4) $p = mv$

5) $\sigma_{bf} = \int \frac{d\sigma}{d\Omega} d\Omega$

Putting it all together, the bound-free cross section of H-like atom with charge Z is

$$\sigma_{bf} = \begin{cases} \left(\frac{64\pi n}{3\sqrt{3} Z^2}\right) \alpha a_0^2 \left(\frac{\omega_n}{\omega}\right)^3 g(\omega, n, l, Z) & \omega \geq \omega_n \\ 0 , & \omega < \omega_n \end{cases}$$

$\alpha \simeq \frac{1}{137} = \frac{e^2}{\hbar c}$ fine structure const.

$a_0 = \frac{\hbar^2}{m e^2}$ = Bohr radius

$\omega_n = \frac{\alpha^2 m c^2 Z^2}{2\hbar n^2} = \frac{\chi_n}{\hbar}$ ionization potential of state n.

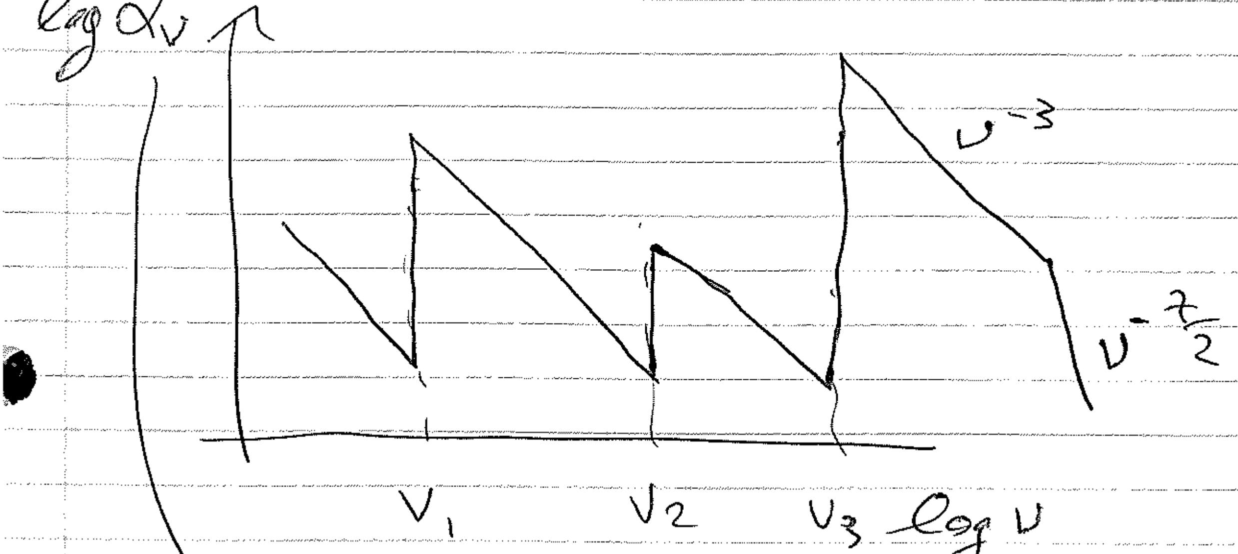
$g(\omega, n, l, Z)$ = bound-free Gaunt factor $\simeq 1$

How does α_{bf} behave?

Sudden rise at threshold $\omega = \omega_n$

Decreases like ω^{-3} for $\omega > \omega_n$

For $\hbar\omega \gg \chi_n$ goes like $\omega^{-\frac{7}{2}}$



$\alpha_\nu = N_n \cdot \sigma$

atomic density at level n

principal quantum #