Atomic, Molecular and Optical Physics

Hand-written Lecture Notes

C. Bulutay

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This is a rudimentary script that emerged out of delivering this course at Bilkent University. The only originality would be my (skewed) handwriting! It is a linear combination of a number of valuable books and lecture notes, most of which I hope are listed below. Please, double check any equation before using in a serious work.

Books:

- Wendell T., III Hill and Chi H. Lee, *Light-Matter Interaction: Atoms and Molecules in External Fields and Nonlinear Optics* (Wiley, 2007)
- M. Auzinsh, D. Budker, and S. M. Rochester, *Optically Polarized Atoms* (Oxford, 2010)
- Gilbert Grynberg, Alain Aspect, and Claude Fabre, *Introduction to Quantum Optics* (Cambridge, 2010)
- W. Demtröder, *Atoms, Molecules and Photons* (Springer, 2006)
- Claude Cohen-Tannoudji, Bernard Diu, Frank Laloe, *Quantum Mechanics* (Wiley, 1977)
- C. J. Foot, *Atomic Physics* (Oxford, 2005)
- Mark Fox, *Optical Properties of Solids* (Oxford, 2001)
- B. H. Bransden and C. J. Joachain, *Physics of Atoms and Molecules* (Prentice Hall, 2003)
- Wolfgang Nolting and Anupuru Ramakanth, *Quantum Theory of Magnetism* (Springer, 2006)
- Patrik Fazekas, *Lecture Notes on Electron Correlation and Magnetism* (World Scientific, 1999)
- W. J. Thompson, *Angular Momentum* (Wiley, 2004)

Online Resources/Lecture Notes:

- Wikipedia (a large number of entries)
- Richard Fitzpatrick, Quantum Mechanics
- Wim Ubachs, Atomic Physics
- Daniel Adam Steck, Quantum and Atom Optics
- W. C. Martin and W. L. Wiese, Atomic Spectroscopy
- Selçuk Aktürk, Lasers & Photonics
- George Siopsis, Quantum Mechanics
- Sumner Davis, Optical Pumping

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Part-I: **Atoms**

Hydrogen-Like Ion (Main Results)

Ions with a single e^- + nucleus

Eg: H, He^+, Li^{++}, Be^{+3}, etc. all multiply-charged ions with nuclear charge Ze that have all but one e^- removed

This defines an ion Hamiltonian $\hat{H}$ that goes into time-dep. Schrödinger eqn.

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r},t) = \hat{H}\, \Psi(\vec{r},t)$$

Seeking for stationary state $\Psi(\vec{r},t) = e^{-iEt/\hbar}\, \psi(\vec{r})$, this reduces to

$$\hat{H}\, \psi(\vec{r}) = E\, \psi(\vec{r})$$

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m_e} + V(\vec{r}) \xrightarrow{\text{Coulomb}} V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad \text{... in SI units}$$

radial e-ion (attractive) potential

$\vec{p} \to -i\hbar\vec{\nabla}$ ... in coordinate representation ($\vec{r}$-space)

This is valid for infinitely massive nucleus.

To account for finite nuclear mass m_N, replace $m_e \to \mu$

where $\frac{1}{\mu} \equiv \frac{1}{m_e} + \frac{1}{m_N}$ ... reduced mass of e^--ion system

In other words, here we are analyzing the relative dynamics ⇒ internal structure of H-like ion.

How significant is the effect of finite nuclear mass?

Comparing hydrogen and deuterium ($D \equiv {}^2_1H$) → stable isotope, p+n; abundance: 1 out of 6420 H

there are small but significant differences in their spectra.

Properties of heavy water (D_2O) differ very noticeably from those of ordinary water (H_2O); the freezing point is about 3.8°, the boiling-point about 1.4° higher; the density is as much as 11 % greater than that of H_2O. The velocities of reaction in these show considerable changes. Thus, an entirely new branch of chemistry has emerged, which is also important for biology.

Note that <u>not</u> a great deal of discrepancies bet. H and D are attributable to mass difference. Their nuclear spins also make some difference: $I_H = 1/2$ vs. $I_D = 1$. D_2O is used in liquid NMR so as not to mask the H nuclei of the sample.

Tritium = 1p + 2n is not stable (half-life ~ 12.3 years)



Positronium: atom with e^+ & e^- where both masses are equal, all energy levels (to be calculated for $m_N \to \infty$) become <u>roughly</u> a half of H values.

Singlet state ($^1S_0$) – lifetime 125 ps (2 γ quanta)

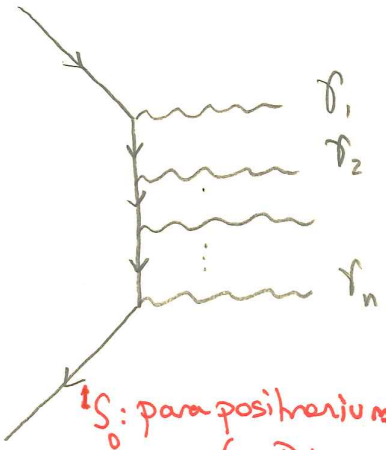
Triplet state ($^3S_1$) – lifetime 142 ns (3 γ quanta)

Positronium Annihilation

Charge conjugation invariance prescribes the selection rule

particle → antiparticle

$$C|p\rangle = |\bar{p}\rangle \pm |p\rangle$$



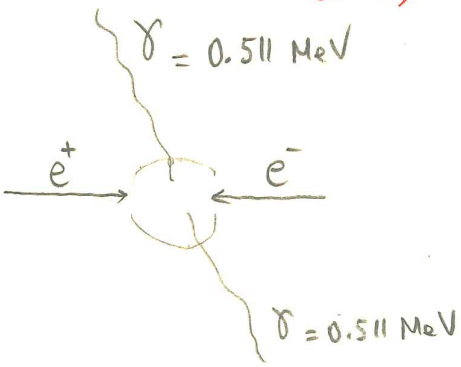
For positronium → n γ decay

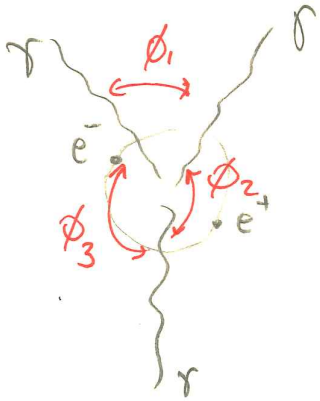
$$(-1)^{l+s} = (-1)^n$$

Since the $e^+ - e^-$ overlap only for $l=0$, S

$^1S_0$: parapositronium (p-Ps) ← $s=0$ → decays via even # photons (typically 2)

$^3S_1$: orthopositronium (o-Ps) ← $s=1$ → decays via odd # photons (typ. 3)





$$E_n = -\frac{6.8}{n^2}\ \text{eV}$$

Highest probability is when

$$\phi_1 = \phi_2 = \phi_3 = 120^\circ$$

2nd order QED calculation for o-Ps lifetime was achieved in the year 2000!

Thus, the Schrödinger eqn. takes the form with reduced mass, μ

$$\nabla^2\psi(\vec{r}) + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi(\vec{r}) = 0$$

(Ze: ionic charge)

Laplacian in spherical coord

$$\nabla^2 \to \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Separable form for $\psi(\vec{r})$:

$$\psi_{nlm}(\vec{r}) = R_{nl}(r)\, Y_{lm}(\theta,\phi)$$

(Y_{lm}: solid Y)

(n, l will be appearing as separation const's in eig. value eq's)

Here, $Y_{\ell m}(\theta,\phi)$ refers to a quantization axis which is arbitrary when $V(\vec{r}) \to V(|\vec{r}|)$, for such cases (as in here) angular momentum is conserved (causes m degeneracy). When the spherical symm. is broken there will be a preferred direction in space and $\vec{l}$ will not be conserved in general. This occurs in diatomic molecules (e.g. H_2), or when an atom is placed in an external field.

However, in both cases: 

the projection of $\vec{l}$ along the axis of symmetry will often remain conserved.

Angular part of wf $\longrightarrow$ (tesseral) spherical harmonics

$$Y_{lm}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}\; \underbrace{P_l^m(\cos\theta)}_{\text{polar dep.}}\; \underbrace{e^{im\phi}}_{\text{azimuthal dependence}},$$

where the Associated Legendre Polynomials are (a poly. of degree l)

$$P_l^m(x) = \frac{1}{2^l l!}\left(1-x^2\right)^{m/2}\frac{d^{l+m}}{dx^{l+m}}\left(x^2-1\right)^l, \quad m = -l, \ldots, 0, \ldots, l$$

Orthogonality:

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\; Y^*_{l'm'}(\theta,\phi)\, Y_{lm}(\theta,\phi) = \delta_{ll'}\,\delta_{mm'}$$

Some low-order spherical harmonics:

$$Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}, \qquad Y_{10}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{1,\pm1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\; e^{\pm i\phi}, \ \ldots$$

NB: To work with real wf's actually two linear superpositions of $Y_{l,\pm m}$ states are preferred.

e.g. $\underbrace{\frac{1}{\sqrt{2}}\left[Y_{1,1} + Y_{1,-1}\right]}_{p_x}$, $\underbrace{\frac{1}{i\sqrt{2}}\left[Y_{1,1} - Y_{1,-1}\right]}_{p_y}$, $\underbrace{Y_{10}}_{p_z}$

Then, radial part of wf $R_{nl}(r)$ needs to satisfy

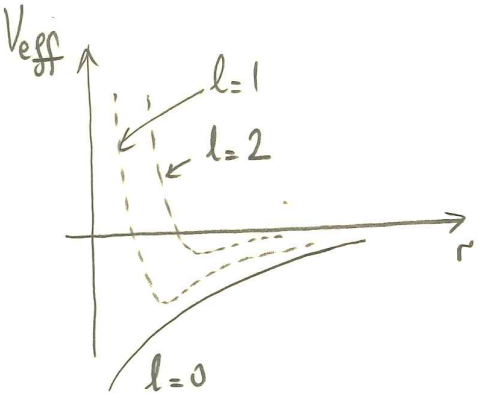
$$\left\{ \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \frac{2\mu}{\hbar^2}\left[E - V_{eff}(r;l)\right] \right\} R_{nl}(r) = 0$$

where $V_{eff}(r;l) \equiv -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)}{r^2}\frac{\hbar^2}{2\mu}$

a legacy of the angular part or the radial part via separation of var's technique.

$\Downarrow$

effective potential



$\rightarrow$ Potentials for $l \neq 0$ became repulsive at the origin. This causes the wf for states $l \neq 0$ to vanish at the origin. For $l=0$ the wf does not have to vanish at the origin (more on this, later)

The exact solution for the radial part can be written either using the confluent hypergeometric function as

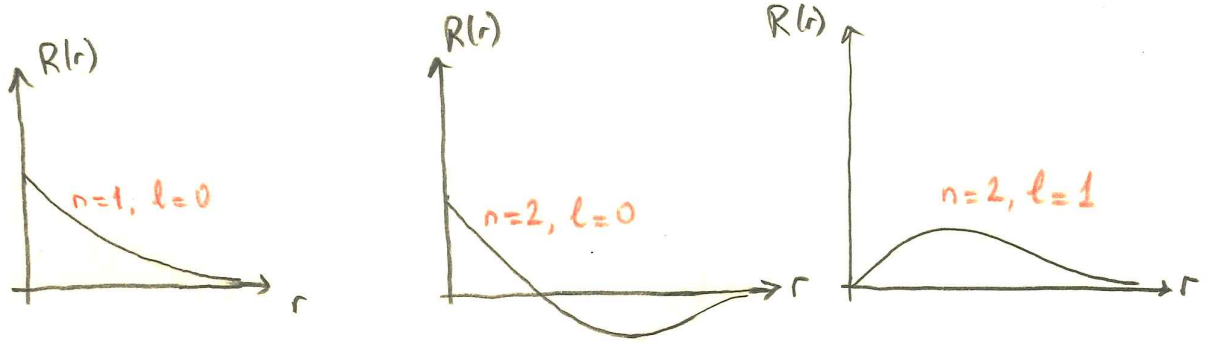
$$R_{nl}(r) = \frac{1}{(2l+1)!}\sqrt{\frac{(n+l)!}{2n(n-l-1)!}}\left(\frac{2Z}{n a_B}\right)^{3/2} e^{-\frac{Zr}{n a_B}}\left(\frac{2Zr}{n a_B}\right)^{l} F\left(l+1-n, 2l+2; \frac{2Zr}{n a_B}\right)$$

$$a_B \equiv \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{\mu} \xrightarrow[\mu \to m_e]{\text{but commonly}} \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{m_e} \quad \ldots \text{ Bohr radius}$$

or using the associated Laguerre polynomials as:

$$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}\left(\frac{2Z}{na_B}\right)^{3/2} e^{-\frac{Zr}{na_B}}\left(\frac{2Zr}{na_B}\right)^{l} \mathcal{L}_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_B}\right)$$

NB: $\mathcal{L}_n^m(x)$ is a polynomial of order n; $\mathcal{L}_n^k(x) = (-1)^k \frac{d^k}{dx^k}\mathcal{L}_{n+k}(x)$



Some low-order radial fn's:

$$R_{10}(r) = 2\left(\frac{Z}{a_B}\right)^{3/2} e^{-Zr/a_B},$$

$$R_{20}(r) = 2\left(\frac{Z}{2a_B}\right)^{3/2}\left(1-\frac{Zr}{2a_B}\right) e^{-Zr/(2a_B)},$$

$$R_{21}(r) = \frac{2}{\sqrt{3}}\left(\frac{Z}{2a_B}\right)^{3/2}\left(\frac{Zr}{2a_B}\right) e^{-\frac{Zr}{2a_B}}$$

Orthogonality: $\int_0^\infty R_{nl}(r)\, R_{n'l'}(r)\, r^2\, dr = \delta_{n,n'}\,\delta_{ll'}$

Remarks:

* $R_{nl}(r=0)$ is finite for $l=0$, while it vanishes for $l \neq 0$
* The # times the wf crosses the axis (# zeros) = $\underbrace{n-l-1}$ stemming from $\mathcal{L}_{n-l-1}(\cdot)$ (not counting the origin)

* As n increases, $\langle r \rangle$ shifts to larger r

$$\underbrace{\langle r^\gamma \rangle_{nlm}}_{\langle \Psi_{nlm} | r^\gamma | \Psi_{nlm} \rangle} \equiv \int_0^\infty r^{2+\gamma} R_{nl}^2(r)\, dr \quad \leftarrow \text{ to be needed in matrix elements}$$

$$\langle r \rangle_{nl} = \frac{a_B}{2Z}\left[3n^2 - l(l+1)\right], \quad \langle r^{-1} \rangle_{nl} = \frac{Z}{a_B n^2}$$

$$\langle r^2 \rangle_{nl} = \frac{a_B^2 n^2}{2Z^2}\left[5n^2 + 1 - 3l(l+1)\right], \quad \langle r^{-2} \rangle_{nl} = \frac{Z^2}{a_B^2 n^3 \left(l+\frac{1}{2}\right)}$$

$$\langle r^3 \rangle_{nl} = \frac{a_B^3 n^2}{8Z^3}\left[35n^2(n^2-1) - 30n^2(l+2)(l-1) + 3(l+2)(l+1)(l-1)\right]$$

$$\langle r^{-3} \rangle_{nl} = \frac{Z^3}{a_B^3 n^3 (l+1)(l+1/2)l}$$

With the radial and angular parts defined as above,

$\Psi(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi)$ becomes normalized as

$$\int |\Psi_{nlm}(r,\theta,\phi)|^2 r^2 \sin\theta\, d\theta\, d\phi\, dr = 1$$

NB: In some texts, the radial part is defined as rR, hence their normalization eqn. differs from this.

Hellmann - Feynman Theorem

When a parameter λ of the Hamiltonian is (or promoted to being) a continuous variable, then for $H(\lambda)|\gamma,\lambda\rangle = E_\gamma(\lambda)|\gamma,\lambda\rangle$

we have

$$\langle \gamma,\lambda| \frac{\partial H(\lambda)}{\partial \lambda} |\gamma,\lambda\rangle = \frac{\partial E_\gamma(\lambda)}{\partial \lambda}$$

Proof: Based on the normalization of eigenkets: $\langle \gamma,\lambda|\gamma,\lambda\rangle = 1$

So, if we differentiate $\langle \gamma,\lambda| H(\lambda) |\gamma,\lambda\rangle = E_\gamma(\lambda)$ wrt λ

$$\left(\frac{\partial}{\partial\lambda}\langle\gamma,\lambda|\right) \overbrace{H(\lambda)|\gamma,\lambda\rangle}^{E_\gamma(\lambda)|\gamma,\lambda\rangle} + \overbrace{\langle\gamma,\lambda| H(\lambda)}^{E_\gamma(\lambda)\langle\gamma,\lambda|} \frac{\partial}{\partial\lambda}|\gamma,\lambda\rangle +$$

$$\hookrightarrow \langle \gamma,\lambda| \frac{\partial H(\lambda)}{\partial\lambda} |\gamma,\lambda\rangle = \frac{\partial E_\gamma(\lambda)}{\partial\lambda}$$

$$\therefore E_\gamma(\lambda) \underbrace{\frac{\partial}{\partial\lambda}\left(\underbrace{\langle\gamma,\lambda|\gamma,\lambda\rangle}_{1 \text{ (indep. of } \lambda)}\right)}_{0} + \langle\gamma,\lambda| \frac{\partial H(\lambda)}{\partial\lambda} |\gamma,\lambda\rangle = \frac{\partial E_\gamma(\lambda)}{\partial\lambda}$$

QED

The Hellmann-Feynman theorem, when applicable greatly simplifies the radial expectations, turning the labor to simple derivatives!

The radial part of the H-like ion is given by

$$H_r = -\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

with the corresponding eigenvalue $E_{kl}(\lambda) = -\frac{1}{2(k+l+1)^2}\frac{Z^2\mu e^4}{(4\pi\varepsilon_0\hbar)^2}$

where $k \in \mathbb{Z}$ that determines when the series obtained in the solution of the radial eqn. terminates (see D.J. Griffiths IQM), and $n = k+l+1$ is the well-known principal quantum number

To extend the scope of Hellmann-Feynman theorem toward other radial dependences, the following commutator becomes very handy.

$$\left\langle \left[\frac{d}{dr}, H(\lambda)\right] \right\rangle_{nl} = 0$$

Examples on Hellmann-Feynman Theorem

* For $\left\langle \frac{1}{r} \right\rangle_{nl}$, we can promote Z to a fake continuous variable.

