

Astronomy 501: Radiative Processes

Lecture 25

Oct 21, 2022

Announcements:

- **Problem Set 7 due today**
- **Problem Set 8 due next Friday**
- Midterm exams scores posted
see Chris to pick up graded exam
Bonus Round points are *additional!*

Last time: atomic transitions

goal: find Einstein coefficients A_{if}, B_{fi}, B_{if} , then

$$j_\nu = \frac{h\nu_{if} A_{if}}{4\pi} n_i \phi(\nu) \quad (1)$$

$$\alpha_\nu = \frac{h\nu_{if}}{4\pi} (B_{fi}n_f - B_{if}n_i) \phi(\nu) \quad (2)$$

with $\phi(\nu)$ the *line profile* function

Spontaneous Dipole Emission: Wild West Derivation

Full derivation: requires quantum electrodynamics
i.e., quantum treatment of electromagnetic field
Sketched in R&L and in Extras below
Here: cowgirl/cowboy “horseback” derivation

consider a transition from an *upper level* E_u
to a *lower level* E_ℓ
expected time-changing dipole component is

$$\vec{d} \equiv \langle \vec{d} \rangle \sim e e^{-i\omega_{lu}t} \langle u | \vec{r} | \ell \rangle \quad (3)$$

and so dipole acceleration is

$$\ddot{\vec{d}} \sim e \omega_{lu}^2 e^{-i\omega_{lu}t} \langle u | \vec{r} | \ell \rangle \quad (4)$$

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Q: and so?

in dipole approximation, **Larmor power per atom** is

$$P_{ul} = \frac{2|\ddot{d}|^2}{3c^3} \sim \frac{\omega_{lu}^4}{c^3} |d_{ul}|^2 \quad (5)$$

- transition driven by dipole operator

$$\vec{d}_{ul} = e \int \psi_l^* \vec{r} \psi_u dV$$

between initial and final states

- zero when dipole moment vanishes—*forbidden* transitions!
but higher multipole transitions may still go

now we are ready for Einstein A_{ul} ! Q: how?

Spontaneous Dipole Emission

the *power* emitted in $u \rightarrow \ell$ transition:

$$P_{ul} \sim \frac{\omega_{lu}^4}{c^3} |d_{ul}|^2 \quad (6)$$

energy released per transition $E_{ul} = \hbar\omega_{lu}$

so estimate transition rate per atom as

$$\frac{dN_{ul}}{dt} \sim \frac{P_{ul}}{E_{ul}} \sim \frac{\omega_{lu}^3}{\hbar c^3} |d_{ul}|^2 \quad (7)$$

exact Einstein coefficient for *spontaneous emission*

$$A_{ul} = \frac{64\pi^4 \nu_{ul}^3 |d_{ul}|^2}{3c^3 h} \quad (8)$$

‡ Q: *what about absorption and stimulated emission?*

Einstein Coefficients

the Einstein coefficients in the electric dipole approximation are:

- *spontaneous emission*

$$A_{ul} = \frac{64\pi^4 \nu_{ul}^3 |d_{ul}|^2}{3c^3 h} = \frac{2\nu^3}{c^2 h} B_{lu} \quad (9)$$

- true *absorption*

$$B_{lu} = \frac{8\pi^2}{3c\hbar^2} |d_{lu}|^2 = \frac{32\pi^4}{3ch} |d_{lu}|^2 \quad (10)$$

for *non-degenerate atomic levels* with $g_l = g_u = 1$ we have

- *stimulated emission*

$$B_{ul} = B_{lu} \quad (11)$$

⁵ 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_{ul}

recall that the absorption coefficient is

$$\alpha_\nu = \frac{h\nu}{4\pi} n_\ell B_{\ell u} \phi(\nu) \quad (12)$$

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

$$\alpha_\nu = n_\ell c \sigma_{\ell u}(\nu) \quad (13)$$

so that the cross section and Einstein coefficient are related by

$$\sigma_{\ell u}(\nu) = \frac{h\nu}{4\pi c} B_{\ell u} \phi(\nu) \quad (14)$$

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

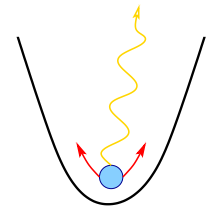
$$B_{\ell u} = \frac{4\pi c}{h\nu_\ell} \int \sigma_{\ell u}(\nu) d\nu \quad (15)$$

