Astro 501: Radiative Processes

Lecture 31

April 8, 2013

Announcements:

- **Problem Set 9** due 5pm today
- **Problem Set 10** due 5pm Friday April 19
- ICES to be available online – please!

Last time: transitions involving bound states

Q: what approximations used?

found transition probability per unit time w_{ij} for $i \to j$

Q: what does this depend on? what about w_{ji} *for* $j \to i$*?*

the transition probability per unit time for $i \to f$ we have

$$w_{fi} = \frac{4\pi^2 e^2}{m_e c^2}\frac{\mathcal{J}(\omega_{fi})}{\omega_{fi}^2} \left| \langle f | e^{i\vec{k}\cdot\vec{r}} \mathbf{e} \cdot \sum_j \nabla_j | i \rangle \right|^2 \tag{1}$$

where $\mathcal{J}_\omega = \int I_\omega \; d\Omega = 4\pi \; J_\omega$, and with $\mathbf{e}$ the polarization unit vector, and the sum is over atomic electrons

for $f \to i$

$$w_{if} = w_{fi} \tag{2}$$

principle of detailed balance

now: evaluate operator $e^{i\vec{k}\cdot\vec{r}}\mathbf{e} \cdot \sum_j \nabla_j$

the heart of the transition probability is
the matrix element $\int \psi_f^* e^{i\vec{k}\cdot\vec{r}} \mathbf{e} \cdot \sum_j \nabla_j \psi_i \; d^3x$

the wavenumber $k = \omega/c = \Delta E/\hbar c$
and the atomic wavefunctions are significant on scales $\sim a_0$
so: $\vec{k}\cdot\vec{r} \sim k a_0 \sim a_0 \Delta E/\hbar c \sim Zv/c \ll 1$

thus we write

$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} - \frac{1}{2}(\vec{k}\cdot\vec{r})^2 + \cdots \tag{3}$$

and we approximate $e^{i\vec{k}\cdot\vec{r}} \approx 1$

Q: when would we be interested in the higher order terms?

we see that $e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} + \cdots$
is an expansion in v/c
and we recall $v/c \ll 1$ for atoms with moderate $Z \ll 137$

lesson: expansion is dominated by first nonzero term

- $(kr)^0$ term: electric dipole approximation (more soon on this) dominates unless identically zero, then
- $(kr)^1$ term: electric quadrupole approximation and comparable magnetic dipole term $(B \sim v/c\ E)$
- $(kr)^2$ term: electric octupole, magnetic quadrupole

Note that to describe these terms,
have to modify Schrödinger equation to appropriate order in v/c

The Dipole Approximation

putting $e^{i\vec{k}\cdot\vec{r}} \approx 1$, the matrix element is

$$\int \psi_f^* \mathbf{e} \cdot \sum_j \nabla_j \psi_i \; d^3x = \frac{1}{i\hbar} \left\langle \mathbf{e} \cdot \hat{\vec{p}}_j \right\rangle_{fi} \tag{4}$$

i.e., related to the expected momentum of electron j

to bring this into a more familiar form, we note
the basic quantum operator relationship

$$\hat{\vec{r}}_j \hat{\vec{p}}_j^2 - \hat{\vec{p}}_j^2 \hat{\vec{r}}_j = 2 \; i \; \hbar \; \hat{\vec{p}} \tag{5}$$

and so given the atomic Hamiltonian

$$\hat{H}_0 = \frac{1}{2m_e}\sum_j \hat{\vec{p}}_j^{\,2} + V(\hat{\vec{r}}_1, \hat{\vec{r}}_2, \ldots, \hat{\vec{r}}_N) \tag{6}$$

we have

$$\hat{\vec{r}}_j \hat{H}_0 - \hat{H}_0 \hat{\vec{r}}_j = i\frac{\hbar \hat{\vec{p}}_j}{m_e} \tag{7}$$

a special case of the general result $-i\hbar\partial_t \hat{A} = [\hat{H}, \hat{A}]$

and so we have

$$\begin{aligned} \frac{1}{i\hbar}\left\langle \mathbf{e}\cdot\hat{\vec{p}}_j\right\rangle_{fi} &= \frac{m_e}{\hbar^2}\int \psi_f^* \mathbf{e}\cdot(\vec{r}_j H_0 - H_0 \vec{r}_j)\psi_i \; d^3x & (8) \\ &= \frac{m_e(E_i - E_f)}{\hbar^2}\int \psi_f^* \mathbf{e}\cdot\vec{r}\psi_i \; d^3x & (9) \end{aligned}$$