$\Rightarrow \lambda = Z$ so that $-\frac{4\pi\varepsilon_0}{e^2}\frac{\partial}{\partial Z} H_r(Z) = \frac{1}{r}$

So, we only need to work out the derivative $-\frac{4\pi\varepsilon_0}{e^2}\frac{\partial}{\partial Z} E_{kl}(Z)$

$$\frac{4\pi\varepsilon_0}{e^2}\frac{1}{2(\underbrace{k+l+1}_{n})^2}\frac{2Z\mu e^4}{(4\pi\varepsilon_0\hbar)^2} = \frac{Z}{n^2}\underbrace{\frac{e^2 m_e}{4\pi\varepsilon_0\hbar^2}}_{\frac{1}{a_B}}\frac{\mu}{m_e}$$

$$\therefore \left\langle \frac{1}{r} \right\rangle_{nl} = \frac{Z}{a_B n^2}\cdot\frac{\mu}{m_e}$$

* For $\left\langle \frac{1}{r^2} \right\rangle_{nl}$ choose $l \to \lambda$ the "fake" cont. var.

$$\Rightarrow \left\langle \frac{1}{r^2} \right\rangle_{nl} = \left\langle -\frac{2\mu}{\hbar^2(2l+1)}\frac{\partial H_r}{\partial l} \right\rangle_{nl} \overset{H\text{-}F}{=} -\frac{2\mu}{\hbar^2(2l+1)}\frac{\partial}{\partial l}E_{kl}(l)$$

$$= \frac{2\mu}{\hbar^2(2l+1)}\frac{1}{2}\cdot\frac{Z^2\mu e^4}{(4\pi\varepsilon_0\hbar)^2}\cdot -2\cdot(k+l+1)^{-3}$$

$$= \frac{Z^2\mu^2 e^4}{(4\pi\varepsilon_0\hbar^2)^2}\frac{1}{(l+\frac{1}{2})n^3} = \left(\frac{Z\mu}{m_e}\right)^2\frac{1}{n^3(l+\frac{1}{2})a_B^2}$$

The corresponding energy levels depend only on the principal quantum number, n:

$$E_n = -\frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{Z^2\mu}{n^2\hbar^2} = -hc\,\frac{Z^2}{n^2}\,\mathcal{R}_M < 0 \quad \text{... Bound state}$$

where $\mathcal{R}_M = \mathcal{R}_\infty \left(1 + \frac{m_e}{m_N}\right)^{-1}$, $\mathcal{R}_\infty \equiv \frac{1}{4\pi}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{\hbar c a_B}$

Rydberg constant for an infinitely massive nucleus

$\mathcal{R}_\infty = 109737.31568549(83)\ \text{cm}^{-1}$ ⟶ in wave numbers

$\mathcal{R}_H = 109678\ \text{cm}^{-1}$, $\mathcal{R}_D = 109707\ \text{cm}^{-1}$

Atomic Units (more precisely, Hartree Atomic Units)

Up to now we used the SI units. The theorists, however, prefer the so-called atomic units, where equations become much simpler (most constants disappear) and one works in the natural units for AMO physics.

In atomic units:

base units:
- charge $\xrightarrow{\text{unit}}$ $e > 0$
- mass ⟶ m_e (free e^-)
- angular momentum ⟶ $\hbar$
- Coulomb const ⟶ $\frac{1}{4\pi\varepsilon_0}$ (for SI)

derived units:
- length ⟶ a_B (Bohr radius)
- energy ⟶ E_h (Hartree)
- ⋮

Speed of light, $c = \frac{1}{\alpha}$ in a.u.

SI equivalents of (Hartree) atomic units:

$e = 1.609 \cdot 10^{-19}$ C $a_B = 0.529 \cdot 10^{-10}$ m

$m_e = 9.109 \cdot 10^{-31}$ kg $E_h = 4.360 \cdot 10^{-18}$ J

$\hbar = 1.055 \cdot 10^{-34}$ J.s

To switch to Atomic Units:

* Gaussian (cgs) $\rightarrow$ (Hartree) Atomic Units: $e = m_e = \hbar = 1$

* SI $\rightarrow$ (Hartree) Atomic Units: $\frac{e}{\sqrt{4\pi\varepsilon_0}} = m_e = \hbar = 1$

Remarks:

* Only a few of the physical constants can be set to 1 in a natural unit system so as not to give rise to contradictions. Also, a constant like the fine-structure constant α cannot be set to 1 as it is dimensionless!

* The disadvantage of such natural units is that equations can become more ambiguous where (SI) dimensions could resolve such cases.

Rydberg Atomic Units: Gaussian (cgs) $\rightarrow$ Ryd. A.U.: $\underbrace{\frac{e}{\sqrt{2}} = 2m_e = \hbar = k_B}_{1}$

less common unit Hartree A.U.

$1\ \mathrm{Ry} = \frac{1}{2}\ \mathrm{Ha} = 13.60569172(53)\ \mathrm{eV}$ ($1\ \mathrm{Ha} \simeq 27.21\ \mathrm{eV}$)

$1\ \mathrm{Ry} = hc\,\mathcal{R}_\infty$, $\mathcal{R}_\infty = 109737.31568549(83)\ \mathrm{cm}^{-1}$

↑ Rydberg energy unit ↑ Rydberg constant

Wavenumbers → inverse wavelengths ($1/\lambda$) and not ~~$k = 2\pi/\lambda$~~

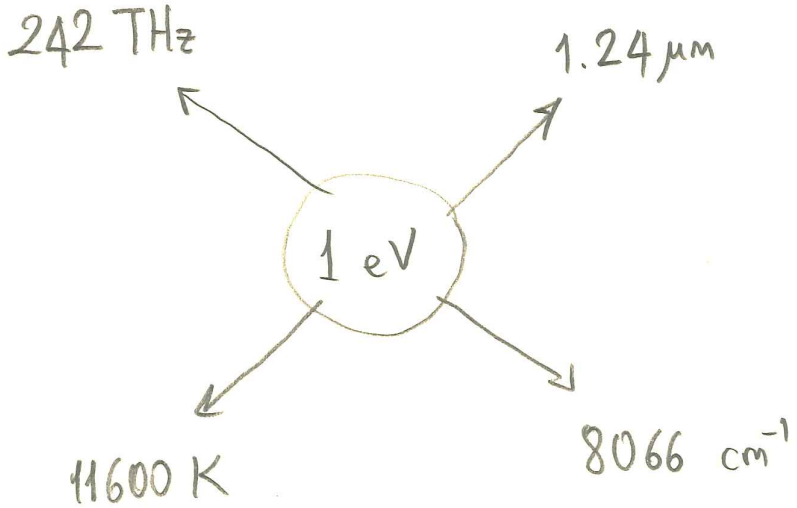
The experimentalists (mainly spectroscopists) work with wavenumbers rather than energies. Furthermore, they set the energy reference to the ground state energy and work with positive numbers, as opposed to theorists who set the energy reference to ionization threshold.

The correspondence for the first three states of H are:

$n \rightarrow$	1	2	3	∞
$cm^{-1} \rightarrow$	0	82259.07	97492.23	109678.8
a.u. →	−0.50	−0.12	−0.06	0

Conversion Among Popular Units:

More important than Schrödinger Eqn!



NB: None of these are in atomic or SI units, but these are popular units in use

Ex: The optical phonon "energy" is quoted in Raman scattering as $520\ cm^{-1}$ (corresponds to Si LO mode).

What's the corresponding freq. of osc. in Hz and in meV?

Solution: $\frac{1}{\lambda} = 520\ cm^{-1}$, $\nu = \frac{c}{\lambda}$, $E = h\nu$

$\Rightarrow \quad \nu \simeq 3.10^{10}\ \frac{cm}{s} \cdot 520\ cm^{-1}$, $\quad E = \frac{520}{8066}\ eV$

$\simeq 15.6\ THz \qquad\qquad \simeq 64\ meV$

Expressions in SI for a_B and E_h:

$$a_B = \frac{4\pi\varepsilon_0 \hbar^2}{Z m_e e^2} = \frac{\alpha}{Z 4\pi R_\infty}$$

where $\alpha = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\hbar c} = \frac{1}{137.035}$ ... fine-structure constant

In QED, α plays the role of a coupling const. representing the strength of interaction bet. $\bar{e}$'s & photons. Its value cannot be predicted by theory, and it is one of the 20-odd "external" parameters in SM

$\alpha \ll 1$ enables perturbation in QED $\rightarrow$

$$E_h = \frac{e^2}{4\pi\varepsilon_0 a_B} = 2R_\infty hc = \alpha^2 m_e c^2$$

NB: 1 Ha (or 1 a.u.) is the potential energy of two elementary charges (e) separated by a Bohr radius (a_B)

Ex: What's the a.u. for time?

This can be derived from the existing a.u., for instance using angular momentum and energy as

$$\text{time (a.u.)} = \frac{\hbar}{E_h} \xrightarrow{[SI]} \frac{4\pi\varepsilon_0 a_B \hbar}{e^2} \frac{\hbar}{m_e} \frac{m_e}{\hbar} = \frac{a_B^2 m_e}{\hbar}$$

(a_B)

Numerically SI value for time (a.u.) $= 2.41889 \cdot 10^{-17}$ s

Similarly, you can work out other derived a.u. like speed, force, pressure,...

Effective Atomic Units (Aside)

When working with semiconductors it is advantageous to use effective a.u. to absorb the band effective mass (m^*) and background DC dielectric constant (ε_{DC}). An SI expression is converted to effective a.u. by:

$$m^* \to 1, \quad \frac{e}{\sqrt{4\pi\varepsilon_{DC}}} \to 1, \quad \hbar \to 1$$

This reflects itself in all relevant quantities of a.u. $\to$ effective a.u.

$$a_B \to a_B^* \xrightarrow{[SI]} \frac{4\pi\varepsilon_{DC}\hbar^2}{e^2 m^*} \quad \ldots \text{Increases from } \sim 0.5\text{A to a few nm}$$

$$Ry \to Ry^* \xrightarrow{[SI]} \frac{e^2}{8\pi\varepsilon_{DC} a_B^*} \quad \ldots \text{Decreases from } \sim 13.6\text{eV to a few meV}$$

Ex. Convert H-like Schrödinger Eqn. to Atomic Units

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Z e^2}{4\pi\varepsilon_0 r} \right] \psi = E \psi$$

Divide by E_h to convert to a.u.

$$\left[-\frac{4\pi\varepsilon_0 a_B}{e^2} \frac{\hbar^2}{2\mu} \frac{m_e}{m_e} \nabla^2 - \frac{Z e^2}{4\pi\varepsilon_0 r} \frac{4\pi\varepsilon_0 a_B}{e^2} \right] \psi = \frac{E}{E_h} \psi$$

(a_B appears in the numerator of $\frac{4\pi\varepsilon_0 a_B}{e^2}$ and $\frac{\hbar^2}{2\mu}$)

$$\frac{a_B}{r} = \frac{1}{\tilde{r}}, \qquad \tilde{E} \text{ in a.u.}$$

$$\nabla^2 \to \frac{\partial^2}{\partial x_i^2}, \qquad a_B^2 \nabla^2 \to \frac{\partial^2}{\partial \left(\frac{x_i}{a_B}\right)^2}$$

$$\tilde{\nabla}^2$$

$$\therefore \left[-\left(\frac{m_e}{\mu}\right) \frac{\tilde{\nabla}^2}{2} - \frac{Z}{\tilde{r}} \right] \psi = \tilde{E} \psi \quad \ldots \text{ in a.u.}$$

OR simplify set $\frac{e}{\sqrt{4\pi\varepsilon_0}} = \hbar = m_e = 1$, then everything will be in a.u.

i.e., $r \to \tilde{r} = \frac{r}{a_B}$, $\mu \to \tilde{\mu} = \frac{\mu}{m_e}$, $E \to \tilde{E} = \frac{E}{E_h}$

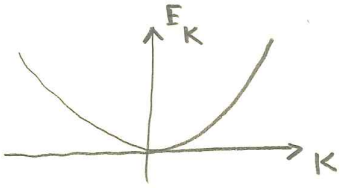
What about the center-of-mass motion?

Up to now, we only considered the relative motion of the e^--ion system giving rise to $\psi_{nlm}(\vec{r})$

As for the center-of-mass coordinate $\vec{R}$ of the e^--ion system, there is no force, hence it shows the free particle characteristics:

$$\phi_{\vec{K}}(\vec{R}) = \frac{1}{\sqrt{V}} e^{i\vec{K}\cdot\vec{R}}$$

($\sqrt{V}$: normalization volume)



Hence, the full wf (relative + CM) is: $\Psi_{nlm,\vec{K}}(\vec{r},\vec{R}) = \psi_{nlm}(\vec{r}) \frac{1}{\sqrt{V}} e^{i\vec{K}\cdot\vec{R}}$

six quantum labels for six degrees of freedom: $\vec{r} + \vec{R}$

* Use the total mass ($m_e + m_N$) for CM
* The CM part is important in BEC
* This degree of freedom (classically) gives rise to Doppler broadening

Due to thermal movement of atoms/molecules, the apparent frequency of each emitter is Doppler shifted. The many different velocities of the emitting gas result in many small shifts, the cummulative effect of which is to broaden the line. The broadening is dependent only on λ, m, T, Hence useful for measuring T of the emitting gas.

The standard deviation of Doppler profile: $\Delta\lambda = \lambda_0 \sqrt{\frac{kT}{mc^2}}$

This is used in astronomy to get an idea on the relative T's of the observed mat'l.

Quantum Labels (so far, without spin degrees of freedom)

ψ_{nlm} → principal q. n. $n = 1, \ldots, \infty$

→ orbital q. n. $l = 0, \ldots, n-1$

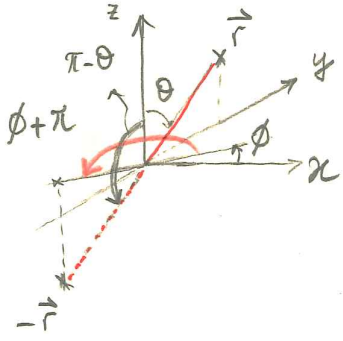
→ magnetic q. n. $m = -l, -l+1, \ldots, +l$

l specifies the orbital angular momentum of the wave function

m is the projection of the angular momentum vector to the quantization axis (which is arbitrary for no ext. field). The name 'magnetic quantum number' becomes meaningful when there is an external field (defining a "real" quantization axis) where 'm' labels the Zeeman levels.

Parity: Refers to the spatial inversion $\vec{r} \to -\vec{r}$ $\begin{cases} x \to -x \\ y \to -y \\ z \to -z \end{cases}$

For $\psi_{nlm}(r, \theta, \phi)$ we need to consider spherical coords:



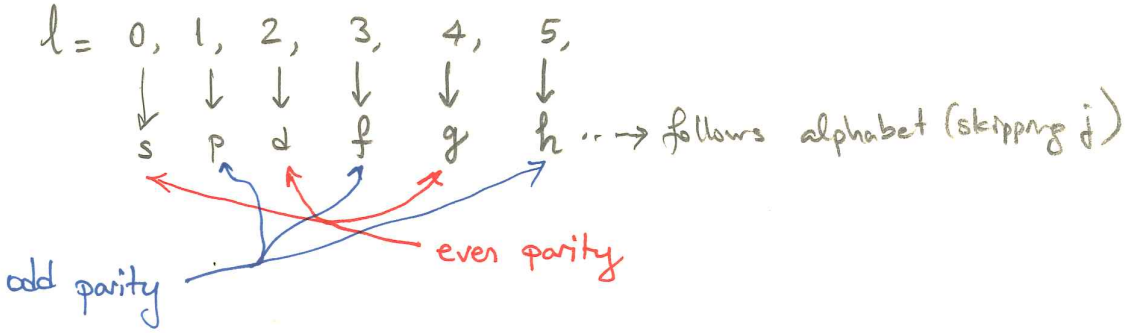
$\begin{cases} r \to r \\ \theta \to \pi - \theta \\ \phi \to \phi + \pi \end{cases}$ only angular var's det. the parity

$$Y_{lm}(\theta, \phi) \propto P_l^m(\cos\theta)\, e^{im\phi}$$

$$\left.\begin{aligned} P_l^m(\cos[\pi-\theta]) &= (-1)^{l-m} P_l^m(\cos\theta) \\ e^{im(\phi+\pi)} &= (-1)^m e^{im\phi} \end{aligned}\right\} \Rightarrow Y_{lm}(\pi-\theta, \phi+\pi) = (-1)^l Y_{lm}(\theta, \phi)$$

$$\therefore \psi_{nlm}(-\vec{r}) = (-1)^l \psi_{nlm}(\vec{r})$$ ← Only l determines the parity of a single-$\bar{e}$ Coulomb wf.

Recall that l quantum number has the following symbols:



Degeneracy: We have seen that $\psi_{nlm}(\vec{r}) \longrightarrow E_n$ (does not depend on l or m)

Hence, in the level of treatment so far all different l, m states have the same energy

$$\sum_{l=0}^{n-1} \underbrace{\sum_{m=-l}^{l} 1}_{(2l+1)} = \underbrace{2\sum_{l=0}^{n-1} l}_{\frac{n(n-1)}{2}} + n = n^2$$

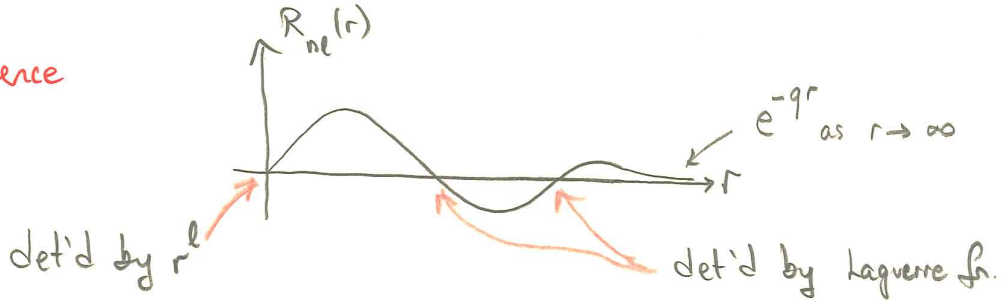
n^2 } without spin degrees of freedom

Here, **m degeneracy** arises from the fact that all directions in space ($V(|\vec{r}|)$) are equivalent (Different values of m correspond to different $\not{}$ bet. angular momentum and the quantization axis. If the quantization axis is arbitrary, then m should not carry a physical meaning.

The **degeneracy wrt l** (which characterizes the magnitude of orbital angular momentum), is a special feature of **1/r potential**. Therefore the l degeneracy will be broken when 1/r potential changes due to perturbations not considered so far.