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

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Oscillator Strength

If the electron moves as a *damped classical oscillator* with natural (resonant) frequency ω_0 then (PS7) absorption rate is $B_{lu}^{\text{classical}} J(\nu_{lu})$ with



$$B_{lu}^{\text{classical}} = \frac{4\pi^2 e^2}{h\nu_{lu} m_e c} \quad (16)$$

it is thus convenient write

$$B_{lu} \equiv f_{lu} B_{lu}^{\text{classical}} \quad (17)$$

$$\sigma_{lu}(\nu) = \frac{\pi e^2}{m_e c} f_{lu} \phi(\nu) \quad (18)$$

where the dimensionless **oscillator strength** is

$$f_{lu} = \frac{m_e}{\pi e^2} \int \sigma_{lu}(\nu) d\nu = \frac{2m_e}{3\hbar^2 g_{le}^2} (E_u - E_l) \sum |d_{lu}|^2 \quad (19)$$

Q: what about f_{ul} ?

Einstein $g_l B_{lu} = g_u B_{ul}$, and since we have absorption

$$g_u f_{ul} = -g_l f_{lu} \quad (20)$$

so *emission oscillator strengths are negative*

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

$$\sum_{j \text{ final}} f_{ij} = 1 \quad (21)$$

where strong transitions have $f_{ij} \sim 1$
and *N-electron atoms have*

$$\sum_{j \text{ final}} f_{ij} = N \quad (22)$$

the *Thomas-Riche-Kuhn sum rule*

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Q: What if two states have no dipole moment: $d_{if} = 0$?

Beyond the Dipole

Our focus has been on electric dipole radiation where Larmor gives power $P_{E1} \sim \dot{d}^2$

but radiation also results from other time-changing charge multipoles

e.g., magnetic dipole $P_{M1} \sim \dot{m}^2$

electric quadrupole $P_{E2} \sim \ddot{Q}^2$

⇒ **higher multipoles can radiate when dipole forbidden ($d = 0$)!**

But there is a cost! for system of size a , freq ω :

- electric dipole $d \sim ea$, $P \sim \omega^2 e^2 a^2$
- magnetic dipole $m \sim Ia^2/c \sim e\omega a^2/c \sim d v/c$
- electric quadrupole $Q \sim ea^2$, $P \sim \omega^6 Q^2/c^2$

◦ magnetic dipole and electric quadrupole power down by $\sim (v/c)^2$

dipole radiation dominates unless forbidden

Electric Dipole 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 can have a nonzero quadrupole rate

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

$$\vec{d}_{fi} = e \int \psi_f^* \sum_{\text{electrons } j} \vec{r}_j \psi_i d^3x \quad (23)$$

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

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

thus if $\pi_i = \pi_f$, then

$$\vec{d}_{fi} \rightarrow \vec{d}'_{fi} = -e \int \psi_f^* \sum_j \vec{r}_j \psi_i d^3x = -\vec{d}_{fi} \quad (24)$$

and thus $\vec{d}'_{fi} = 0$: *no transitions when parity unchanged*

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

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

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

Q: implications?

the dipole operator only involves $\int u_a^* \vec{r}_j u_a d^3 r_j$
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:

$$\Delta\ell = \pm 1 \quad (25)$$

$$\Delta m = 0, \pm 1 \quad (26)$$

rules for *total angular momentum quantum numbers*

$$\Delta S = 0 \quad (27)$$

$$\Delta L = 0, \pm 1 \quad (28)$$

$$\Delta J = 0, \pm 1 \quad \text{except } J = 0 \text{ to } J = 0 \quad (29)$$

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!

Shape of Spectral Lines

consider a transition $u \rightarrow \ell$

Q: *most naïve guess for line profile $\phi(\nu)$*

real astrophysical spectra show wide range profiles
with nonzero observed widths

www: solar spectrum try $(\lambda_i, \Delta\lambda) = (6500, 100)\text{nm}; (4043, 5); (6704, 8)$

www: spectrum of mystery star

Q: *how is this star different from the Sun?*

hint—look at the continuum

www: spectrum of interstellar matter

Q: *how is this gotten? how do we know the lines are ISM?*

Q: *reason(s) for nonzero observed linewidths?*

Linewidths

naïvely: in transition $u \rightarrow \ell$, *energy conservation* requires $h\nu = E_u - E_\ell \equiv h\nu_{ul}$, so $\phi_{\text{naive}}(\nu) = \delta(\nu - \nu_{ul})$: *zero width!*