thus the transition rate is

$$w_{fi} = \frac{4\pi^2}{\hbar^2 c} \left| \left\langle \mathbf{e} \cdot \vec{d} \right\rangle_{fi} \right|^2 \; \mathcal{J}(\omega_{fi}) \tag{10}$$

where the **electric dipole operator** is

$$\vec{d} = e \sum_j r_j \tag{11}$$

note that generally we have atoms in random orientations so taking the angle average, we have

$$\left\langle |\mathbf{e} \cdot \vec{d}_{fi}|^2 \right\rangle = \frac{1}{3} |d_{fi}|^2 \tag{12}$$

where

$$|d_{fi}|^2 \equiv \vec{d}^{*}_{fi} \cdot \vec{d}_{fi} = |(d_x)_{fi}|^2 + |(d_y)_{fi}|^2 + |(d_z)_{fi}|^2 \tag{13}$$

Electric Dipole Transition Rate

the electric dipole transition rate is thus

$$\left\langle w_{fi} \right\rangle = \frac{4\pi^2}{3c\hbar^2} \, |d_{fi}|^2 \; \mathcal{J}(\omega_{fi}) \tag{14}$$

thus the Einstein absorption coefficient for $\ell \rightarrow u$ ("lower to upper") is

$$\langle w_{\ell u} \rangle = B_{\ell u} \; J(\nu_{\ell u}) \tag{15}$$

where $J(\nu_{\ell u}) = \mathcal{J}(\nu_{\ell u})/4\pi$ since intensity is in one direction and $\mathcal{J}(\nu_{\ell u}) = \mathcal{J}(\omega_{\ell u}) \; d\omega/d\nu = 2\pi \mathcal{J}(\omega_{\ell u})$, so

$$\langle w_{\ell u} \rangle = \frac{1}{2} B_{\ell u} \; \mathcal{J}(\omega_{\ell u}) \tag{16}$$

∞ and we can now find all three Einstein coefficients *Q: how?*

Einstein Coefficients

the Einstein coefficients in the electric dipole approximation are:

- true *absorption*

$$B_{\ell u} = \frac{8\pi^2}{3c\hbar^2}|d_{\ell u}|^2 = \frac{32\pi^4}{3ch}|d_{\ell u}|^2 \tag{17}$$

for *non-degenerate atomic levels* with $g_\ell = g_u = 1$ we have

- *stimulated emission*

$$B_{u\ell} = B_{\ell u} \tag{18}$$

- *spontaneous emission*

$$A_{u\ell} = \frac{2\nu^3}{c^2 h} B_{\ell u} = \frac{64\pi^4 \ \nu_{u\ell}^3 \ |d_{u\ell}|^2}{3c^3 h} \tag{19}$$

this gives (at least in principle) a direct means to connect
the radiative coefficients j_ν and α_ν
to the atomic properties encoded in the dipole moment $d_{u\ell}$

recall that the absorption coefficient is

$$\alpha_\nu = \frac{h\nu}{4\pi}\, n_\ell\, B_{\ell u}\, \phi(\nu) \tag{20}$$

and so writing this in terms of the *absorption cross section* $\sigma_{\ell u}$

$$\alpha_\nu = n_\ell\, c\, \sigma_{\ell u}(\nu) \tag{21}$$

so that the cross section and Einstein coefficient are related by

$$\sigma_{\ell u}(\nu) = \frac{h\nu}{4\pi\ c}\, B_{\ell u}\, \phi(\nu) \tag{22}$$

integrating and using $\int \phi(\nu)\ d\nu = 1$, we have

$$B_{\ell u} = \frac{4\pi\ c}{h\nu_{\ell\nu}} \int \sigma_{\ell u}(\nu)\ d\nu \tag{23}$$

and thus our expressions for $B_{\ell u}$ also give $\sigma_{\ell u}$

Oscillator Strength

If the electron moves as a *damped classical oscillator* with natural (resonant) frequency ω_0 then (PS10) absorption rate is $B_{\ell u}^{\text{classcial}}\ J(\nu_{\ell u})$ with

$$B_{\ell u}^{\text{classical}} = \frac{4\pi^2 e^2}{h\nu_{\ell u}\ m_e c} \tag{24}$$

it is thus convenient write

$$B_{\ell u} \equiv f_{\ell u}\ B_{\ell u}^{\text{classical}} \tag{25}$$

$$\sigma_{\ell u}(\nu) = \frac{\pi e^2}{m_e c}\ f_{\ell u}\ \phi(\nu) \tag{26}$$

where the dimensionless **oscillator strength** is

$$f_{\ell u} = \frac{m_e}{\pi e^2} \int \sigma_{\ell u}(\nu)\ d\nu = \frac{2m_e}{3\hbar^2 g_\ell e^2}(E_u - E_\ell) \sum |d_{\ell u}|^2 \tag{27}$$