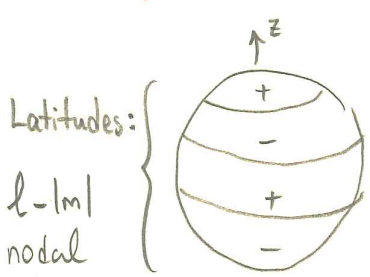
Orbital Profiles: $R_{nl}(r)\ Y_{lm}(\theta,\phi)$

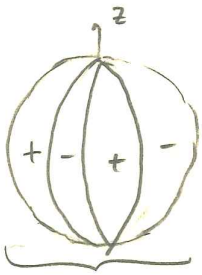
Radial Dependence

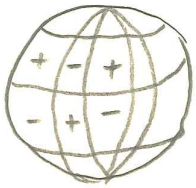


Polar Dependence $P_l^m(\cos\theta)$

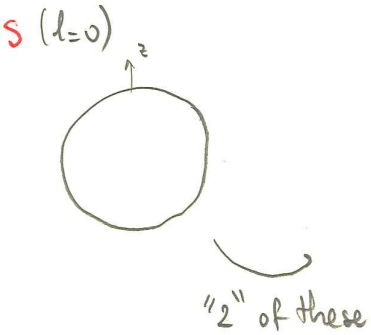
Azimuthal Dep. $\sin m\phi$, $\cos m\phi$

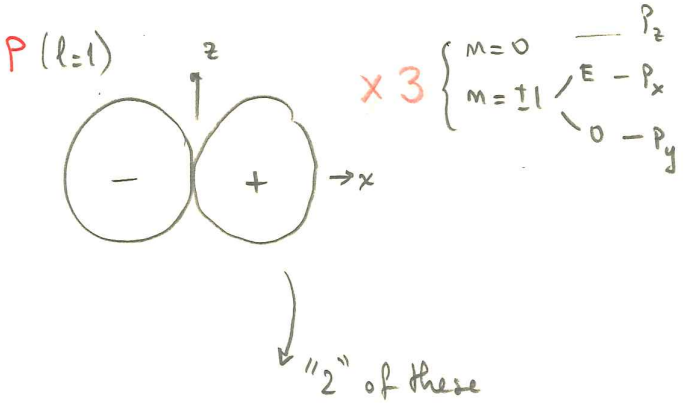


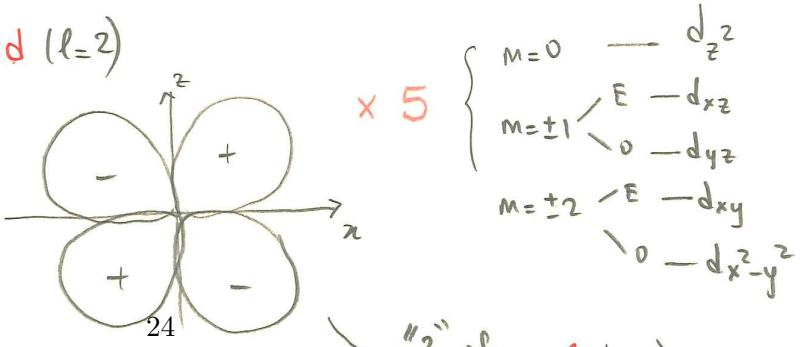




$Y_{lm}(\Omega)$: l nodal lines







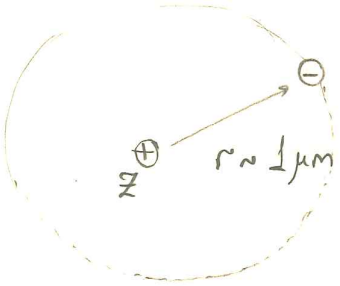
Rydberg Atoms

This is an atom excited into a very high principal q.n., say $n \sim 50-100$. They were first observed in astrophysics and believed to be common in interstellar space where due to low density (many orders of magnitude lower than best lab vacuums), the Rydberg states can persist for long periods before being destroyed by collisions.

They possess very inflated physical properties, such as electric/magnetic dipole moments

$$d = e\langle r \rangle$$

$$\mu = i\,\pi\,\langle r \rangle^2$$



Scalings with n:

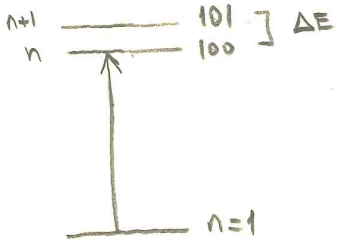
$r \sim n^2$

$\tau_{\text{lifetime}} \sim n^3 - n^{4.5}$

polarizability $\sim n^7$

Therefore, they are highly sensitive to ext. $\vec{E}$ & $\vec{B}$ fields.

Let's calculate the energy separation for $n \gg 1$, say $n = 100$



$$\Delta E = \frac{Z^2 E_h}{2}\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right) = \frac{E_h}{2} Z^2 \frac{2n+1}{n^2(n+1)^2}$$

$Z=1$, $n=100$

$$\Rightarrow \Delta E \simeq 27.2\,\mu eV = 1\,\mu Ha$$

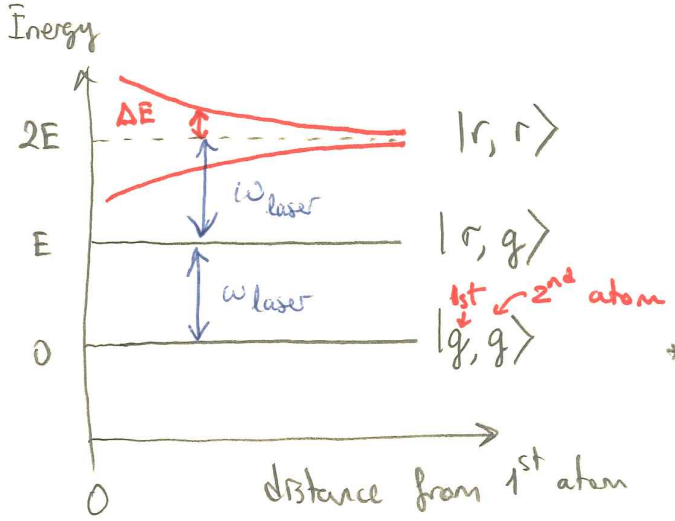
$$\simeq 6.6\ GHz$$

Typical laser linewidths: (comparable!)

He-Ne laser $\simeq$ GHz → not good for Rydberg state exc.

CW low power dye and semiconductor laser < 1 kHz ✓

The exaggerated properties of Rydberg atoms give rise to interesting physics. One of them is the so-called Rydberg blockade. Once an atom within an ensemble is excited, its interaction with the surrounding atoms shifts the transition frequencies, such that the same laser that excited the original atom becomes detuned for exciting the rest.



When $\Delta E > \Delta\nu_{laser}$, the presence of a single Ryd. atom blocks the rest

* This Rydberg blockade is suggested as a means for implementing quantum gates. (See Saffman Review)

* Haroche groups have demonstrated the entanglement of two Rydberg atoms in two steps, by first entangling one of them with a photon in a cavity, followed by the absorption of the photon by another Rydberg atom, hence being entangled to the 1st one forming a state: $|e, g\rangle + |g, e\rangle$. Probing such entangled atom pairs paves the way to "see photons in a cavity without destroying them" → Quantum Non-demolition measurement.

Relativistic Corrections to the Energy Levels

Up to now, ions were composed of a nonrelativistic spinless e^- and a nucleus taken as a spinless point charge. In reality both of these need to be revised. They lead to shift of energy levels and symmetry breaking:

* e^- relativistic orbital motion
* e^- spin

} gives rise to fine structure that partially splits the l degeneracy

* nuclear spin $\longrightarrow$ gives rise to hyperfine structure

How relativistic is the H atom?

Let's make a very crude estimate of the average speed of the e^- in the ground state of the H atom. [We shall use $\mu \to m_e$]

$\langle v^2 \rangle = \left\langle \left(\frac{p}{m_e}\right)^2 \right\rangle$, so let's work out $\langle T \rangle = \left\langle \frac{p^2}{2m_e} \right\rangle$

$$\langle T \rangle_{100} = \langle n=1, l=0, m=0 | \underbrace{\frac{p^2}{2m_e}}_{H-V} | 100 \rangle = E_{100} - \underbrace{\langle V \rangle_{100}}_{-\frac{Ze^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle_{100}}$$

$E_{100} = -\frac{1}{2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{\hbar^2}$

$\left\langle \frac{1}{r} \right\rangle_{100} \frac{Z}{a_B}$

$$\Rightarrow \quad \langle T \rangle_{100} = \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2} = \frac{1}{2} Z^2 \alpha^2 m_e c^2$$

$\frac{1}{2} m_e v_{100}^2$ ← actually a non-rel. expression, but OK for est.

$$\Rightarrow \quad v_{100}^{rms} = \sqrt{\langle v^2 \rangle_{100}} = Z\alpha c$$

$\therefore$ H $(Z=1)$: $v_{100} \simeq 1\%$ of the speed of light (not that slow!)

We expect the relativistic corrections to be proportional to $\gamma \to \left(\frac{v}{c}\right)^2 = (Z\alpha)^2$.

Hence, as $Z \nearrow$ atom will become much more relativistic.

NB: Too simplistic as seen by $v > c$ for $Z > 137$!!

An Estimation of Relativistic Energy Shift

Recall the relativistic dispersion relation for a free ($V=0$) particle:

$$\left(\frac{E}{c}\right)^2 = p^2 + m_e^2 c^2$$

Including the potential energy term

$$E = V + \sqrt{p^2 c^2 + m_e^2 c^4}$$

For $p \ll m_e c$ equivalently $v \ll c$, we can use Binomial expansion (we need to 2nd order)

$$(1+x)^a \simeq 1 + ax + \frac{1}{2!} a(a-1) x^2 ; \quad \sqrt{1+x} \simeq 1 + \frac{x}{2} - \frac{x^2}{8} \quad (x \ll 1)$$

$$\Rightarrow \quad E \simeq V + m_e c^2 + \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3 c^2} + \cdots$$

Coulomb pot. | rest energy (const.) | Non-rel. K.E. | 1st relativistic correction

Let $H_0 = \frac{p^2}{2m_e} + V$, $\quad \zeta_R = -\frac{p^4}{8m_e c^2} = -\frac{1}{2m_e c^2}\left[\underbrace{H_0 - V}_{\hat{T}}\right]^2$

According to 1st order perturbation theory:

$$\Delta E_R = \langle n\ell m | \zeta_R | n\ell m \rangle$$

$$= -\frac{1}{2m_e c^2} \langle n\ell m | H_0^2 - 2H_0 V + V^2 | n\ell m \rangle$$

$$H_0 |n\ell m\rangle = E_n |n\ell m\rangle, \qquad H_0^2 |n\ell m\rangle = E_n^2 |n\ell m\rangle$$

$$\langle H_0 V \rangle_{n\ell m} = -E_n \frac{Ze^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle_{n\ell m} = -\frac{Z^2 e^2}{4\pi\varepsilon_0} \frac{E_n}{n^2 a_B}$$

$$\langle V^2 \rangle_{n\ell m} = \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \left\langle \frac{1}{r^2} \right\rangle_{n\ell m} = \left(\frac{Z^2 e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^3 a_B^2 \left(\ell + \frac{1}{2}\right)}$$

ℓ degeneracy is lifted!

$$\Delta E_R = -\frac{E_n^2}{2m_e c^2}\left(\frac{4n}{\ell + \frac{1}{2}} - 3\right) = -\frac{\alpha^2 R_M}{4}\left(\frac{4n}{\ell + \frac{1}{2}} - 3\right)\frac{Z^4}{n^4}$$

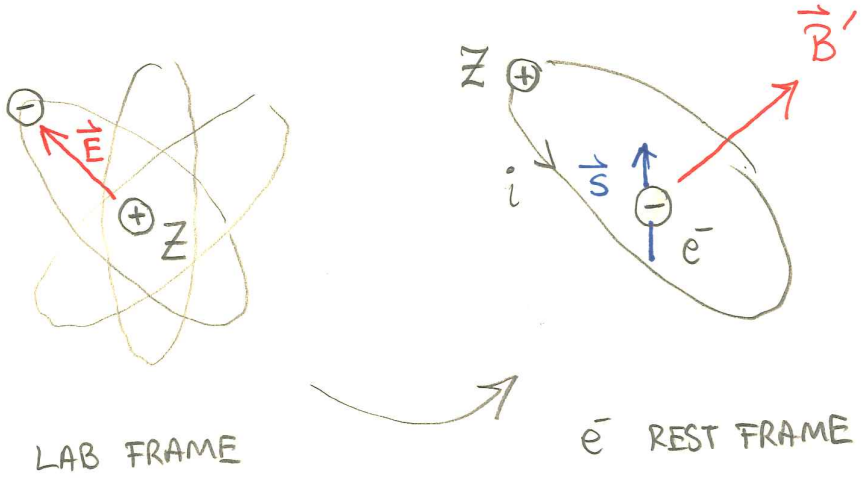
Note the Z^4 dependence of the relativistic shift

Spin-orbit Interaction

→ Crucial for understanding spin relaxation and in general external control of the spin degrees of freedom (SPINTRONICS)

→ Gives rise to further splittings in the spectra

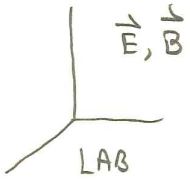
What's the physical origin?

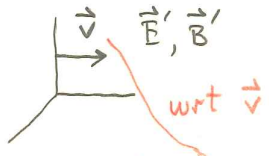


The Coulomb field in the lab frame, transforms to a magnetic field in the rest frame of the $\bar{e}$. Hence this coupling of the spin of $\bar{e}$ $\vec{s}$ with the effective magnetic field $\vec{B}'$ is the cause of this SOI.

Technical Details

Let's refresh our memory on the Lorentz xf:





$$E'_{\parallel} = E_{\parallel}, \quad \vec{E}'_{\perp} = \gamma\left(\vec{E}_{\perp} + \vec{v}\times\vec{B}\right)$$

$$B'_{\parallel} = B_{\parallel}, \quad \vec{B}'_{\perp} = \gamma\left(\vec{B}_{\perp} - \frac{1}{c^2}\vec{v}\times\vec{E}\right)$$

Lorentz factor

where $\gamma = \dfrac{1}{\sqrt{1-\beta^2}}$, $\beta = v/c$

The complication in applying this to orbiting $\bar{e}$ case is that this Lorentz xf is valid bet. inertial frames, whereas the $\bar{e}$ in orbital motion is following a curved trajectory in the lab frame.

There are (at least) three options available to work out H_{SOI}

1) Solve Dirac Eqn. and extract all relativistic terms (not only SOI)

→ Exact and straightforward but not very transparent (and coherent, if one does not remain in this RQM framework throughout).

2) Apply ordinary Lorentz xf including Thomas precession correction

→ Quite technical, see Jackson's Electrodynamics

3) Follow Herb Krömer's approach (AJP 2004) to extract the transformations for a curved trajectory which is valid up to $O(\beta^2)$

→ Not very general or rigorous but simple

We follow this final approach due to its simplicity.

Here, one proposes that the $\bar{e}$ rest frame $\vec{B}'$ field will be generalized for a curved trajectory wrt ordinary Lorentz xf as:

$$\vec{B}' = a \frac{\vec{E} \times \vec{v}}{c^2}$$

a → to be det'd (can depend on v but not on $\vec{E}$ or $\vec{B}$)

If there is also $\vec{B}$ field in the LAB frame, then we include that as

$$\vec{B}' = a \frac{\vec{E} \times \vec{v}}{c^2} + b \vec{B}$$

b → similar conditions as 'a' apply

NB: Using the above assertion that 'a' and 'b' (being in the transformation kernel) do not depend on the fields, we can choose $\vec{E}$ and $\vec{B}$ in such a way that it will simplify the extraction of a & b.

For the SOI of orbiting $\bar{e}$ we actually do not need to include a $\vec{B}$ field in LAB frame. However, to extract a and b (at least to order β^2), we want to construct a known-solution limiting case such that curved trajectory → straight line trajectory by setting $\vec{E}$ & $\vec{B}$ in LAB frame via

$$\vec{E} = -\vec{v} \times \vec{B} \qquad \text{so that} \qquad \vec{F}_e + \vec{F}_m = 0$$

$$q\vec{E} + q\,\vec{v}\times\vec{B} = -q\vec{v}\times\vec{B} + q\vec{v}\times\vec{B} = 0$$

For such a setting, we can safely apply Lorentz xf as we do not have a curved trajectory.

Without loss of generality choose : $\vec{v} = \hat{x}\,v_x$, $\vec{B} = \hat{z}\,B_z$, $\vec{E} = \hat{y}\,E_y$ with $B_z v_x = E_y$

Applying Lorentz xf

$$B_z' = \gamma\left(B_z - E_y v_x/c^2\right), \qquad \gamma = 1/\sqrt{1-(v_x/c)^2}$$

In the limit $v_x \ll c$, $\gamma = \left(1-\frac{v_x^2}{c^2}\right)^{-1/2} \simeq 1 + \frac{v_x^2}{2c^2}$

$$B_z' = B_z\left(1+\frac{v_x^2}{2c^2}\right) - \frac{E_y v_x}{c^2}\left(1+\frac{v_x^2}{2c^2}\right)$$

$$= B_z + \underbrace{\frac{B_z v_x^2}{2c^2}}_{E_x v_x} - \frac{E_y v_x}{c^2} - \frac{E_y v_x^3}{2c^4} - \frac{E_y v_x}{2c^2}$$

neglect

$$\Rightarrow B_z' = B_z - \frac{1}{2}\frac{E_y v_x}{c^2}$$

Switching back to general coordinates:

$$\vec{B}' = \vec{B} + \left(\frac{1}{2}\right)\frac{\vec{E}\times\vec{v}}{c^2} \quad \Rightarrow \quad a = 1/2\,, \quad b = 1$$

(1/2) → Thomas' factor

Knowing the exact result (by more rigorous approaches), we assert that this xf also holds for a general curved trajectory with/without the presence of $\vec{B}$. This '1/2' term took 1 year for physicists in 1920's!

In the e^- rest from this $\vec{B}'$ field couples to the e^-'s spin-related magnetic moment, $\vec{\mu}_e$

$$\hat{H}_{SOI} = -\hat{\vec{\mu}}_e \cdot \vec{B}' \,, \qquad \hat{\vec{\mu}}_e = -g_0 \mu_B \frac{\hat{\vec{S}}}{\hbar}$$

... (spin) magnetic moment of e^-

$-g_0$: due to −ve charge of e^-

μ_B: Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e} \simeq 58\ \mu eV/T$$

know this value

$$\hat{\vec{\mu}}_e = -\frac{e}{m_e}\hat{\vec{S}}$$

g_0: Landé g factor, $g_0 = 2$ (Dirac theory)

$$\hat{H}_{SOI} = \frac{e}{m_e}\hat{\vec{S}}\cdot\vec{B}' \qquad \vec{B}' \leftarrow \frac{\vec{E}\times\vec{v}}{2c^2}$$

$$\vec{E} = -\vec{\nabla}V \xrightarrow{V(\vec{r}) = V(|\vec{r}|)} \vec{E} = -\hat{r}\frac{dV}{dr}$$

$$\hat{r}\times\vec{v} = \frac{1}{rm_e}\vec{\ell}, \qquad \vec{\ell} = \vec{r}\times\vec{p}$$

$$\Rightarrow \hat{H}_{SOI} = -\frac{e}{2m_e^2c^2}\left(\frac{1}{r}\frac{dV}{dr}\right)\vec{\ell}\cdot\hat{\vec{S}}$$

$\frac{dV}{dr} = \frac{-Ze}{4\pi\varepsilon_0 r^3}$

In summary, the nonrelativistic Schrödinger eqn. for a spinless H-like atom yields a highly degenerate energy spectrum

$$E_n = -\frac{E_h Z^2}{2n^2}, \quad n = 1, 2, \ldots \quad \text{(no dependence on } l \text{ or } m\text{)}$$

If we include perturbatively the relativistic corrections

we get → $\Delta E_R \propto \frac{Z^4}{\left(l+\frac{1}{2}\right) n^3} \frac{1}{n^3}$ ... l-dependent

→ $\mathcal{H}_{SOI} = \lambda \vec{l} \cdot \vec{s}$ ... spin-orbit coupling

This last issue of SOI takes us to the discussion of the coupling between angular momenta. It will also be required in the case of $\bar{e}$ spin and nuclear spin coupling which gives rise to the hyperfine splittings ⇒ of technological importance for clock transitions

For all these, we shall first refresh our knowledge on the QM of angular momenta.

Angular Momentum (in a Nutshell)

If for some vector $\vec{J}$, the following commutation rule applies among its Cartesian components:

$$[J_i, J_j] = i\hbar\, \varepsilon_{ijk} J_k, \qquad \varepsilon_{ijk} = \begin{cases} +1 : ijk = xyz \text{ cyclic ordering} \\ -1 : ijk = xyz \text{ out of cyc. ordering} \\ 0 : \text{o.w.} \end{cases}$$

(Levi-Civita)

then $\vec{J}$ corresponds to an angular momentum (orbital or intrinsic).