But real observed linewidths are nonzero, for several reasons

- *intrinsic width*

quantum effect, due to nonzero transition probability

- *thermal broadening*

thermal motion of absorbers \rightarrow Doppler shifts

- *collisional broadening*

absorber collisions add to transition probability

- *instrumental resolution*

real spectrographs have finite resolving power

$$R = \lambda/\Delta\lambda = \nu/\Delta\nu \stackrel{\text{Keck}}{\sim} 30,000$$

Intrinsic Linewidth

in real atoms, any excited state u has nonzero transition rate to lower levels: $\Gamma_u = 1/\tau_u$, with τ_u the state *lifetime*

thus: state u is only populated for timescales $\delta t \sim \tau_u$

but in quantum mechanics, over finite time Δt , *energy* only determined to within finite resolution

$$\Delta E \Delta t \gtrsim \frac{\hbar}{2} \quad (30)$$

the **energy-time uncertainty relation**

thus state u , level energy E_u has intrinsic spread

$$\delta E_u \sim \hbar/\tau_u = \hbar\Gamma_u$$

Q: *consequence for line profile?*

level u energy intrinsic spread $\delta E_u \sim \hbar/\tau_u = \hbar\Gamma_u$
 so for $u \rightarrow \ell$, transition frequency $\nu_{u\ell} = (E_u - E_\ell)/h$
 has natural or *intrinsic width* $\delta\nu_{n\ell} = \Gamma_{u\ell} = \Gamma_u + \Gamma_\ell$

level lifetimes related to Einstein A = decay rates:

$$\Gamma_u = \Gamma_{u \rightarrow \text{anything}} = \sum_{u \rightarrow \text{allowed } j} A_{uj} \quad (31)$$

where sum is over *all energetically allowed* transitions from u

for *damped classical oscillator*, damping $\Gamma \dot{x}$
 leads (PS10) to absorption cross section

$$\sigma_{lu}(\nu) = \frac{2\pi e^2}{m_e c} \frac{\Gamma/2}{(\omega - \omega_0)^2 + (\Gamma/2)^2} = \frac{\pi e^2}{m_e c} \frac{4\Gamma}{16\pi^2(\nu - \nu_0)^2 + \Gamma^2}$$

$\frac{1}{\infty}$ Q: behavior at $\nu = \nu_0$? $\nu \gg \nu_0$? what about a real atomic transition $u \rightarrow \ell$?

for a damped classical oscillator, we have

$$\sigma(\nu) = \pi e^2 / m_e c \phi(\nu) = B_{\text{classical}} \phi(\nu) \quad (32)$$

with profile function (normalized to $\int \phi(\nu) d\nu = 1$) of

$$\phi(\nu) = \frac{4\Gamma}{16\pi^2(\nu - \nu_0)^2 + \Gamma^2}$$

a real atomic transition $u \rightarrow \ell$ has same properties but with overall factor of oscillator strength:

$$\sigma_{ul}(\nu) = \pi e^2 / m_e c f_{ul} \phi_{ul}(\nu) = B_{\text{classical}} f_{ul} \phi(\nu) \quad (33)$$

with *Lorentzian* profile shape

$$\phi_{ul}^{\text{intrinsic}}(\nu) = \frac{4\Gamma_{ul}}{16\pi^2(\nu - \nu_{ul})^2 + \Gamma_{ul}^2}$$

full width at half-maximum: $(\Delta\nu)_{\text{FWHM}} = \Gamma_{ul}/2\pi$

note that line profiles and linewidths are often expressed in line-of-sight *velocity* units

motivated by the non-relativistic Doppler formula, we have

$$v(\nu) = \frac{\nu - \nu_{ul}}{\nu_{ul}} c \quad (34)$$

so that $v(\nu_{ul}) = 0$ at line center

thus the FWHM in velocity units is

$$(\Delta v)_{\text{FWHM}} = \frac{(\Delta \nu)_{\text{FWHM}}}{\nu_{ul}} c = \frac{\Gamma_{ul} \lambda_{ul}}{2\pi} \quad (35)$$

for optical and UV transitions, intrinsic linewidths generally small:

for Lyman- α , $(\Delta v)_{\text{FWHM}, \text{Ly}\alpha} = 0.0121$ km/s

20 Q: *implications?*

Thermal Linewidth

intrinsic linewidths are generally narrow
so other broadening effects can be important

thermal motion of atoms leads to Doppler shifts
of incident spectra as seen by the atoms
so absorption occurs “off resonance”

a *Gaussian distribution* of line-of-sight velocities
has velocity probability distribution

$$p(v) dv = \frac{1}{\sqrt{2\pi}\sigma_v} e^{-(v-v_0)^2/2\sigma_v^2} \equiv \frac{1}{\sqrt{\pi}b} e^{-(v-v_0)^2/b^2} dv \quad (36)$$

where v_0 is the bulk or “systemic” velocity along sightline
 $\sigma_v = b/\sqrt{2}$ is the *velocity dispersion*

Q: v_0 , σ_v , and b for thermal gas at rest??

a thermal gas at T of particles with mass m ,
and at rest in bulk, has

$$p_T(v) dv = \sqrt{\frac{m}{2\pi kT}} e^{-mv^2/2kT} \quad (37)$$

from which we identify

$$v_0 = 0 \quad (38)$$

$$\sigma_v = v_T \equiv \sqrt{\frac{kT}{m}} = 9.12 \text{ km/s} \left(\frac{T}{10^4 \text{ K}} \right) \left(\frac{1 \text{ amu}}{m} \right) \quad (39)$$

$$b = \sqrt{\frac{2kT}{m}} \quad (40)$$

Q: implications of numerical result?

Q: how to combine intrinsic and thermal broadening?

Voigt Profile

in general both intrinsic and thermal broadening present and so resulting line profile includes both effects

observed profile is *weighted average* of natural/intrinsic width with Doppler shifted center

$$\nu'_{ul} = \left(1 - \frac{v}{c}\right) \nu_{ul} \quad (41)$$

giving the **Voigt profile**

$$\phi_{\text{Voigt}}(\nu) = \frac{1}{\sqrt{\pi} b} \int e^{-v^2/b^2} \frac{4\Gamma_{ul}}{16\pi^2 [\nu - (1 - v/c)\nu_{ul}]^2 + \Gamma_{ul}^2} dv$$

integral has no simple analytic result

≈ Q: *simple and interesting approximation?*

we saw that for astrophysical situations, often intrinsic linewidths $(\Delta\nu)_{\text{FWHM}} \ll b$ thermal linewidths

simple approximation: intrinsic absorption is δ -function
 $\phi^{\text{intrinsic}}(\nu) \rightarrow \delta[\nu - (1 - v/c)\nu_{ul}]$

this gives a thermally-dominated Voigt profile

$$\phi_{\text{Voigt}}(\nu) \rightarrow \phi_T(\nu) = \frac{1}{\sqrt{\pi}} \frac{c}{\nu_{ul} b} \exp\left[-\frac{v(\nu)^2}{b^2}\right] \quad (42)$$

valid in the “*thermal core*” $\nu - \nu_{ul} \ll \Gamma_{ul}$, with

$$v(\nu) \equiv \left(\frac{\nu - \nu_{ul}}{\nu_{ul}}\right) c \quad (43)$$

for $\nu - \nu_{ul} \gg b$, in the “*damping wings*,” we have

$$\phi_{\text{Voigt}}(\nu) \approx \frac{1}{4\pi^2} \frac{\Gamma_{ul}}{(\nu - \nu_{ul})^2} \quad (44)$$

Q: sketch of $\phi_{\text{Voigt}}(\nu)$? of $\sigma_{ul}(\nu)$?

so imagine we can resolve a strong absorption line and measure the shape vs ν or λ to high precision

Q: what will we see?

Q: what will we learn?

Q: what if the line is not very strong?

Q: what if we only have moderate spectral resolution?

www: overview of the optical solar spectrum

Q: what are we seeing?