Q: what about $f_{u\ell}$*?*

Einstein $g_\ell B_{\ell u} = g_u B_{u\ell}$, and since we have absorption

$$g_u \; f_{u\ell} = - \; g_\ell f_{\ell u} \tag{28}$$

so *emission oscillator strengths are negative*

if we sum over all transitions from $i \rightarrow j$,
can show that *one-electron atoms have*

$$\sum_{j \;\; \text{fina}} f_{ij} = 1 \tag{29}$$

and *N-electron atoms have*

$$\sum_{j \;\; \text{fina}} f_{ij} = N \tag{30}$$

the *Thomas-Riche-Kuhn sum rule*

Selection Rules

When is a transition between states i and f possible?

in general: the transition probability is *always nonzero*
but can be very small if the transition is suppressed,
usually due to a symmetry
e.g., a forbidden dipole transition can have a nonzero quadrupole rate

we will focus on selection rules for *dipole transitions*
where recall that the dipole matrix element is

$$\vec{d}_{fi} = e \int \psi_f^* \sum_j \vec{r}_j \; \psi_i \; d^3x \tag{31}$$

Laporte's rule:
no transitions between two states of the same parity
Q: what is a parity transformation?
Q: why is $\vec{d}_{fi} = 0$ if i and j have same parity?

a parity transformation is the mapping $\vec{r} \rightarrow -\vec{r}$

note: electron wavefunctions are angular momentum eigenstates
and angular momentum eigenstates are parity eigenstates
thus: wavefunctions have definite parity

$\psi_k(-\vec{r}) = \pi_k \psi_k(\vec{r})$, with $\pi_k = \pm 1$

thus if $\pi_i = \pi_f$, then

$$\vec{d}_{fi} \rightarrow \vec{d}'_{fi} = -e \int \psi_f^* \sum_j \vec{r}_j \, \psi_i \, d^3x = -\vec{d}_{fi} \tag{32}$$

and thus $\vec{d}_{fi} = 0$

the parity of an electron configuration (set of states)
is set by the electron angular momenta:

parity is $(-1)^{\sum \ell_i}$, where each electron has ℓ_i

thus we conclude: *no transitions between the same configuration*

Note that the atomic wavefunction is really a function $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ over all N electron coordinates
and at our level of approximation can be written in terms of single-electron wavefunctions $u_a(\vec{r}_1)\ u_b(\vec{r}_2)\ \ldots\ u_k(\vec{r}_N)$
where $\int u_a^* u_a\ d^3x = 1$

thus the dipole operator $\vec{r}_j$ picks out the wavefunctions for a *single electron*, involving $\int u_{a'}^* \vec{r}_j\ u_a\ d^3 r_j$

Q: implications?

the dipole operator only involves $\int u_{a'}^{*}\vec{r}_j \; u_a \; d^3r_j$
for a *single electron*

thus we conclude

- all other electron wavefunctions remain the same
- *one electron jumps* per transition
- the transition dipole moment is that of the jumping electron
- in the jump the *parity change* is $(-1)^{\Delta\ell}$

vector nature of dipole operator imposes conditions on
single electron states in transitions:

$$\Delta\ell = \pm 1 \tag{33}$$

$$\Delta m = 0, \pm 1 \tag{34}$$

`www: helium allowed transitions`

rules for *total angular momentum quantum numbers*

$$\Delta S = 0 \quad (35)$$

$$\Delta L = 0, \pm 1 \quad (36)$$

$$\Delta J = 0, \pm 1 \ \text{ except } J = 0 \text{ to } J = 0 \quad (37)$$

note that we can have $\Delta L = 0$
but always must have $\Delta \ell = \pm 1$

examples:

- $3s\ ^2S_{1/2} \rightarrow 4s\ ^2S_{1/2}$
  $\Delta \ell = 0$: forbidden!

- $2p\ ^2P_{1/2} \rightarrow 3d\ ^2D_{5/2}$
  $\Delta \ell = 1$, OK!
  $\Delta L = 1$, OK!
  $\Delta S = 0$, OK!
  $\Delta J = 2$, forbidden!