Because of this commutation relation, we cannot simultaneously measure any two Cartesian components. But since $J^2 = \vec{J}\cdot\vec{J}$ commutes with J_i.

$$\text{E.g. } [J^2, J_z] = \underbrace{[J_x^2, J_z]}_{-i\hbar(J_xJ_y + J_yJ_x)} + \underbrace{[J_y^2, J_z]}_{i\hbar(J_xJ_y + J_yJ_x)} + \underbrace{[J_z^2, J_z]}_{0} = 0$$

It is easy to see where this commutation relation comes from ↙

Orbital Angular Momentum

$$\vec{J} \to \vec{L} = \vec{r} \times \vec{p} = -i\hbar\, \vec{r} \times \vec{\nabla}$$

$$L_i = \varepsilon_{ijk} r_j p_k$$

$$= -i\hbar\, \varepsilon_{ijk} x_j \partial_k$$

From $[x_i, p_j] = i\hbar\delta_{ij} \longrightarrow [L_i, L_j] = i\hbar\, \varepsilon_{ijk} L_k$ ✓

Introducing **ladder operators**:

$$L_+ \equiv L_x + iL_y, \qquad L_- \equiv L_x - iL_y$$

$$[L_+, L_z] = -\hbar L_+ \;, \quad [L_-, L_z] = +\hbar L_- \;, \quad [L_+, L_-] = 2\hbar L_z$$

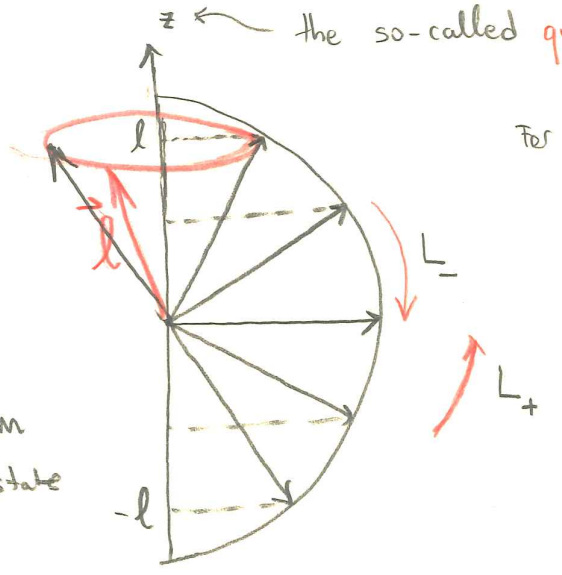
The simultaneous eigenkets of L^2 and L_z are specified by quantum labels l and m such that

$$L_z |l,m\rangle = m\hbar\, |l,m\rangle \;, \qquad m = \overbrace{-l, -l+1, \ldots, 0, \ldots, +l}^{2l+1 \text{ possibilities}}$$

$$L^2 |l,m\rangle = l(l+1)\hbar^2 |l,m\rangle \;, \qquad l = \underbrace{0, 1, 2, \ldots}$$

Should be integers due to $e^{im\phi}$, 2π periodicity

$$L_\pm |l,m\rangle = \sqrt{l(l+1) - m(m\pm 1)}\;\hbar\, |l,m\pm 1\rangle$$

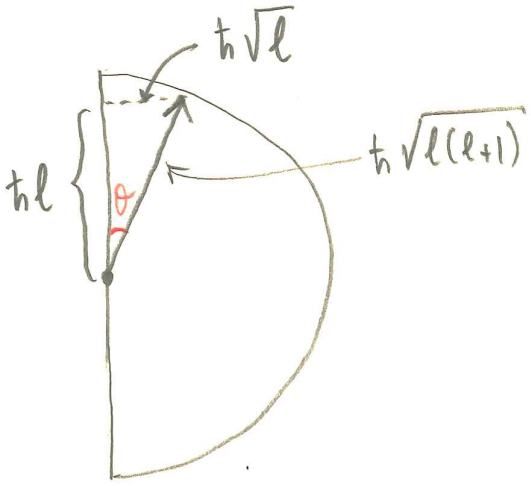


z ← the so-called **quantization axis** wrt which 'm' is defined

For isotropic sys. it can be chosen as any dir.

L_x, L_y are uncertain for an $|l,m\rangle$ state

NB: $\vec{l}$ cannot be fully aligned with z-axis as it would violate the simultaneous unmeasurability of two Cartesian components.



The minimum angular uncertainty is for the $m = +\ell$ eigenstate, which has $\tan\theta = \frac{1}{\sqrt{\ell}} \simeq \theta$. Hence higher-"spin" objects will be more classical-like, i.e., $\hat{\vec{L}} \longrightarrow \vec{L}$ as a c-number.

Angular momentum as the generator of Rotations

The operator $R_j(\Delta\varphi_j) \equiv e^{-i L_j \Delta\varphi_j/\hbar}$, $j = x, y, z$

rotates a state by an angle $\Delta\varphi_j$ about the x_j axis.

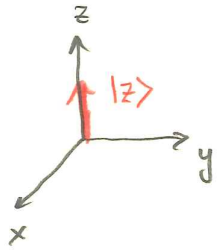
The non-commuting nature of angular momentum components coincides with the noncommutation of rotations wrt different axes.

Eg. $R_y(\pi/2)\, R_x(\pi/2) \neq R_x(\pi/2)\, R_y(\pi/2)$

$R_x(\pi/2)|z\rangle = |-y\rangle$, so $R_y(\pi/2)\, R_x(\pi/2)|z\rangle = |-y\rangle$

$R_y(\pi/2)|z\rangle = |x\rangle$, so $R_x(\pi/2)\, R_y(\pi/2)|z\rangle = |x\rangle$

$|-y\rangle \neq |x\rangle$



Spin Angular Momentum

In their rest frames, the angular momentum is still non-zero for most quantum particles which is attributed to a rotational degree of freedom other than the orbital real space one. This so-called intrinsic spin is purely a QM phenomenon with no classical analogue.

Denoting the spin angular momentum with $\vec{S} \equiv (S_x, S_y, S_z)$, the same angular momentum commutation relations hold.

There are some differences wrt orbital angular momentum

* Unlike l, s can also become a half-integer (fermions) as well as integer (bosons): $s = 0, 1/2, 1, 3/2, 2, 5/2, \dots$

  In all cases $m_s = -s, -s+1, \dots, s$

  when we say spin-s, we refer to this number

* A particle can be given any orbital angular momentum $l \in \mathbb{N}$ but for each type of particle, the value s is fixed.

* $\vec{S}$ cannot be expressed in terms of position and momentum operators, (like $L_i = -i\hbar \varepsilon_{ijk} x_j \partial_k$), so that the restriction that quantum number of the overall angular momentum to take integer values is lifted.

Spin-1/2 $(s = 1/2)$

$|s\ m_s\rangle \rightarrow |\ 1/2\ \pm 1/2\rangle$ shorthand: $m_s = 1/2 \rightarrow |\uparrow\rangle$, $-1/2 \rightarrow |\downarrow\rangle$

In doing some calculations we switch to column (row) vectors for representing spin kets (bras)

$$|\uparrow\rangle, |1/2, +1/2\rangle \longrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \langle\uparrow| \longrightarrow (1 \quad 0)$$

$$|\downarrow\rangle, |1/2, -1/2\rangle \longrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \langle\downarrow| \longrightarrow (0 \quad 1)$$

The spin operators $\hat{S}$ take the following 2x2 forms for spin-1/2 known as Pauli spin matrices (here in z-diagonal representation):

$$S_k = \frac{\hbar}{2}\sigma_k, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The associated eigenvectors: $S_i|\chi_i\rangle = \lambda_i|\chi_i\rangle$

$$|\chi_x\rangle = \begin{pmatrix} 1/\sqrt{2} \\ \pm 1/\sqrt{2} \end{pmatrix}, \quad |\chi_y\rangle = \begin{pmatrix} 1/\sqrt{2} \\ \pm i/\sqrt{2} \end{pmatrix}$$

$\lambda_i = \pm\hbar/2$, for $i = x, y, z$;

$$|\chi_{z+}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\chi_{z-}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Ex: For a state $|\psi\rangle = \begin{pmatrix} 1/3 \\ \sqrt{8}/3 \end{pmatrix}$

a) What's the expectation value of S_x?

b) What values do we get for S_x measurement and with what probabilities?

Solution:

a) $\langle S_x \rangle = \langle \psi | \hat{S}_x | \psi \rangle = \frac{\hbar}{2} \begin{pmatrix} 1/3 & \sqrt{8}/3 \end{pmatrix} \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1/3 \\ \sqrt{8}/3 \end{pmatrix}}_{\begin{pmatrix} \sqrt{8}/3 \\ 1/3 \end{pmatrix}}$

$= \frac{\hbar}{2} \frac{2\sqrt{8}}{9}$

$= \hbar \frac{\sqrt{8}}{9}$

b) $+\frac{\hbar}{2}$ will be measured with probability: $|\langle \chi_{x+} | \psi \rangle|^2$

$\left| \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \begin{pmatrix} 1/3 \\ \sqrt{8}/3 \end{pmatrix} \right|^2 = \frac{(1+\sqrt{8})^2}{18}$

$-\frac{\hbar}{2}$ " " " " " : $|\langle \chi_{x-} | \psi \rangle|^2$

$\left| \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} 1/3 \\ \sqrt{8}/3 \end{pmatrix} \right|^2 = \frac{(1-\sqrt{8})^2}{18}$

Check with part (a):

$\frac{\hbar}{2} \cdot \frac{(1+\sqrt{8})^2}{18} - \frac{\hbar}{2} \frac{(1-\sqrt{8})^2}{18} = \frac{\hbar}{2} \frac{4\sqrt{8}}{18} = \frac{\hbar\sqrt{8}}{9}$ ✓

Some commutation relations of σ:

anti-comm.: $\sigma_i \sigma_j + \sigma_j \sigma_i$

$$[\sigma_i, \sigma_j] = 2i\,\varepsilon_{ijk}\,\sigma_k \quad , \qquad \{\sigma_i, \sigma_j\} = 2\delta_{ij}\,\mathbb{1}_2$$

The spin operators act on spinors, whereas the position operators P_k, L_k etc. act only on position (space) part of the wf's.

In other words, real space operators are diagonal in spin space

$$\text{eg: } P_k \to -i\hbar\,\partial_k\,\mathbb{1}_2$$

How about spin-orbit like operators? $\vec{S}\cdot\vec{L}$

If $\vec{a} \equiv (a_x, a_y, a_z)$ is some real space operator, then

$$\vec{\sigma}\cdot\vec{a} \equiv \sum_{k=1}^{3} \sigma_k\, a_k = \begin{pmatrix} a_z & a_x - i a_y \\ a_x + i a_y & -a_z \end{pmatrix}$$

The following identity follows from commutation rel's of σ:

$$(\vec{\sigma}\cdot\vec{a})\,(\vec{\sigma}\cdot\vec{b}) = \vec{a}\cdot\vec{b} + i\,\vec{\sigma}\cdot(\vec{a}\times\vec{b})$$

Rotation Operator in Spin Space

For rotation of a spinor by an angle $\Delta\varphi$ around an axis $\hat{n}$:

$$R_{\vec{s},\hat{n}}(\Delta\varphi) = e^{-i\vec{s}\cdot\hat{n}\,\Delta\varphi/\hbar} = e^{-i\vec{\sigma}\cdot\hat{n}\,\Delta\varphi/2}$$

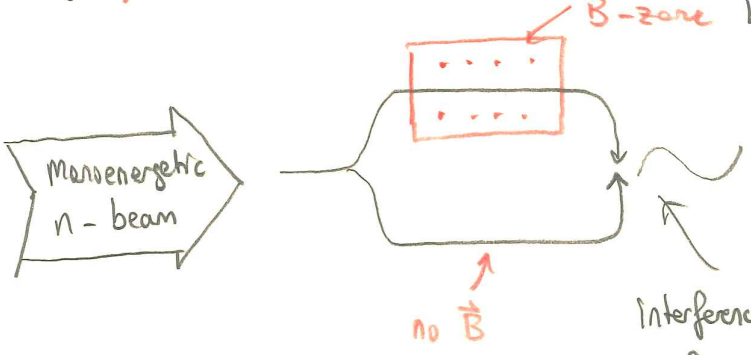
$\vec{s} = \frac{\hbar}{2}\vec{\sigma}$

Taylor series expansion

$$= \cos\left(\frac{\Delta\varphi}{2}\right)\mathbb{1}_2 - i\sin\left(\frac{\Delta\varphi}{2}\right)\vec{\sigma}\cdot\hat{n}$$

$$= \begin{pmatrix} \cos\frac{\Delta\varphi}{2} - i n_z \sin\frac{\Delta\varphi}{2} & \text{c.c.} \\ (-i n_x + n_y)\sin\frac{\Delta\varphi}{2} & \cos\frac{\Delta\varphi}{2} + i n_z \sin\frac{\Delta\varphi}{2} \end{pmatrix}$$

Note that $R_s(2\pi) = -1$, so that spin-1/2 spinors recover their dir. by 4π rotation. This is real! Neutron ($s=1/2$) interferometry verifies this:



Larmour precession, ω_L

$$\omega_L = \frac{q_n e B}{m_p}$$

It is demonstrated that it requires 4π rotation for restoring the constructive interference

Spin - S

In this case we are in a $2s+1$ dimensional spin space with $(2s+1)\times(2s+1)$ matrix representations of spin operators

$$S_k = s\hbar\,\sigma_k \qquad \text{where} \quad (\sigma_k)_{jl} = \frac{\langle s, m_{s_j} | S_k | s, m_{s_l}\rangle}{s\hbar}$$

σ_k: generic Pauli spin matrix

m_{s_j}, m_{s_l} are integers or half-integers in the range $\underbrace{-s, \ldots, +s}_{2s+1}$

Explicit forms of σ_k, start with σ_z

$$S_z |s, m_{s_j}\rangle = m_{s_j}\hbar\,|s, m_{s_j}\rangle$$

$$(\sigma_z)_{jl} = \frac{\langle s, m_{s_j}|S_z|s, m_{s_l}\rangle}{s\hbar} = \frac{m_{s_j}}{s}\delta_{j,l} \quad \text{as} \quad \langle s, m_{s_j} | s, m_{s_l}\rangle = \delta_{jl}$$

For $\sigma_{x,y}$ use $S_\pm = S_x \pm i S_y$ where $S_\pm |s, m_{s_j}\rangle = \sqrt{s(s+1) - m_{s_j}(m_{s_j}\pm 1)}\;|s, m_{s_j}\pm 1\rangle$

$$\Rightarrow (\sigma_x)_{jl} = \frac{\sqrt{s(s+1) - m_{s_j}(m_{s_j}-1)}\;\delta_{j,l+1}}{2s} + \frac{\sqrt{s(s+1) - m_{s_j}(m_{s_j}+1)}\;\delta_{j,l-1}}{2s}$$

$$(\sigma_y)_{jl} = \frac{''}{2is} - \frac{''}{2is}$$

Specifically for $s=1$:

$$\sigma_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \sigma_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & \\ 0 & & -1 \end{pmatrix}$$

Coupling

Addition of Angular Momenta

means to couple

In physics, we repeatedly end up in need to "add" two or more angular momenta. In AMO physics, this can be e^- spins in atom, e^- and nuclear spins as they interact through hyperfine interaction, or the spin and orbital angular momenta as they are coupled via $\mathcal{H}_{SO}$ etc. We shall consider adding two of them, as the addition of more is just adding them cummulatively, with the order not being important (as they belong to different degrees of freedom.

Take two angular momenta $\vec{J}_1$, $\vec{J}_2$ with either corresponding to orbital or intrinsic angular momenta. $\vec{J}_1 + \vec{J}_2 = ?$

If they were classical vectors, we would simply add the Cartesian components $J_i = J_{1i} + J_{2i}$, and the result would be a single (definite) answer.

But in quantum mechanics we do not have access to all three components; we need to live with uncertainty and work with one component (usually J_z) and the magnitude (J), which

inherently yields not a single sum, but a set of possible sum values, each with a certain probabilistic weight.

$$[J_{1i}, J_{1j}] = i\hbar\,\varepsilon_{ijk}\,J_{1k} \qquad [J_{2i}, J_{2j}] = i\hbar\,\varepsilon_{ijk}\,J_{2k}$$

$$J_1^2\,|j_1, m_1\rangle = j_1(j_1+1)\hbar^2\,|j_1, m_1\rangle \qquad J_2^2\,|j_2, m_2\rangle = j_2(j_2+1)\hbar^2\,|j_2, m_2\rangle$$

$$J_{1z}\,|j_1, m_1\rangle = m_1\hbar\,|j_1, m_1\rangle \qquad J_{2z}\,|j_2, m_2\rangle = m_2\hbar\,|j_2, m_2\rangle$$

$m_1 \leftrightarrow -j_1, \dots, +j_1$ ($2j_1+1$) $\qquad$ $m_2 \leftrightarrow -j_2, \dots, j_2$ ($2j_2+1$)

$[\vec{J}_1, \vec{J}_2] = 0$, as they are not conjugate variables, in fact they belong to different degrees of freedom.

Introducing the <u>total</u> angular momentum: $\vec{J} = \vec{J}_1 + \vec{J}_2$

with $[J_i, J_j] = i\hbar\,\varepsilon_{ijk}\,J_k$ and complete labels (j, m) as

$$J^2\,|j, m\rangle = j(j+1)\hbar^2\,|j, m\rangle$$

$$J_z\,|j, m\rangle = m\hbar\,|j, m\rangle \;; \quad m = \underbrace{-j, -j+1, \dots, j}_{2j+1}$$

NB: At this stage we do not know the relationship bet. $\{j, m\}$ and those of individual angular momenta $\{j_1, m_1; j_2, m_2\}$

Since $\vec{J}^2 = \vec{J}\cdot\vec{J} = (\vec{J}_1+\vec{J}_2)\cdot(\vec{J}_1+\vec{J}_2) = J_1^2 + J_2^2 + 2\vec{J}_1\cdot\vec{J}_2$ ← any order, OK

$\Rightarrow [J^2, J_1^2] = [J^2, J_2^2] = 0$, Also $[J_z, J_1^2] = [J_z, J_2^2] = 0$

(J_z ← $(\vec{J}_1+\vec{J}_2)_z$)

∴ Quantum labels j_1, j_2 and j can be used simultaneously (all commute),

but $[J^2, J_{1z}] \neq 0$ and $[J^2, J_{2z}] \neq 0$

$J_1^2 + J_2^2 + 2\vec{J}_1\cdot\vec{J}_2$ ← due to this term

So, quantum labels m_1 and m_2 cannot be used to define a state simultaneously with j. That is, we cannot determine the z-projections of the individual angular momenta at the same time as the magnitude of the total angular momentum.

Hence, we can form two groups of mutually commuting observables:

$$\{J_1^2, J_2^2, J_{1z}, J_{2z}\} \quad \text{vs.} \quad \{J_1^2, J_2^2, J^2, J_z\}$$

Each set has its merits. The one on the L is useful when $\vec{J}_1, \vec{J}_2$ do not interact whereas set R is convenient when one deals with $\vec{J}_1$ & $\vec{J}_2$ are strongly coupled so that $\vec{J}$ and J_z are the conserved quantities (as in strong LS coupling - more on this later).

Eigenkets of either set is complete and we can take them to be normalized. Since J_1^2 and J_2^2 are common in both sets, we can assume that j_1 and j_2 are given. In addition, we can either know the quantum numbers $\{m_1, m_2\}$ or $\{j, m\}$, but not both at the same time.