Collisional Linewidth

if particle densities are high, atomic collisions are rapid and can drive transitions $u \leftrightarrow \ell$

thus there is a nonzero collision rate Γ_{coll} per atom where $\Gamma_{\text{coll}} = n \sigma_{\text{coll}} v$

heuristically: this decreases excited state lifetimes and thus adds to energy uncertainty

so total transition rate is $\Gamma_{\text{int}} + \Gamma_{\text{coll}}$: collisions add damping, in density- and temperature-dependent way

26 thus collisional broadening a measure of density and temperature thus also know as “pressure broadening”

Director's Cut Extras

The Semiclassical Approach

Deriving the general Einstein A and B coefficient for transitions between two atomic states from first principles is a big job

we will take a “first-ish” principles approach
sketch what goes into the final result

we will work in the *semiclassical limit*

- treat the atomic states quantum mechanically
- but treat the radiation classically

→ i.e., in the limit of large photon occupation f

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good for getting Einstein B , bad for A Q : *why?*

Q : *but what's the workaround if we know B ?*

classical radiation \leftrightarrow large photon occupation f

absorption and stimulated emission: rate proportional to $\bar{J}_\nu = \int I_\nu d\Omega$

and recall $I_\nu = 2\nu^2/c^2 f$

\rightarrow so rate $\propto \int f d\Omega$ works even down to small f

spontaneous emission: involves single photons

correct analysis demands quantum treatment of radiation field

but luckily Einstein says: $A_{if} = (2h\nu_{if}^3/c^2)B_{fi}$

so if we find B , then use this to get A

29 thus: we will calculate *absorption*

So we will:

- treat atoms quantum mechanically, and
- treat radiation as a perturbation, in the form of an *external classical* EM field

Q: how do we describe formally the unperturbed system?

Q: how do we introduce the perturbation?

The Electromagnetic Hamiltonian

recall quantum mechanics: stationary atomic states $|n\rangle$ are governed by the time-independent Schrödinger equation

$$H_0 |n\rangle = E_n |n\rangle \quad (45)$$

in terms of wavefunctions $\psi_n(x) = \langle x|n\rangle$,

$$H_0 \psi_n = E_n \psi_n \quad (46)$$

with H_0 the **Hamiltonian** operator for the atom and includes the e -nucleus EM interactions and E_n is the energy of state n

add an external classical field with 4-potential (ϕ, \vec{A}) the **relativistic Hamiltonian** for an electron is

$$H = \sqrt{(c\vec{p} + e\vec{A})^2 + (m_e c^2)^2} - e\phi \quad (47)$$

for experts: gives right equation of motion in Hamilton's eqs
Q: limit of no field? non-relativistic limit?

The Relativistic Hamiltonian

full relativistic Hamiltonian for an electron

$$H = \sqrt{(c\vec{p} + e\vec{A})^2 + (m_e c^2)^2} - e\phi \quad (48)$$

non-relativistic limit: $cp \ll m_e c^2$

$$H = \frac{1}{2m_e} \left(\vec{p} + \frac{e\vec{A}}{c} \right)^2 - e\phi \quad (49)$$

$$= \frac{p^2}{2m_e} + \frac{e}{m_e c} \vec{A} \cdot \vec{p} + \frac{e^2 A^2}{2m_e c^2} - e\phi \quad (50)$$

plus a constant term $m_e c^2$ which we ignore Q: *why?*

note: we have used the “Coulomb gauge” for the perturbation

$$\nabla \cdot \vec{A} = 0 = \phi$$

we can write the non-relativistic Hamiltonian as

$$H = H_0 + H_1 + H_2 \quad (51)$$

where the *unperturbed atomic Hamiltonian* is H_0 ,
the perturbation *first order in A* is

$$H_1 = \frac{e}{m_e c} \vec{A} \cdot \vec{p} \quad (52)$$

and the perturbation *second order in A* is

$$H_2 = \frac{e^2 A^2}{2m_e c^2} \quad (53)$$

there is a beautiful physical interpretation of the terms:

- H_1 describes one-photon emission processes
- H_2 describes two-photon emission processes

Q: relative importance of the two terms?

order-of-magnitude estimate of the ratio of terms, in H atom:

$$\eta = \frac{H_1}{H_2} \sim \frac{epA/m_e c}{e^2 A^2/m_e c^2} \sim \frac{ev/c}{\alpha^2 a_0 A} \quad (54)$$

external electric field $E \sim 1/c \text{ partial}_t A \sim \nu/c A$

and in H: $v/c \sim \alpha$, and $h\nu \sim e^2/a_0$ so $h\nu/c \sim \alpha/a_0$

$$\eta^2 \sim \frac{h\nu}{a_0^3 E^2} \quad (55)$$

but $E^2/h\nu \sim n_{\text{ph}}$, the photon density in the external field

$$\eta^2 \sim \frac{1}{n_{\text{ph}} a_0^3} \sim \left(\frac{10^{25} \text{ photons/cm}^3}{n_{\text{ph}}} \right) \quad (56)$$

at the Sun's surface $n_{\text{ph}} \sim 10^{12}/\text{cm}^3$

34 lesson: $\eta \gg 1$ for (almost) all astro applications
 → *ignore the two-photon term H_2*