Hence the (j_1, j_2) subspace is spanned by either of the kets:

$$\sum_{m_1, m_2} |j_1, j_2; m_1, m_2\rangle \langle j_1, j_2; m_1, m_2| = 1$$

$$\sum_{j, m} |j_1, j_2; j, m\rangle \langle j_1, j_2; j, m| = 1$$

over all their allowed values

completeness relations

drop these labels as we know that we are in (j_1, j_2) subspace

Hence, if the system is at $|j, m\rangle$, then a measurement of j_{1z} and j_{2z} will yield values m_1 and m_2 with probability $|\langle m_1, m_2 | j, m\rangle|^2$. In other words, we can expand $|m_1, m_2\rangle$ as

$$|j, m\rangle = \sum_{m_1, m_2} \underbrace{\langle m_1, m_2 | j, m\rangle}_{\text{Clebsch-Gordan coefficients}} |m_1, m_2\rangle$$

Properties of C-G Coefficients (Proofs omitted but straightforward)

* The C-G coef's are zero, unless $m = m_1 + m_2$

Thus, the z-components of different angular momenta add algebraically.

* The C-G coef's vanish, unless: $|j_1 - j_2| \leq j \leq j_1 + j_2$

Check: $\sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1)$ ✓ correct multiplicity

(say $j_1 > j_2$)

Ex: An e^- ($s = 1/2$) in an orbital state $\underbrace{n=4,\ l=2}_{4d}$

will have $j \rightarrow l+s = 5/2$, $l-s = 3/2$

4d shell has 10 states $= 2\cdot(2l+1)$

Later on, we shall switch to spectroscopic notation

$4d_{3/2}$ subshell has $-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2} \rightarrow 4$

$4d_{5/2}$ subshell has $-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \rightarrow 6$

$\Big\} 10$ ✓

* The sum of the modulus squared of all C-G coef's is unity:

$$\sum_{m_1, m_2} |\langle m_1, m_2 | j, m\rangle|^2 = 1$$

← follows from completeness relation

or (j, m)

* C-G coef's obey two ($\pm$) recursion relations:

$$\sqrt{j(j+1) - m(m\pm 1)}\ \langle m_1, m_2 | j, m\pm 1\rangle =$$

$$\sqrt{j_1(j_1+1) - m_1(m_1\mp 1)}\ \langle m_1\mp 1, m_2 | j, m\rangle +$$

$$\sqrt{j_2(j_2+1) - m_2(m_2\mp 1)}\ \langle m_1, m_2\mp 1 | j, m\rangle$$

Due to absense of complex coefficients in these relations, we can (as a convention) choose the C-G coef's as real numbers. This also ensures that the inverse C-G coef's $\langle j, m | m_1, m_2\rangle$ are identical to the C-G coef's, i.e.,

$$\langle j, m | m_1, m_2\rangle = \langle m_1, m_2 | j, m\rangle$$

where the inverse C-G coef's are used in reverse direction as

$$|m_1, m_2\rangle = \sum_{j,m} \langle j, m | m_1, m_2\rangle\ |j, m\rangle$$

Ex: Addition of two e^- spins

$$j_1 = j_2 = 1/2 \quad \Rightarrow \quad m_1 = -1/2, +1/2, \quad m_2 = \pm 1/2$$

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \quad \Rightarrow \quad j = 0, 1$$

($|j_1 - j_2| \to 0$, $j_1 + j_2 \to 1$)

$j = 0$: $m_j = 0$ — Singlet

$j = 1$: $m_j = -1, 0, 1$ — triplet

For the C-G coef's we should fill the following table:

Common labels defines the subspace $\{j_1 = 1/2, j_2 = 1/2$

	j	1	1	1	0
m_1	m / m_2	1	0	−1	0
1/2	1/2	±1	0	0	0
1/2	−1/2	0	$1/\sqrt{2}$	0	$1/\sqrt{2}$
−1/2	1/2	0	$1/\sqrt{2}$	0	$-1/\sqrt{2}$
−1/2	−1/2	0	0	±1	0

1) Fill the zero entries using

$$M_1 + M_2 \neq m$$

2) For the only remaining entries in a column, use normalization (up to a sign)

3) For the remaining undetermined entries use recursion relations:

$$\langle \tfrac{1}{2}, -\tfrac{1}{2} | 1, 0 \rangle + \langle -\tfrac{1}{2}, \tfrac{1}{2} | 1, 0 \rangle = \sqrt{2} \langle \tfrac{1}{2}, \tfrac{1}{2} | 1, 1 \rangle \to \pm 1$$

and

$$\langle \tfrac{1}{2}, -\tfrac{1}{2} | 1, 0 \rangle + \langle -\tfrac{1}{2}, \tfrac{1}{2} | 1, 0 \rangle = \sqrt{2} \langle -\tfrac{1}{2}, -\tfrac{1}{2} | 1, -1 \rangle$$

Note that <u>both</u> recursion relations yield the same eqn :-(

Invoking the normalization condition:

$$\left|\left\langle \tfrac{1}{2}, \tfrac{-1}{2} \middle| 1,0 \right\rangle\right|^2 + \left|\left\langle \tfrac{-1}{2}, \tfrac{1}{2} \middle| 1,0 \right\rangle\right|^2 = 1$$

Their only real solutions are

$$\left\langle \tfrac{1}{2}, \tfrac{-1}{2} \middle| 1,0 \right\rangle = \left\langle \tfrac{-1}{2}, \tfrac{1}{2} \middle| 1,0 \right\rangle = \pm \frac{1}{\sqrt{2}}$$

4) This leaves as only the two entries in the 4th column undetermined. We can either use i) recursion rel. or ii) the fact that rows (columns) must all be mutually orthogonal.

Following (ii), unknown entries should be equal and opposite sign to those in column 2.

With the table finalized, we have $|j,m\rangle$ eigenkets expressed as

$$|1,1\rangle = |m_1 = 1/2,\ m_2 = 1/2\rangle$$

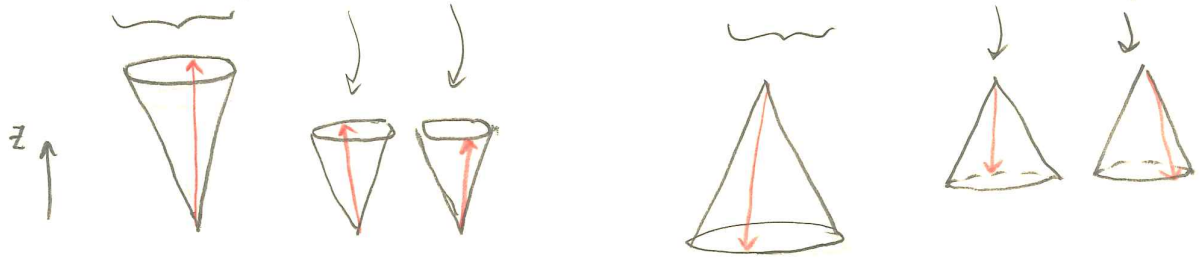
$$|1,0\rangle = \frac{1}{\sqrt{2}}\left|\tfrac{1}{2}, -1/2\right\rangle + \frac{1}{\sqrt{2}}\left|\tfrac{-1}{2}, \tfrac{1}{2}\right\rangle \quad \Big\} \text{ triplet}$$

$$|1,-1\rangle = \left|\tfrac{-1}{2}, \tfrac{-1}{2}\right\rangle$$

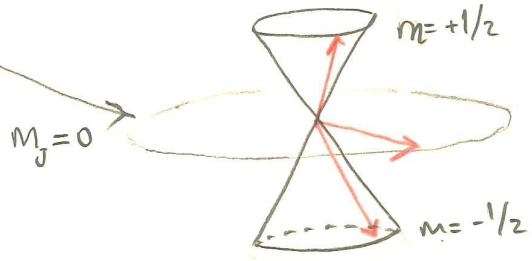
$$|0,0\rangle = \frac{1}{\sqrt{2}}\left|\tfrac{1}{2}, \tfrac{-1}{2}\right\rangle - \frac{1}{\sqrt{2}}\left|\tfrac{-1}{2}, \tfrac{1}{2}\right\rangle \quad \Big\} \text{ singlet}$$

Visualization

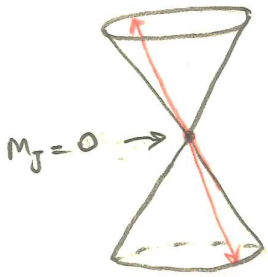
$|1, 1\rangle = |1/2, 1/2\rangle$, $|1, -1\rangle = |-1/2, -1/2\rangle$



$$|1, 0\rangle = \frac{1}{\sqrt{2}} |1/2, -1/2\rangle + \frac{1}{\sqrt{2}} |-1/2, 1/2\rangle$$



$$|0, 0\rangle = \frac{1}{\sqrt{2}} |1/2, -1/2\rangle - \frac{1}{\sqrt{2}} |-1/2, 1/2\rangle$$



NB: $|1, 0\rangle$ and $|0, 0\rangle$ are entangled states; either spin "knows" about the other.

$|1, 1\rangle$ and $|1, -1\rangle$ are product states and they are <u>not</u> entangled

In Group Theory Language

The procedure we followed a.k.a. Clebsch-Gordan decomposition turns a direct product (of irreducible representations ≡ irreps) into a direct sum (of other irreps):

$$D_{j_1} \otimes D_{j_2} = \bigoplus_{j=|j_1-j_2|}^{j_1+j_2} D_j$$

$2j_1+1$ $\quad$ $2j_2+1$ $\quad$ $2j+1$

* $j_1 = j_2 = 1/2$

$$2 \otimes 2 = 1 \oplus 3$$

$$[2\times 2] \otimes [2\times 2] = \begin{bmatrix} 1 & 0 & 0 & 0 \\ \hline 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

1x1 $\quad$ 3x3

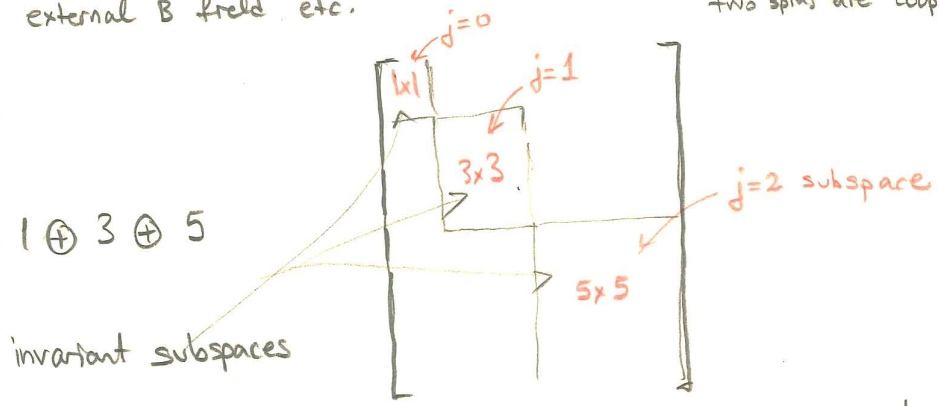
This basis is convenient when dealing with non-interacting spins in some external B field etc.

This is convenient when two spins are coupled

Why need two different bases ?

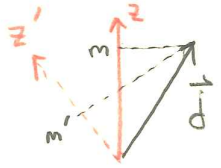
* $j_1 = j_2 = 1$

$$3 \otimes 3 = 1 \oplus 3 \oplus 5$$



Group operations (rotations) transform each member to another within that invariant subspace without affecting other subspaces.

A rotation op. will not affect $|\vec{J}|$ but it will change m to another value



eg. In $1/2 \otimes 1/2$ rotation will not transform a singlet $\leftrightarrow$ triplet

43. CLEBSCH-GORDAN COEFFICIENTS, SPHERICAL HARMONICS, AND *d* FUNCTIONS

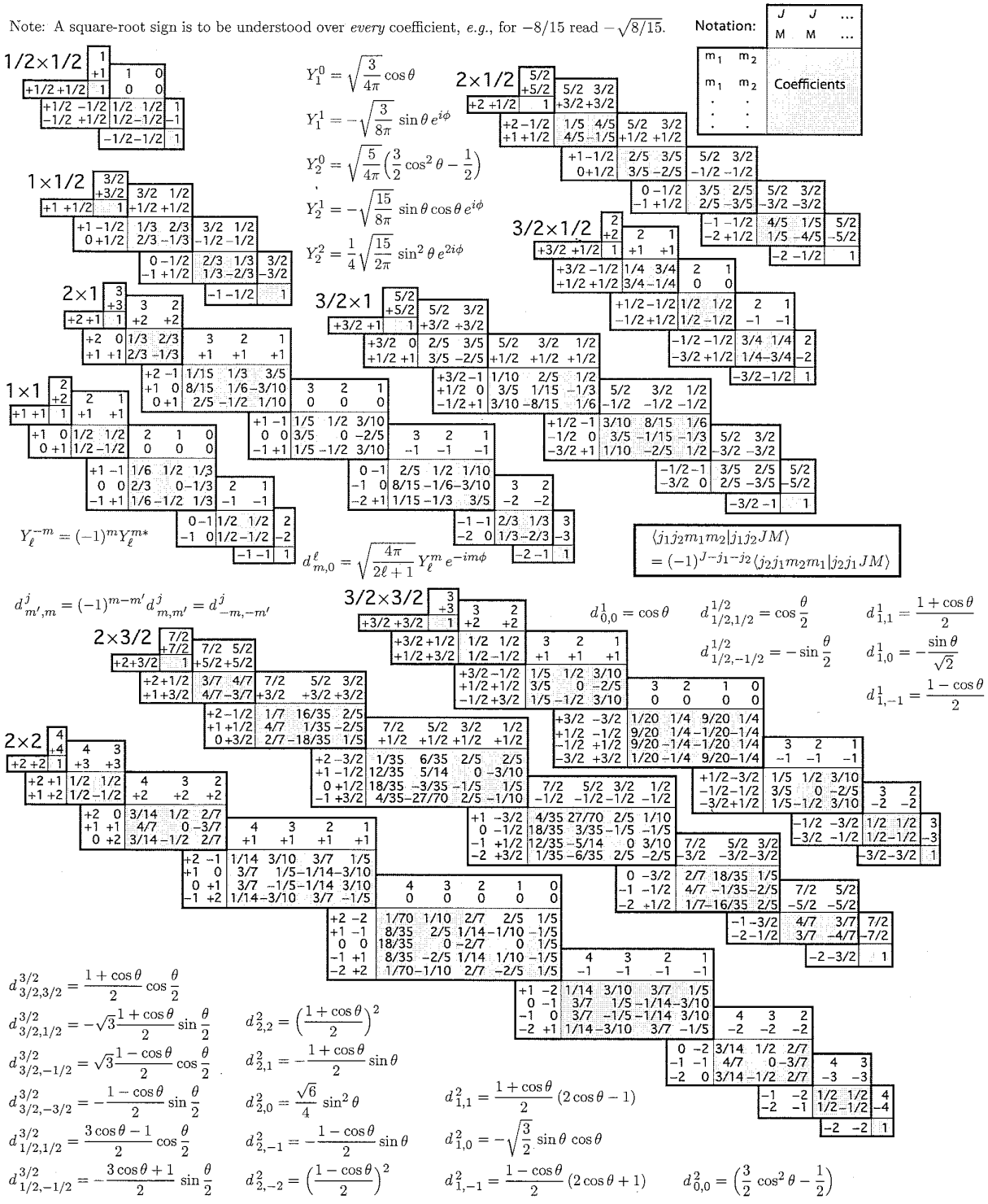


Figure 43.1: The sign convention is that of Wigner (*Group Theory*, Academic Press, New York, 1959), also used by Condon and Shortley (*The Theory of Atomic Spectra*, Cambridge Univ. Press, New York, 1953), Rose (*Elementary Theory of Angular Momentum*, Wiley, New York, 1957), and Cohen (*Tables of the Clebsch-Gordan Coefficients*, North American Rockwell Science Center, Thousand Oaks, Calif., 1974).

Fine Structure and Spin-Orbit Interaction (single-e^- case)

We derived the spin-orbit Hamiltonian as

$$\hat{H}_{SO} = \frac{-e}{2m_e^2c^2}\left(\frac{1}{r}\frac{dV}{dr}\right)\vec{l}\cdot\vec{s}$$

Using $\vec{j} = \vec{l} + \vec{s}$, $\quad j^2 = (\vec{l}+\vec{s})\cdot(\vec{l}+\vec{s}) = l^2 + s^2 + 2\vec{l}\cdot\vec{s}$

we can express $\vec{l}\cdot\vec{s} = \dfrac{j^2 - l^2 - s^2}{2}$

The 1st order energy shift $\Delta E_{SO} = \langle \hat{H}_{SO} \rangle$ becomes

(use the fact that $|\psi\rangle = |\vec{r}\rangle \otimes |\chi\rangle$ so that operators act on only space or spin kets)

$\langle s^2\rangle/\hbar^2$ — spatial, $|\vec{r}\rangle$ part of the exp. value

$$\Delta E_{SO} = \frac{-e\hbar^2}{2m_e^2c^2}\;\underbrace{\frac{j(j+1) - l(l+1) - s(s+1)}{2}}_{\langle j^2\rangle/\hbar^2}\;\left\langle \frac{1}{r}\frac{dV}{dr}\right\rangle_{nlm}$$

$|\chi\rangle$ part of the expectation

$\dfrac{-Ze}{4\pi\varepsilon_0 r^3} \Leftarrow \left\langle \dfrac{1}{r^3}\right\rangle$ was worked out

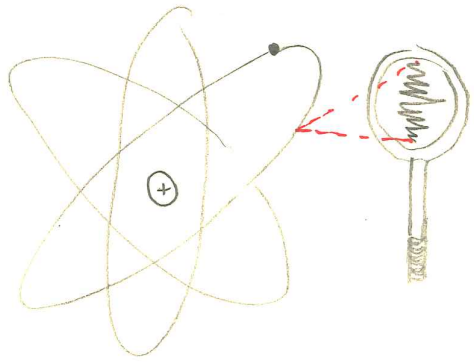
$$\Rightarrow \Delta E_{SO} = \frac{Z^4e^2\hbar^2}{4\pi\varepsilon_0}\;\frac{\hbar^2}{2m_e^2c^2a_B^3n^3}\;\frac{j(j+1) - l(l+1) - s(s+1)}{2l\left(l+\frac{1}{2}\right)(l+1)}$$

Note that SOI lifts the l degeneracy, however this will be reversed by the Darwin term.

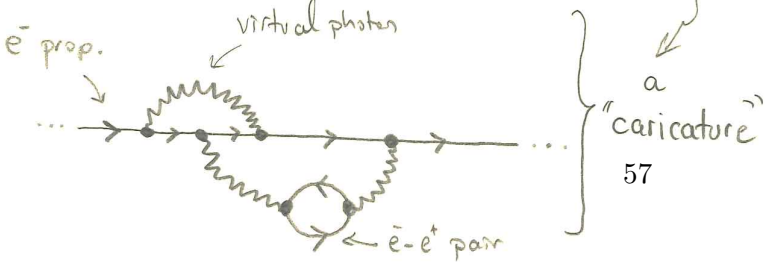
Darwin Term : Phenomenon

In the Dirac eqn. the interaction bet. the $\bar{e}$ and the Coulomb field of the nucleus is **local**, i.e., it only depends on the value of the field at the $\bar{e}$ position $\vec{r}$. However, the **non-relativistic** approximation (series expansion in v/c) leads, for the two-component spinor which describes the $\bar{e}$ state, to an eqn in which the interaction bet. the $\bar{e}$ & the field has become **non-local**. The $\bar{e}$ is then affected by all the values taken on by the field in a domain centered at the point $\vec{r}$, and whose size is of the order of **Compton wave length** $\frac{\hbar}{m_e c} \sim 2.10^{-12}$ m of the $\bar{e}$. This is the origin of the correction represented by the **Darwin** term.

We shall see that this term gives rise to a small shift in **s-states**. It represents the relativistic nonlocalizability of the $\bar{e}$ and is related to the trembling motion of the $\bar{e}$ known as **zitterbewegung**



$\bar{e}$ undergoes very fine random oscillations as it absorbs and emits (virtual) photons due to its coupling with the **EM vacuum** which has its zero-point fluctuations. (This also shows itself in the **Lamb shift**.)



a "caricature"

Darwin Term : Technical Details

The trembling motion will give rise to an average Coulomb field over a volume with a radius about the Compton wave length

$$V_{eff} = \frac{1}{Vol.} \int V(\vec{r}+\vec{\varepsilon})\, d^3\varepsilon$$



since this is the minimum wave length an $\vec{\varepsilon}$ can have, hence its position can be accurate up to λ_0

$$V(\vec{r}+\vec{\varepsilon}) = V(\vec{r}) + \vec{\varepsilon}\cdot\vec{\nabla}V + \sum_{i,j=1}^{3} \frac{1}{2}\varepsilon_i \varepsilon_j \partial_i \partial_j V + \cdots$$

$$\int V(\vec{r}+\vec{\varepsilon})\, d^3\varepsilon = \text{Vol.}\, V(\vec{r}) + \underbrace{\int \vec{\varepsilon}\cdot\vec{\nabla}V\, d^3\varepsilon}_{\vec{\nabla}V \cdot \int \vec{\varepsilon}\, d^3\varepsilon \,=\, 0} + \nabla^2 V \frac{1}{2} \underbrace{\int \varepsilon_i \varepsilon_j\, d^3\varepsilon}_{A\,\delta_{ij}}$$

$$\left.\begin{aligned} \int \left(\varepsilon_x^2 + \varepsilon_y^2 + \varepsilon_z^2\right) d^3\varepsilon &= 3A \\ 4\pi \int_0^{\lambda_0} \varepsilon^4\, d\varepsilon &= \frac{4\pi}{5}\lambda_0^5 \end{aligned}\right\} \Rightarrow A = \frac{4\pi}{15}\lambda_0^5$$

Inserting the Compton wave length $\lambda_0 = \frac{\hbar}{m_e c}$, we get the effective potential as

$$V_{eff} = V(\vec{r}) + \frac{1}{8}\left(\frac{\hbar}{m_e c}\right)^2 \nabla^2 V$$

In this final result we have made a little relativistic correction to make our crude treatment agree with that using Dirac eqn.

As, $$\nabla^2\left(\frac{1}{r}\right) = -4\pi\,\delta(\vec{r})$$

the Darwin correction comes out as:

$$\mathcal{H}_D = \frac{Ze^2\hbar^2}{8m_e^2c^2\varepsilon_0}\,\delta(\vec{r})$$

Applying for the first-order energy shift:

$$\Delta E_D = \frac{Ze^2\hbar^2}{8m_e^2c^2\varepsilon_0}\,|\psi(0)|^2 \quad \text{... only affects s-states}$$

For the H 1s state $\psi(r) = \frac{1}{\sqrt{\pi a_B^3}}\,e^{-r/a_B}$

$$\Delta E_D(1s) = \frac{e^2\hbar^2}{8\pi m_e^2c^2\varepsilon_0 a_B^3} \propto m_e c^2\,\alpha^4$$

Note that Darwin term is essentially l-dependent!

Total Fine Structure Shift

If we combine spin-orbit interaction, relativistic mass correction (p^4 term) and Darwin terms (in short known as fine structure) we get a very neat expression for this shift:

$$\Delta E_{FS} = \frac{m_e c^2 (Z\alpha)^4}{2n^3} \left(\frac{3}{4n} - \frac{1}{j+1/2} \right)$$

historical reason for naming α as the fine structure const.

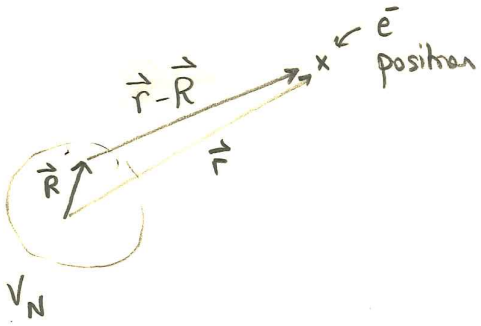
where $j = \begin{cases} 1/2, & \ell = 0 \\ \ell \pm 1/2, & \text{o.w.} \end{cases}$

Interestingly, this form was obtained by Arno Sommerfeld using pre-QM. But with wrong degeneracies and wrong physics!

Hyperfine Hamiltonian

One can derive the hyperfine Hamiltonian once again starting from Dirac eqn (see, Stoneham – TDS). A non-relativistic alternative is available, e.g. Nolting & Ramakanth in QTM. Its merit is that it vividly shows how each term arises in the HF Hamiltonian, which is what we follow.

Let the nuclear current density be denoted by $\vec{j}(\vec{R})$ which resides within the nucleus "volume" V_N giving rise to a nuclear vector potential $\vec{A}_N(\vec{r})$:



$$\vec{A}_N(\vec{r}) = \frac{\mu_0}{4\pi} \int_{V_N} d^3R \, \frac{\vec{j}(\vec{R})}{|\vec{r}-\vec{R}|}$$

With multipole expansion of $\frac{1}{|\vec{r}-\vec{R}|}$ up to only dipole $r \gg R$:

$$|\vec{r}-\vec{R}|^{-1} = \left(r^2 - 2\vec{r}\cdot\vec{R} + R^2\right)^{-1/2} \simeq \frac{1}{r}\left(1 + \frac{\vec{r}\cdot\vec{R}}{r^2}\right)$$

$$\Rightarrow \vec{A}_N(\vec{r}) \simeq \frac{\mu_0}{4\pi r}\left[\int_{V_N} d^3R \, \vec{j}(\vec{R}) + \int_{V_N} d^3R \, \vec{j}(\vec{R}) \, \frac{\vec{r}\cdot\vec{R}}{r^2} \right]$$

The first integral $\int_{V_N} d^3R \, \vec{j}(\vec{R}) = 0$ (A standard procedure in classical E & M)

Defining $\vec{M}_N \equiv \frac{1}{2} \int_{V_N} d^3R \left[\vec{R} \times \vec{j}(\vec{R})\right]$ ... nuclear magnetic moment

NB: The nuclear magnetic moment in practise refers to both spin and orbital contributions from all nucleons within the nucleus.

$$\Rightarrow \vec{A}_N(\vec{r}) \overset{\text{dipole}}{=} \frac{\mu_0}{4\pi} \frac{\vec{M}_N \times \hat{r}}{r^2} = \frac{\mu_0}{4\pi} \vec{\nabla} \times \left(\frac{1}{r} \vec{M}_N \right) \qquad \vec{B}_N = \vec{\nabla} \times \vec{A}_N$$

This nuclear vector potential influences the electrons in the same way as any external magnetic field in two ways:

1) Affects the electron's spin degrees of freedom via $-\vec{\mu} \cdot \vec{B}$ as:

$$2 \frac{\mu_B}{\hbar} \vec{s} \cdot \underbrace{(\vec{\nabla} \times \vec{A}_N)}_{\vec{B}_N}$$

($2 \to g_e$)

2) Affects the electron's orbital degree of freedom via replacing the kinetic energy part. Recall that in the presence of EM field for a charge q of mass m:

$\vec{P} = m\vec{v}$ ... kinetic momentum

$\vec{p} = \frac{\partial L}{\partial \dot{\vec{r}}} \to -i\hbar\vec{\nabla}$ ... canonical (generalized) momentum

$T = \frac{P^2}{2m}$ ... kinetic energy

In the presence of EM field kinetic and canonical momentum become different: $\vec{P} = \vec{p} - q\vec{A}$ (in SI units)

So that $T = \frac{(\vec{p} - q\vec{A})^2}{2m}$

For an $\bar{e}$ $(m \to m_e,\ q \to -e)$ K.E. part of Hamiltonian changes to

$$\frac{\hat{p}^2}{2m_e} + \underbrace{\frac{e}{2m_e}\vec{p}\cdot\vec{A}_N + \frac{e}{2m_e}\vec{A}_N\cdot\vec{p}}_{\frac{e}{m_e}\vec{p}\cdot\vec{A}_N \text{ as } [\vec{p},\vec{A}_N]=0} + \cancel{\mathcal{O}(A_N^2)} \quad \text{neglect}$$

within Coulomb gauge $\vec{\nabla}\cdot\vec{A}_N \equiv 0$

Hence, the additional terms in the electronic Hamiltonian due to $\vec{A}_N$, so-called hyperfine terms are

$$\mathcal{H}_{HF} = \mathcal{H}^{(1)}_{HF} + \mathcal{H}^{(2)}_{HF}$$

$$\mathcal{H}^{(2)}_{HF} = \frac{e}{m_e}\vec{p}\cdot\vec{A}_N \qquad \vec{A}_N = \frac{\mu_0}{4\pi}\vec{m}_N \times \frac{\vec{r}}{r^3}$$

$$\vec{A}\cdot(\vec{B}\times\vec{C}) = \vec{B}\cdot(\vec{C}\times\vec{A})$$

$$= \frac{\mu_0}{4\pi}\frac{e}{m_e}\vec{m}_N\cdot\left(\frac{1}{r^3}\vec{r}\times\vec{p}\right) \qquad \vec{r}\times\vec{p} = \vec{l}$$

$$\mu_B = \frac{e\hbar}{2m_e}$$

$$= 2\frac{\mu_B}{\hbar}\frac{1}{r^3}\frac{\mu_0}{4\pi}\vec{m}_N\cdot\vec{l} \leftarrow \text{vanishes for } l=0 \text{ (s-states)}$$

$$\mathcal{H}^{(1)}_{HF} = 2\frac{\mu_B}{\hbar}\vec{s}\cdot(\vec{\nabla}\times\vec{A}_N)$$

$$\vec{A}_N = \frac{\mu_0}{4\pi}\vec{\nabla}\times\left(\frac{1}{r}\vec{m}_N\right)$$

$-\vec{m}_s$: $\bar{e}$ spin magnetic moment

$$\vec{\nabla} \times \vec{A}_N = \frac{\mu_0}{4\pi} \vec{\nabla} \times \vec{\nabla} \times \left(\frac{1}{r} \vec{m}_N \right)$$

$$= \frac{\mu_0}{4\pi} \left[\vec{\nabla} \left(\vec{\nabla} \cdot \left(\frac{1}{r} \vec{m}_N \right) \right) - \nabla^2 \left(\frac{1}{r} \vec{m}_N \right) \right]$$

$$= \frac{\mu_0}{4\pi} \left[\vec{\nabla} \left(\vec{m}_N \cdot \vec{\nabla} \left(\frac{1}{r} \right) \right) - \vec{m}_N \nabla^2 \left(\frac{1}{r} \right) \right]$$

$$\vec{\nabla} \left(r^{-1} \right) = -r^{-2} \hat{r}$$

$$-4\pi \delta(\vec{r})$$

($\bar{e}$ positron coinciding with nuclear site)

drop this term (to be revisited)

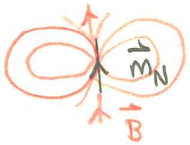
So, $$\vec{\nabla} \times \vec{A}_N = -\frac{\mu_0}{4\pi} \vec{\nabla} \left(\vec{m}_N \cdot \frac{\vec{r}}{r^3} \right)$$

evaluate in Cartesian components

$$\frac{d}{dx} \left(\frac{\vec{r} \cdot \vec{m}_N}{r^3} \right) = \frac{m_{Nx}}{r^3} - \frac{\vec{r} \cdot \vec{m}_N}{r^4} 3 \frac{x}{r}$$

$\frac{d}{dy}(\cdot)$, $\frac{d}{dz}(\cdot)$

$$\vec{\nabla} \times \vec{A}_N = \frac{\mu_0}{4\pi} \frac{3\vec{r} \left(\vec{m}_N \cdot \vec{r} \right) - \vec{m}_N r^2}{r^5}$$ ← Dipolar magnetic field



$$\Rightarrow \mathcal{H}_{HF}^{(1)} = -\vec{m}_S \cdot \vec{B}_N$$

$$= 2 \frac{\mu_B}{\hbar} \frac{\mu_0}{4\pi} \vec{s} \cdot \left(\frac{3\vec{r} \left(\vec{m}_N \cdot \vec{r} \right)}{r^5} - \frac{\vec{m}_N}{r^3} \right)$$ ... magnetic dipolar HFI part

Fermi Contact Term

The term we dropped above was safe when e^- wf vanishes at the nuclear site, however for s-electrons ($\ell=0$) with wf $\psi(\vec{r})$ we have to make a revision. If we work out the expectation value for

$$\langle \vec{s}\cdot\vec{B}_N \rangle \propto \int d^3r\, \psi^*(\vec{r}) \left[\vec{s}\cdot(\vec{\nabla}\times\vec{A}_N)\right]\psi(\vec{r})$$

(all space)

$$= \underbrace{\int_{V_N}}_{\text{Let's follow this term} \rightarrow \text{Fermi-Contact HFI}} + \underbrace{\int_{\text{rest of space}}}_{\text{leads to dipolar HFI as derived above}}$$

Using the cyclic triple product:

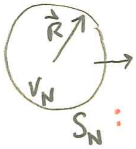
$$\vec{s}\cdot(\vec{\nabla}\times\vec{A}_N) = \vec{\nabla}\cdot(\vec{A}_N\times\vec{s}) = \vec{s}\cdot(\vec{\nabla}\times\vec{A}_N) - \vec{A}_N\cdot(\vec{\nabla}\times\vec{s})$$

and taking the e wf within the nucleus region as constant $\psi(\vec{r})\rightarrow\psi(0)$

$$|\psi(0)|^2 \int_{V_N} d^3r\ \vec{\nabla}\cdot(\vec{A}_N\times\vec{s}) = |\psi(0)|^2 \int_{S_N} d^2R\ \hat{n}\cdot(\vec{A}_N\times\vec{s})$$

$\vec{\nabla}\cdot(\vec{A}_N\times\vec{s})$: divergence theorem

$\hat{n}\cdot(\vec{A}_N\times\vec{s})$: const. (cyclic perm)



S_N : a sphere (for simplicity)

$$= |\psi(0)|^2 \, \vec{S} \cdot \int_{S_N} d^2R \; \hat{n} \times \vec{A}_N \leftarrow \frac{\mu_0}{4\pi} \frac{\vec{m}_N \times \vec{R}}{R^3}$$

$$= |\psi(0)|^2 \, \vec{S} \cdot \int_{S_N} d\Omega \, R^2 \underbrace{\left(\frac{\vec{R}}{R} \times \left(\frac{\mu_0}{4\pi} \frac{\vec{m}_N \times \vec{R}}{R^3}\right)\right)}_{\frac{\mu_0}{4\pi} \frac{1}{R^2}\left[\vec{m}_N R^2 - \vec{R}(\vec{R}\cdot\vec{m}_N)\right]}$$

($\hat{n} = \frac{\vec{R}}{R}$; $d\Omega = \sin\theta \, d\theta \, d\phi$)

let $\vec{m}_N = \hat{z} \, m_N$ ↘

$$\frac{\mu_0}{4\pi}\left[\hat{z} m_N - \hat{r} m_N \cos\theta\right]$$

only $\hat{z}$ component will survive after $\int d\Omega$

$\hat{r} \to \hat{z}\cos\theta$

$$\frac{\mu_0}{4\pi} \hat{z} m_N \, 2\pi \int_0^{\pi} d\theta \sin\theta (1-\cos^2\theta) \to \int_{-1}^{1} (1-u^2)\,du = \frac{4}{3}$$

$$\Rightarrow \quad \left\langle \vec{S} \cdot \vec{B}_N \right\rangle_{\text{contact}} = \frac{2}{3} \mu_0 |\psi(0)|^2 (\vec{S} \cdot \vec{m}_N)$$

From this we deduce the Hamiltonian operator as

$$\mathcal{H}_{HF}^{\text{contact}} = \frac{4}{3} \mu_0 \frac{\mu_B}{\hbar} (\vec{S} \cdot \vec{m}_N) \, \delta(\vec{r}) \quad \ldots \text{ Fermi contact part of HFI}$$

Expressing $\vec{m}_N$ in terms of nuclear spin $\vec{I}$ and nuclear magneton $\mu_N = \frac{e\hbar}{2m_p}$

$$\vec{m}_N = g_N \frac{\mu_N}{\hbar} \vec{I}$$

↖ nuclear g-factor

$$\mathcal{H}_{HF} = \frac{\mu_0}{2\pi}\frac{\mu_B}{\hbar^2} g_N \mu_N \left[\underbrace{\frac{1}{r^3}(\vec{I}\cdot\vec{\ell})}_{\text{orbital HFI}} + \underbrace{\left(\frac{3(\vec{s}\cdot\vec{r})(\vec{I}\cdot\vec{r})}{r^5} - \frac{\vec{s}\cdot\vec{I}}{r^3} \right)}_{\text{magnetic dipolar HFI}} \right.$$

$$\left. + \underbrace{\frac{8\pi}{3}(\vec{s}\cdot\vec{I})\,\delta(\vec{r})}_{\text{contact HFI}} \right]$$

Let's calculate the 1st order hyperfine shift in the 1s H atom ($Z=1$). In this case $\ell = 0$ so the orbital term in $\mathcal{H}_{HF}$ vanishes. Similarly, the dipolar term also vanishes when integrated over all 4π solid angle. So, we only have the contact term's contribution:

$$\Delta E_{HF}(1s) = \frac{4 g_N \mu_0 \mu_B \mu_N}{3\hbar^2} \langle \vec{s}\cdot\vec{I} \rangle \underbrace{|\psi_{1s}(0)|^2}_{\frac{1}{\pi a_B^3}}$$

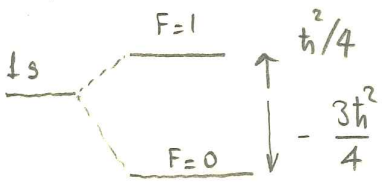
(2 × 2.79; $\vec{s}_p$: spin-1/2)

$\vec{F} = \vec{s} + \vec{I}$

Using the approach we followed for $\vec{\ell}\cdot\vec{s}$ in SOI, we express

$$\vec{s}\cdot\vec{s}_p = \frac{1}{2}\left[(\vec{s}+\vec{s}_p)^2 - s_p^2 - s^2 \right] = \frac{1}{2}\left[F(F+1) - s_p(s_p+1) - s(s+1) \right]$$

(singlet) $F=0$: $-\frac{3\hbar^2}{4}$; $F=1$ (triplet): $\frac{\hbar^2}{4}$

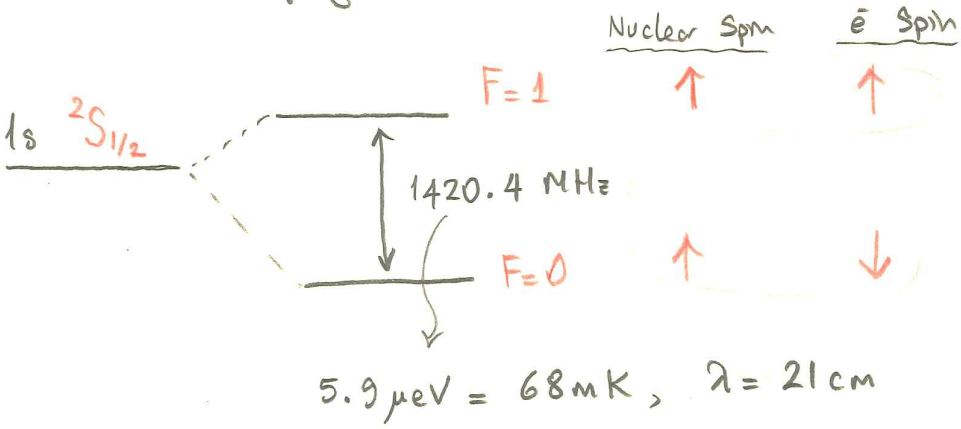


$$\Rightarrow \Delta E_{HF}(1s) = \frac{2\mu_0}{3} 2.79 \frac{e\hbar}{2m_e} \frac{e\hbar}{2m_p} \frac{4}{\pi a_B^3} \sim \frac{m_e}{m_p} \alpha^4$$

$$= 9.39 \times 10^{-25} \text{ J}$$

NB: Hyperfine splitting is a factor of $\frac{m_e}{m_p}$ smaller than the fine structure corrections ($\sim \alpha^4$).