The Transition Probability

we want the *probability* for transition $i \rightarrow f$
where the unperturbed wavefunctions satisfy $H_0 \psi_k = E_k \psi_k$ this
probability is *time-dependent*

the perturbing field generates nonzero amplitude for states $n \neq i$
so write time-dependent wavefunction as

$$\psi(t) = \sum_k a_k(t) \psi_k e^{-iE_k t/\hbar} \quad (57)$$

Q: $a_k(t)$ for system without perturbation? behavior with perturbation?

for at time-dependent potential, standard quantum mechanics gives

the probability P_{fi} to go from state $i \rightarrow f$

$$P_{fi} = w_{fi} t \quad (58)$$

with t the time the perturbation acts

and the *transition probability per unit time*

$$w_{fi} = \frac{4\pi^2 |H(\omega_{fi})|^2}{\hbar^2 t} \quad (59)$$

where $H_{fi}(\omega) = (2\pi)^{-1} \int_0^t H_{fi}(t') e^{i\omega t'} dt'$

with the *matrix element* $H_{fi} = \int \psi_f^* H_1 \psi_i d^3x$

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

if we have multiple atomic electrons, then perturbation is sum

$$H_1 = \frac{e}{m_e c} \sum_j \vec{A} \cdot \vec{p}_j = \frac{ie\hbar}{m_e c} \vec{A} \cdot \sum_j \nabla_j \quad (60)$$

let the perturbing field have:

- $\vec{A}(\vec{r}, t) = \vec{A}(t) e^{i\vec{k}\cdot\vec{r}}$, with
- $\vec{A}(t') = 0$ outside of $(0, t)$

then the Fourier transform of the matrix element is

$$H_{fi} = \vec{A}_{fi}(\omega_{fi}) \cdot \frac{ie\hbar}{c} \langle f | e^{i\vec{k}\cdot\vec{r}} \sum_j \nabla_j | i \rangle \quad (61)$$

where $\langle f | e^{i\vec{k}\cdot\vec{r}} \sum_j \nabla_j | i \rangle = \sum_j \int \psi_f^* \nabla_j \psi_i d^3x$ is *time-independent*

write $\vec{A} = A \mathbf{e}$ with unit polarization vector \mathbf{e} :

$$w_{fi} = \frac{4\pi^2 e^2}{m_e c^2 t} |A(\omega_{fi})|^2 \left| \langle f | e^{i\vec{k}\cdot\vec{r}} \mathbf{e} \cdot \sum_j \nabla_j | i \rangle \right|^2 \quad (62)$$

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note that $w_{fi} \propto |A(\omega_{fi})|^2$; related to intensity

recall: *integrated* intensity is

$$I = \langle \vec{S} \cdot \vec{n} \rangle = \frac{c}{4\pi t} \int E^2(t) dt = \frac{c}{t} \int |E(\omega)|^2 dt \quad (63)$$

to *monochromatic intensity*

$$J_\omega = \frac{c |E(\omega)|^2}{t} \quad (64)$$

and since $\vec{E} = -1/c \partial_t \vec{A} = -i\omega/c \vec{A}$

$$J_\omega = \frac{\omega^2}{c t} |A(\omega)|^2 \quad (65)$$

and thus we see that $w_{fi} \propto |A(\omega)|^2$

implies $w_{fi} \propto J_\omega$, as expected for absorption!

∞ also: what about w_{if} , for $f \rightarrow i$?

finally, for the transition probability per unit time for $i \rightarrow f$ we have

$$w_{fi} = \frac{4\pi^2 e^2}{m_e c^2} \frac{J(\omega_{fi})}{\omega_{fi}^2} \left| \langle f | e^{i\vec{k}\cdot\vec{r}} \mathbf{e} \cdot \sum_j \nabla_j | i \rangle \right|^2 \quad (66)$$

about the probability for $f \rightarrow i$?
 the same except now $\langle i | e^{i\vec{k}\cdot\vec{r}} \mathbf{e} \cdot \sum_j \nabla_j | i \rangle$
 but integrating by parts, can show

$$w_{if} = w_{fi} \quad (67)$$

principle of detailed balance

39 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: $\vec{k} \cdot \vec{r} \sim ka_0 \sim a_0 \Delta E/\hbar c \sim Zv/c \ll 1$

thus we write

$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k} \cdot \vec{r} - \frac{1}{2}(\vec{k} \cdot \vec{r})^2 + \dots \quad (68)$$

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 $e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} + \dots$

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

$$\int \psi_f^* \mathbf{e} \cdot \sum_j \nabla_j \psi_i d^3x = \frac{1}{i\hbar} \langle \mathbf{e} \cdot \hat{\mathbf{p}}_j \rangle_{fi} \quad (69)$$

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

$$\hat{r}_j \hat{p}_j^2 - \hat{p}_j^2 \hat{r}_j = 2 i \hbar \hat{p}_j \quad (70)$$

and so given the atomic Hamiltonian

$$\hat{H}_0 = \frac{1}{2m_e} \sum_j \hat{\vec{p}}_j^2 + V(\hat{\vec{r}}_1, \hat{\vec{r}}_2, \dots, \hat{\vec{r}}_N) \quad (71)$$

we have

$$\hat{\vec{r}}_j \hat{H}_0 - \hat{H}_0 \hat{\vec{r}}_j = i \frac{\hbar \hat{\vec{p}}_j}{m_e} \quad (72)$$

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

and so we have

$$\frac{1}{i\hbar} \langle \mathbf{e} \cdot \hat{\vec{p}}_j \rangle_{fi} = \frac{m_e}{\hbar^2} \int \psi_f^* \mathbf{e} \cdot (\vec{r}_j H_0 - H_0 \vec{r}_j) \psi_i d^3x \quad (73)$$

$$= \frac{m_e(E_i - E_f)}{\hbar^2} \int \psi_f^* \mathbf{e} \cdot \vec{r} \psi_i d^3x \quad (74)$$

thus the transition rate is

$$w_{fi} = \frac{4\pi^2}{\hbar^2 c} \left| \langle \mathbf{e} \cdot \vec{d} \rangle_{fi} \right|^2 \mathcal{J}(\omega_{fi}) \quad (75)$$

where the **electric dipole operator** is

$$\vec{d} = e \sum_j \mathbf{r}_j \quad (76)$$

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

$$\langle |\mathbf{e} \cdot \vec{d}_{fi}|^2 \rangle = \frac{1}{3} |d_{fi}|^2 \quad (77)$$

where

$$|d_{fi}|^2 \equiv \vec{d}_{fi}^* \cdot \vec{d}_{fi} = |(d_x)_{fi}|^2 + |(d_y)_{fi}|^2 + |(d_z)_{fi}|^2 \quad (78)$$

Electric Dipole Transition Rate

the electric dipole transition rate is thus

$$\langle w_{fi} \rangle = \frac{4\pi^2}{3c\hbar^2} |d_{fi}|^2 \mathcal{J}(\omega_{fi}) \quad (79)$$

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

$$\langle w_{\ell u} \rangle = B_{\ell u} J(\nu_{\ell u}) \quad (80)$$

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

$$\langle w_{\ell u} \rangle = \frac{1}{2} B_{\ell u} \mathcal{J}(\omega_{\ell u}) \quad (81)$$

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

Einstein Coefficients

the Einstein coefficients in the electric dipole approximation are:

- true *absorption*

$$B_{lu} = \frac{8\pi^2}{3c\hbar^2} |d_{lu}|^2 = \frac{32\pi^4}{3ch} |d_{lu}|^2 \quad (82)$$

for *non-degenerate atomic levels* with $g_l = g_u = 1$ we have

- *stimulated emission*

$$B_{ul} = B_{lu} \quad (83)$$

- *spontaneous emission*

$$A_{ul} = \frac{2\nu^3}{c^2h} B_{lu} = \frac{64\pi^4 \nu_{ul}^3 |d_{ul}|^2}{3c^3h} \quad (84)$$

this gives (at least in principle) a direct means to connect

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the radiative coefficients j_ν and α_ν

to the atomic properties encoded in the dipole moment d_{ul}