"While HF structure is the weakest of all (known) angular momenta couplings, its capacity to enlighten is profound."



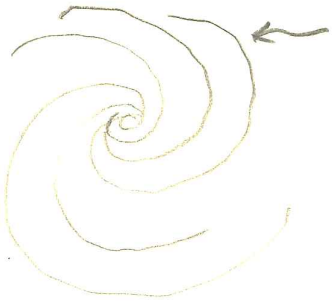
This F=1 to F=0 transition is electric-dipole (E1) forbidden, but magnetic-dipole (M1) allowed. This makes it quite a rare event. The natural (spontaneous) lifetime is 10^7 years and so unlikely to be seen in a lab on Earth. But the rate can be amplified by stimulated emission in the case of hydrogen maser which operates in this $F=1 \rightarrow F=0$ transition.

Another way to observe the spontaneous emission is to bring together a huge amount of H atoms which is naturally the case in the interstellar medium.

Importance for Radio Astronomy

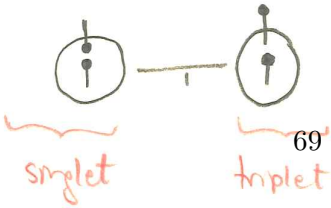
The cosmic thermal bath is at 1.95 K (today) and 2.7 K (back "then") so that $k_B T \gg \Delta E_{HF} = 68\ mK$. So, the F=1 state is thermally populated and we can see the $\lambda = 21$ cm lines even from regions w/o stars and hot gas. A nice thing is that the wave length of $\lambda = 21$ cm can penetrate the large clouds of interstellar cosmic dust that are opaque to their visible light.

This is used to measure the rotation speed of H gas in a given galaxy using the Doppler shifts. This revealed presence of Dark Matter.



← outskirts rotate way too fast to be held together by the gravity of stars within!
(There must be some dark matter producing deficient attractive force)

The hyperfine transition was portrayed in pioneer plaque:



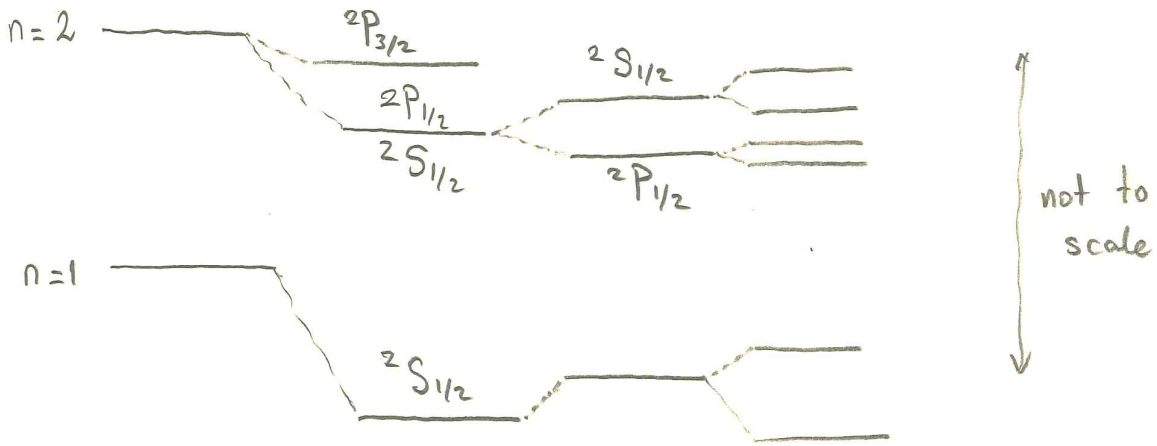
and 21 cm was used as a natural scale to measure human height etc.

The 21 cm line arises from a 1.4 GHz splitting of the $n=1$ level.

There is also a similar energy splitting for $n=2$ state (which is not populated in H at eql.) bet. $2S_{1/2}$ and $2P_{1/2}$. According to Dirac theory these should have been degenerate but $2S_{1/2}$ is measured to be higher by 1.057 GHz. This is known as the **Lamb shift**, which arises from the coupling to the EM vacuum fluctuations (like the Darwin term). But whereas Darwin term (included in Dirac theory) restores the degeneracy of s- and p-states, Lamb shift (not included in Dirac theory) makes ⇓ QED

S-state become higher in energy than p-state.

Summary of Shifts



Coulomb Fine Str. Lamb Shift Hyperfine Shift

Order of Magnitude: Bohr Energy $\sim \alpha^2$

Fine Str. $\sim \alpha^4$ (SO + Darwin + rel. mass corr.)

Lamb shift $\sim \alpha^5 \ln\alpha$

Hyperfine $\sim \frac{m_e}{m_p}\alpha^4$

Angular Momentum Coupling Schemes in Multi-$\bar{e}$ Atoms

The computational multi-$\bar{e}$ schemes such as HF and beyond provide a quantitive insight, however they require special tools and become less transparent in terms of physics. Alternatively, we shall consider qualitative tools that are in wide use in AMO community.

Central Field Approximation

As the crudest approximation, we can assume that each $\bar{e}$ sees a mean electric potential that is centrally symmetric. Therefore orbital states l_i together with n_i for each $\bar{e}$ forms the electronic configuration of a state in a multi-$\bar{e}$ atom. The energy levels in the central field approximation are highly degenerate.

Shell vs. Subshell

X-ray absorption names (not widely used)

Shells:
- $n=1$ (K)
- $n=2$ (L)
- $n=3$ (M)

In subshell designation we indicate the atomic orbitals and the number of $\bar{e}$'s contained within: $2p^4$ etc.

The max. # $\bar{e}$'s per subshell $(l) = (2s+1)(2l+1) = 2(2l+1)$

A configuration describes the states of all $\bar{e}$'s: Si $\rightarrow$ [Ne] $3s^2 3p^2$ ($1s^2 2s^2 2p^6$)

* A (sub)shell is said to be closed when it contains its max. # $\bar{e}$'s. A closed subshell has a spherically symmetric charge distr. $\vec{J}=0$

* In general, a configuration (unless for a closed shell) will lead to several, so-called terms. More on this later...

* One should not forget that configuration is only an approximation. In reality, including the ground states of atoms, admixtures of several configurations are required to determine the energy of a multi-$\bar{e}$ atom, as the underlying states/configurations were extracted from single-$\bar{e}$ H-like atom.

The residual Coulomb interaction (that is not centrally symmetric) is responsible for lifting some of the degeneracies within a given configuration. Furthermore, even though in central field approximation the projection of $\vec{l}$ and $\vec{s}$ along the quantization axis are also conserved, this will no longer be the case. In other words, non-central forces will lead to mixing among $\{m_l\}$ states of the same l. However, $\vec{L} = \sum_i \vec{l}_i$ and its z-prj will still be conserved.

Furthermore, the spin-orbit interaction $\lambda \vec{l}\cdot\vec{s}$ is also operational in lifting some of the degeneracies.

Strictly speaking only the TOTAL angular momentum $\vec{J}$ of the of the $\bar{e}$'s is conserved. If we also consider the hyperfine coupling then, only the total atomic angular momentum $\vec{F} = \vec{I} + \vec{J}$ and its z-projection F_z will be the two good quantum numbers.

However, depending on the relative strengths of i) residual Coulomb e-e interaction, ii) spin-orbit coupling, iii) hyperfine coupling, we can introduce different angular momentum coupling schemes.

LS coupling: Coulomb e-e $\gg$ spin-orbit coupling

This is the case usually for the low-lying states of light atoms where $\bar{e}$'s in the outer shell interact strongly (Coulomb) with $\bar{e}$'s in the inner shell (core). This coupling scheme is often appropriate for the ground states of most atoms

In this case, as the spin-orbit coupling is weak, it is meaningful to introduce $\vec{L} \equiv \sum_i \vec{l}_i$, $\vec{S} \equiv \sum_i \vec{s}_i$ $\vec{J} \equiv \vec{L} + \vec{S}$

$\vec{L}$: total orbital ang. mom.

$\vec{S}$: total spin

$\vec{J}$: min $|\vec{L}-\vec{S}|$, max $|\vec{L}|+|\vec{S}|$

jj Coupling: spin-orbit coupling $\gg$ Coulomb e-e

The jj coupling describes systems where one $\bar{e}$ is highly excited (as in Rydberg atoms). The reason is that the high-n orbitals have large separation bet. core $\bar{e}$'s and the high-n $\bar{e}$ which reduces the Coulomb interaction.

Another possibility for the spin-orbit term to dominate is for high-atomic numbers (high Z). Recall the spin-orbit energy shift

$$\Delta E_{so} \sim Z^4$$

Therefore, the structure of the spectra of the heavy elements very closely approaches the structure characteristic of jj coupling.

In this case, due to strong spin-orbit coupling, the individual $\vec{l}_i$ and $\vec{s}_i$ or their individual sums $\vec{L}$ and $\vec{S}$ are <u>not</u> good quantum numbers, but $\vec{j}_i = \vec{l}_i + \vec{s}_i$ is.

Intermediate coupling: Coulombic e-e $\simeq$ spin-orbit

In passing from the light to heavy elements, a more or less continuous transition from LS to jj coupling occurs, i.e., there is an intermediate coupling. Note that even for the intermediate coupling J is a good q.n. as the total ang. mom. is conserved (absence of HFI). The notation $^{2S+1}L_J$ (for the LS coupling) is often used for the int. coupling also.

Important: LS or jj couplings are idealizations which simplify the interpretation of atomic spectra wherever applicable.

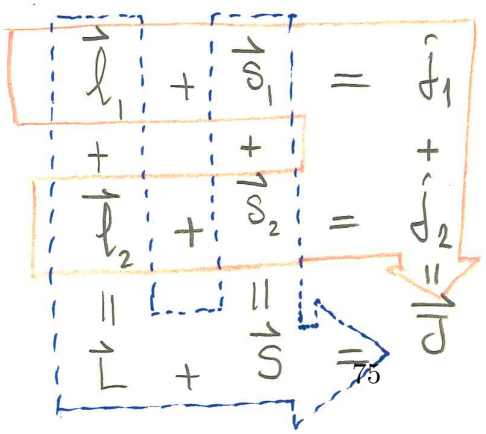
These angular momentum coupling schemes are very widely used in nuclear shell models. Therefore, they have a wide support also outside AMO.

Why bother which coupling scheme is the are?

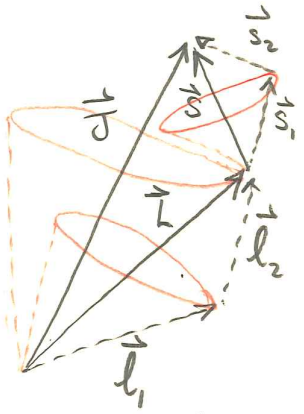
As we noted above, the particular coupling scheme enables the interpretation of the optical spectra.

The coupling scheme has clear consequences for the atomic selection rules as we shall discuss in the light-matter interaction part.

The rules related to the total orbital and spin angular momenta, for instance, are only obeyed as long as L and S are good quantum numbers. The selection rules for the total angular momentum $\vec{J}$ and its quantization axis projection M_J are good quantum numbers under any coupling scheme, in the absence of hyperfine coupling.



Vector Models of Coupling Schemes



LS Coupling

Since in LS coupling,

Coulomb e-e $\gg$ spin-orbit

the ranking of precessions:

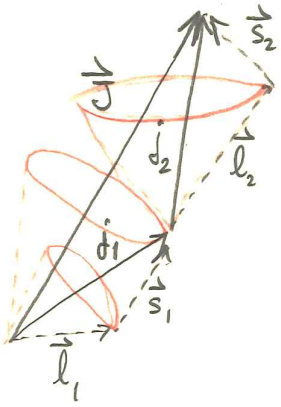
$\vec{l}_1$ and $\vec{l}_2$ precession around $\vec{L}$ } fast

$\vec{s}_1$ and $\vec{s}_2$ " " $\vec{S}$ }

$\downarrow$

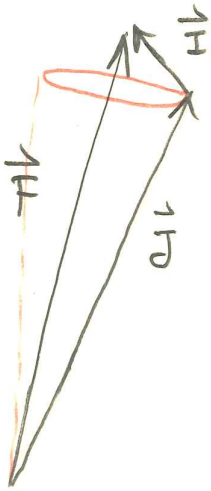
$\omega_p \sim \frac{E_{coulomb}}{\hbar}$

The precession of $\vec{L}$ and $\vec{S}$ around $\vec{J}$ $\rightarrow$ slow $\leftarrow$ $\omega_p \sim \frac{E_{so}}{\hbar}$



jj coupling

HF interaction $\longrightarrow$



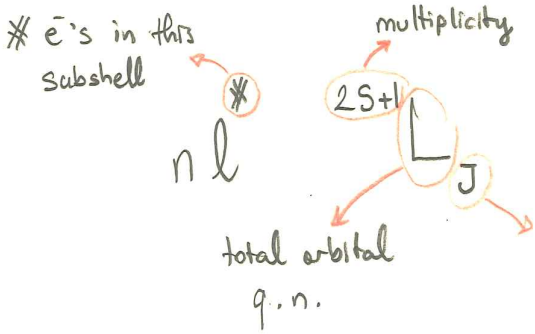
Term Symbols in the LS Coupling

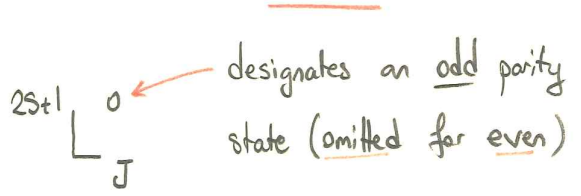
In light atoms ($Z \lesssim 30$), e^- spins $\vec{s}_i$ interact among themselves forming total spin ang. mom. $\vec{S} = \sum_i \vec{s}_i$. The same happens with orbital angular momenta $\vec{L} = \sum_i \vec{l}_i$ and eventually $\vec{L}$ & $\vec{S}$ get coupled forming $\vec{J} = \vec{L} + \vec{S}$

In this regime, it can be shown that the dominant e-e interaction term, $H_{e\text{-}e} \sim \sum_{i;j} \frac{1}{r_{ij}}$, commutes with $[H_{ee}, L] = [H_{ee}, S] = 0$ so that in this approximation, L^2, S^2, L_z, S_z are constants of motion.

LS coupling holds as long as any external magnetic field is weak, otherwise these two momenta decouple, giving rise to a different splitting pattern in the energy levels → Paschen-Back Effect

Term Symbols in the LS Coupling:





$L = 0, 1, 2, 3, 4, 5, 6, 7, \ldots$ (not to mix with J)
S P D F G H I K

Alternative:

$^{2S+1}L_{J,u}$ or $^{2S+1}L_{J,g}$

ungerade (odd) — gerade (even)

$P = (-1)^{\sum_i l_i}$ (-1 / $+1$)

orbital q.n. for open shell e^-'s

For a given $\bar{e}$ configuration:

* The S and L together (i.e., term) contains $(2S+1)(2L+1)$ possible microstates
* The S, L, and J together is called a level. A given level has $(2J+1)$ microstates.
* A combination of L, S, J and M_J defines a single state: $|L,S;J,M_J\rangle$

Examples (The best way to master term symbols)

1) He – ground state: $1s^2 \rightarrow 1s^2\ {}^1S_0$ — singlet ($S=0$, $\uparrow\downarrow$); even parity; "singlet S zero"; read as; $L=0+0=0$; $J=L+S=0$

Recall: $S=1$ not allowed by Pauli Exc.

2) a) Na – ground state: $1s^2\ 2s^2\ 2p^6\ 3s$

All closed (sub)shells give ${}^1S_0$, hence

$1s^2\ ({}^1S_0)\ 2s^2\ ({}^1S_0)\ 2p^6\ ({}^1S_0)\ 3s^1\ \rightarrow\ {}^2S_{1/2}$ — $S=1/2$; read as "doublet S one-half"; $L=0$; $J=L+S=1/2$

b) Na – excited state: $[Ne]\ 3p^1$

Two possibilities for J:

- $L+S = 1+1/2 = 3/2 \rightarrow 3p\ {}^2P_{3/2}$ ... doublet P three-halves
- $L-S = 1-1/2 = 1/2 \rightarrow 3p\ {}^2P_{1/2}$ ... doublet P one-half

The examples so far contained only a single-e in the open subshell. Next, we shall consider a pair of $\bar{e}$'s. First, two non-equivalent pairs, and then two equivalent pairs. We shall see that for the latter we need to form tables so as not to violate Pauli Exclusion Principle.

3) Ne — excited state : $\underbrace{1s^2}_{^1S_0}\ \underbrace{2s^2}_{^1S_0}\ 2p^5\ 3p$ → equivalently, consider one p-vacancy

∴ 2 non-equivalent states : $np\ n'p \longrightarrow m_{\ell_1}^{s_1},\ m_{\ell_2}^{s_2}$ denote $s = \pm 1/2 \rightarrow \pm$

There are $(2\ell+1)(2s+1) \times (2\ell+1)(2s+1) = 6 \times 6 = 36$ microstates (see Table)

$M_L = 0, \pm1, \pm2, \ldots, \pm L$, $M_L = \sum_i m_{\ell_i}$; $M_S = 0, \pm1, \ldots, \pm S$, $M_S = \sum_i m_{s_i}$

M_L \ M_S	1	0		-1
2	1^+1^+	1^+1^-	1^-1^+	1^-1^-
1	1^+0^+	1^+0^-	0^+1^-	1^-0^-
	0^+1^+	1^-0^+	0^-1^+	0^-1^-
0	1^+-1^+	1^+-1^-	1^--1^+	1^--1^-
	0^+0^+	0^+0^-	0^-0^+	0^-0^-
	-1^+1^+	-1^+1^-	-1^-1^+	-1^-1^-
-1	-1^+0^+	-1^+0^-	0^+-1^-	-1^-0^-
	0^+-1^+	-1^-0^+	0^--1^+	0^--1^-
-2	-1^+-1^+	-1^+-1^-	-1^--1^+	-1^--1^-

Such combinations are distinct as these two $\bar{e}$'s are now distinguishable since they are in two different p-states (2p & 3p)

we do not get into how these microstates are distributed among these terms ; a different example is available →

Possible terms : ^3D, ^3P, ^3S, ^1D, ^1P, ^1S ✓

Term multiplicity $= (2S+1)(2L+1)$; $3\times5=15$, $3\times3=9$, $3\times1=3$, $1\times5=5$, $1\times3=3$, $1\times1=1$ $\xrightarrow{\Sigma}$ 36

4) C – ground state : $1s^2\ 2s^2\ 2p^2$ (or other Group-IV like Si)

$^1S_0\ \ ^1S_0$ ↳ contains two EQUIVALENT p $\bar{e}$'s

In this case we should watch for Pauli Exc. Pr. while writing possible microstates. For a given orbital q.# l, the total # available states is, $N_A = (2s+1)(2l+1) = 2(2l+1) \xrightarrow[l=1]{\text{for C}} N_A = 6$ ($s = 1/2$)

If there are N_e $\bar{e}$'s in this subshell (l), then the # possible combinations are

$$N = \binom{N_A}{N_e} = \frac{N_A!}{N_e!\,(N_A - N_e)!} \xrightarrow[N_A=6,\ N_e=2]{\text{for C}} N = \frac{6!}{2!\,4!} = 15 \text{ different microstates}$$

m_l: 1, 0, −1 ($2l+1$) — ↑↓ Not possible

$M_S = \sum_i m_{s_i} = 0, \pm 1 \quad (S = 0, 1)$

M_L ↙ $\sum_i m_{l_i}$	M_S = 1	M_S = 0	M_S = −1
2		1^+1^-	
1	1^+0^+	1^+0^-	
		1^-0^+	1^-0^-
0	1^+-1^+	1^+-1^-	
		0^+0^-	
		-1^+1^-	1^--1^-
−1	-1^+0^+	-1^+0^-	
		-1^-0^+	-1^-0^-
−2		-1^+-1^-	

empty entries due to Pauli Exc. Pr. OR indistinguishable config.

15 microstates ✓

Tentative (Possible) terms are:

$^3D,\ ^3P,\ ^3S,\ ^1D,\ ^1P,\ ^1S$

see next page

Aside: these entries encircled are in singlet-spin configuration as triplet identically vanishes for equivalent $\bar{e}$'s

The question is, to which terms do these microstates belong?

The rigorous way to do this is via group theory. But we shall follow another alternative, where we first form M_L vs M_S table containing # possible microstates as the entries:

M_L \ M_S	1	0	-1
2		1	
1	1	2	1
0	1	3	1
-1	1	2	1
-2		1	

Next, extract smaller tables representing each possible term. Each table will be $(2L+1) \times (2S+1)$ dimensional and will contain only 1's as entries.

First, hunt for $L=2$ with a single value for M_S (implying $S=0$) $\Rightarrow$ ^1D term

$S=0,\ L=2 \Rightarrow J=2 \Rightarrow {}^1D_2$

M_L \ M_S	0
2	1
1	1
0	1
-1	1
-2	1

$\leftarrow$ When we subtract this contribution from the main table (above), we are left with a 3×3 part.

M_L \ M_S	1	0	-1
1	1	1	1
0	1	1	1
-1	1	1	1

Next, catch $L=1$, $S=1$ terms

$J = 2, 1, 0$

$\Rightarrow {}^3P_2,\ {}^3P_1,\ {}^3P_0$

There remains a single unaccounted one $\longrightarrow$ $L=0,\ S=0 \Rightarrow {}^1S$ term

$J=0 \Rightarrow {}^1S_0$

NB: Other possible terms ^3D, ^3S, ^1P are excluded due to Pauli Exc. Pr.

So, we obtained the $^3P_{2,1,0}$, $^1D_2$, $^1S_0$ terms as compliant with the configuration of carbon under LS coupling.

In general these terms have different energies, and the question is, which term would correspond to the ground-state, i.e, ground-term.

Hund's Rules

The recipe is provided by the so-called Hund's rules which were empirically determined by Friedrich Hund

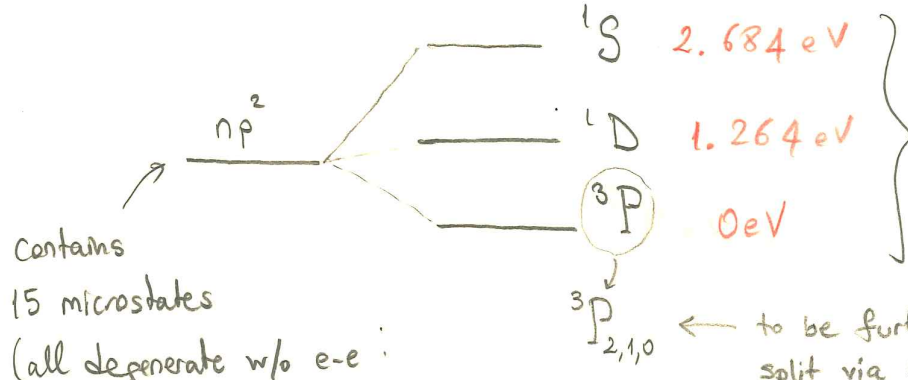
1. Among different term symbols $^{2S+1}L_J$, the term with maximum multiplicity (maximum S) has the lowest energy. → Exchange Energy!
2. For a given multiplicity, the term with the largest value of L has the lowest energy
3. For a given term (i.e., L and S) in an atom

"Justification in Landé Interval Rule":
- with outermost shell half-filled or less → lowest value of J
- " " " more than half-filled → highest " " "

} is the g.s.

NB: Hund's rules assume the validity of LS coupling regime. Also they do not hold for the ordering of excited states!

Turning to our C example, $^3P_0$ is the ground term.



still LS coupling applies for this case!

Ex: Erbium belongs to rare earth metals ($Z = 68$), $[Xe]\,4f^{12}\,6s^2$ → $^1S_0$

We can easily determine the ground term.

Easier to consider only the vacancies in f: $f^{12} \rightarrow f^2$

For ground term
1) maximize S
2) Next, maximize L



$L = 5$ (3+2), $S = 1$ ⇒ $J = 6, 5, 4$

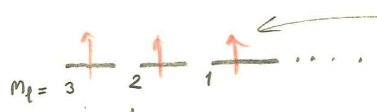
H

Ground term (Hund's rule) → $^3H_6$, $^3H_5$, $^3H_4$, + other terms with smaller S

Technologically more important is the Er^{+3} ion: $[Xe]\,4f^{11}$

Er-doped fiber amplifiers

Switch to vacancies: $f^{11} \rightarrow f^3$



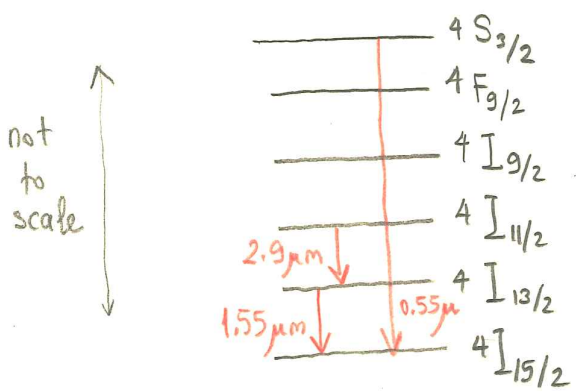
maximizing S for ground term and then max. L

$L = 6$ (3+2+1), I; $S = 3/2$, $2S+1 = 4$ ⇒ $J = 15/2,\ 13/2,\ 11/2,\ 9/2$

$^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$

Ground-term via Hund's Rule

f^{11} more than half-filled ⇒ max. $J = \frac{15}{2}$



j-j Coupling

Remaining on the previous np-np two equivalent e^-'s, let's redo it within jj coupling (as would apply to say Pb). Again we need to watch for the Pauli Exc. Pr. $\Rightarrow$ tables

$\vec{j}_i = \vec{l}_i + \vec{s}_i$ (P, 1/2) $\rightarrow$ 3/2, 1/2

Possible $\vec{j}_1 - \vec{j}_2$ cases:

$\left(\frac{3}{2}, \frac{3}{2}\right)$, $\left(\frac{3}{2}, \frac{1}{2}\right)$, $\left(\frac{1}{2}, \frac{1}{2}\right)$

In j-j coupling quantum labels for these two states will be (j_1, m_{j_1}) and (j_2, m_{j_2}) according to Pauli Exc. Pr. they need to be distinct!

$\boxed{j_1 = 3/2, \quad j_2 = 3/2}$ We require $m_{j_1} \neq m_{j_2}$ according to Pauli E. P.

m_{j_1}	m_{j_2}	$\sum_i m_{j_i}$
3/2	1/2	2
3/2	-1/2	1
3/2	-3/2	0
1/2	-1/2	0
1/2	-3/2	-1
-1/2	-3/2	-2

6 μ states $\rightarrow$ 5: $J = 2$ $(M_J = \pm 2, \pm 1, 0)$; $J = 0$ $(M_J = 0)$

$\left(\frac{3}{2}, \frac{1}{2}\right)$

Since $\hat{j}_i$'s are distinct, no constraint on m_j's

m_{j_1}	m_{j_2}	$\sum m_{j_i}$
3/2	1/2	2
3/2	-1/2	1
1/2	1/2	1
1/2	-1/2	0
-1/2	1/2	0
-1/2	-1/2	-1
-3/2	1/2	-1
-3/2	-1/2	-2

8 μ-states → $J=2$ $(M_J = \pm 2, \pm 1, 0)$

8 μ-states → $J=1$ $(M_J = \pm 1, 0)$

$\left(\frac{1}{2}, \frac{1}{2}\right)$

Again m_j's need to be distinct!

m_{j_1}	m_{j_2}	$\sum$
1/2	-1/2	0

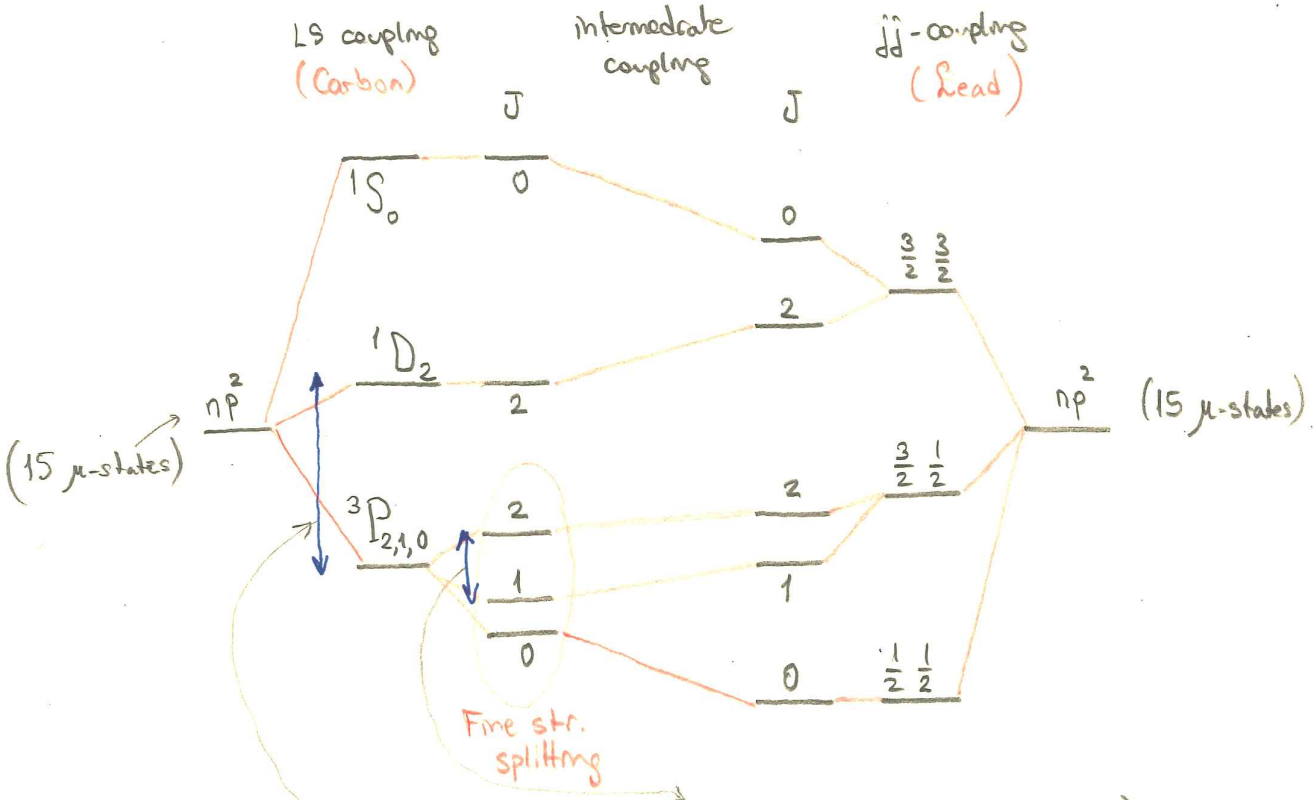
→ 1 μ state: $J=0$, $M_J = 0$

So, altogether we have $6+8+1 = 15$ μ states under jj coupling.

(Just like the LS coupled case :-)

LS → Intermediate → jj Coupling

If we move on the periodic table on the same column from light to heavy atoms (say, from carbon to lead $Z_{Pb} = 82$) we shall observe a smooth transition LS → intermediate → jj coupling of the atomic levels respecting the non-crossing rule.



LS coupling is meaningful when fine-str. splitting (i.e., SOI) is less than the term splitting (i.e., e-e interaction).

Fine Structure (Multi-e^- Case)

We realize from the previous evolution chart that the LS coupled states (unless they are singlets) split due to spin-orbit interaction, fine-structure splitting. We shall now show that this splitting is proportional to $\vec{J}$, so-called Landé interval rule.

Energy shift of $|LSJM_J\rangle$ state will be

(γ: other labels due to other deg. of freedom)

$$\Delta E_{\gamma LS;J} = \langle \gamma; LM_L, SM_S; JM_J | \xi(r)\vec{L}\cdot\vec{S} | \gamma; LM_L, SM_S; JM_J \rangle$$

using $\vec{L}\cdot\vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$ → J, L, S are good q.n. in LS coupling

$$\Delta E_{\gamma LS;J} = \xi(\gamma LS)\ \frac{J(J+1) - L(L+1) - S(S+1)}{2}$$

$$\xi(\gamma LS) = \frac{\hbar^2}{2m_e^2c^2}\left\langle \frac{1}{r}\frac{dV(r)}{dr}\right\rangle_{\gamma LS}$$

effective central field

Hence, the spacing bet. levels J and J-1 will be

$$\Delta E_{\gamma LS;J} - \Delta E_{\gamma LS;J-1} = \xi(\gamma LS)\, J$$

its sign det's ordering of J's

Hund's rule #3:

- $\xi(\gamma LS) > 0$ — Normal multiplet — A subshell w/ less than 50% filling
- $\xi(\gamma LS) < 0$ — Inverted multiplet — more than 50% filling

Two important properties of $\Delta E_{\gamma LS;J}$

1. $\Delta E_{\gamma LS;J}$ has no M dependence, which implies that there is no preferred direction in space — fine-str. is spherically symmetric

2. $$\sum_{J=|L-S|}^{L+S} (2J+1)\, \Delta E_{\gamma LS;J} = 0$$

This implies that the center of "gravity" of the multiplet,

$$\overline{E}_{\gamma LS;J} = \frac{\sum_J (2J+1)\, \Delta E_{\gamma LS;J}}{\sum_J (2J+1)} = 0$$

coincides with the unsplit term; see the drawing 2 pages back.

Atoms in an External DC Magnetic Field: Zeeman Effect

Magnetic field has a fundamental role in physics, esp. in AMO physics as it lifts most of the degeneracies in the states by removing the time-reversal symmetry. NMR and ESR spectroscopy are two direct applications based on Zeeman-split states.

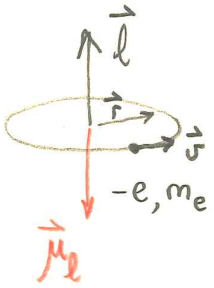
History and Nomenclature

P. Zeeman first observed in 1896 that spectral lines were split in the presence of an external magnetic field. It turns out that atoms without net spin ($S=0$) could be explained using classical concepts, hence termed as normal Zeeman effect, containing an odd number $[(2l+1)]$ of Zeeman sublevels. The case for net spin (atoms with unpaired $\bar{e}$'s) instead contains even number $[\times(2S+1)]$ of Zeeman sub-levels and cannot be explained classically as it requires the spin (half-integer) angular momentum. Therefore, it was termed anomalous Zeeman effect even though it is more commonly observed.

We shall start with the single-$\bar{e}$ hydrogen atom first classically, then via QM approach. Next, we shall consider many-$\bar{e}$ atoms.

Classical Treatment (Only applies to Normal Zeeman effect, no spin)

The magnetic moment of an atom with no spin will be entirely due to orbital motion. We take $\bar{e}$ orbital motion as a classical circular orbit.



An $\bar{e}$ with charge $-e$, velocity $\vec{v}$ and linear freq $\nu = \frac{\omega}{2\pi} = \frac{v}{2\pi r}$

corresponds to a current:

$$I = \frac{q}{T} = -e\nu = -\frac{ev}{2\pi r}$$

(I & v are in opposite dir's ($-e<0$))

So that the orbital magnetic moment becomes

$$\vec{\mu}_l = I\vec{A} = I\pi r^2 \hat{n} = -\frac{evr}{2}\hat{n}$$

$\vec{A}$: Vector area, $\pi r^2 \hat{n}$ ← RHR

Since circulating $\bar{e}$ has a mass, it also has an angular momentum

$$\vec{l} = \vec{r} \times \vec{p} = m_e r v \hat{n}$$

Hence, we can extract the relation: $\vec{\mu}_l = -\frac{e}{2m_e}\vec{l}$

due to fact that $\bar{e}$ has -ve charge (mass & charge flow are opposite)

More commonly this is expressed in terms of Bohr magneton as

$$\vec{\mu}_l = -\left(\frac{e\hbar}{2m_e}\right)\left(\frac{\vec{l}}{\hbar}\right);$$

$\left(\frac{e\hbar}{2m_e}\right)$ → μ_B: Bohr magneton $\simeq$ 58 μeV/T

KNOW this !

$\left(\frac{\vec{l}}{\hbar}\right)$ → dimensionless ang. mom.

OR we include the orbital g-factor for the $\bar{e}$ so that

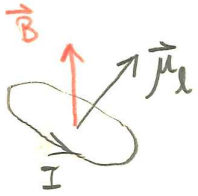
$$\vec{\mu}_l = -\mu_B\, g_{e,l}\left(\frac{\vec{l}}{\hbar}\right)$$

where $g_{e,l} = 1$

When we place such an atom in a uniform B field, the potential energy of the magnetic moment is given by

$$U = -\vec{\mu}_l \cdot \vec{B}$$

$$= \frac{e}{2m_e}\vec{l}\cdot\vec{B}$$



For $\vec{B} = \hat{z}B$, and assuming U as a small perturbation (quite safe as $\mu_B \simeq 58\ \mu$eV/T and in "labs" we have $B \lesssim 30$ T, but in neutron stars etc B field can become tremendously higher!)

$$\langle U\rangle_{\gamma l m_l} = -\langle \mu_{l,z}\rangle^{B}_{\gamma l m_l} \qquad -\mu_B\, g_{e,l}\,\frac{l_z}{\hbar}$$

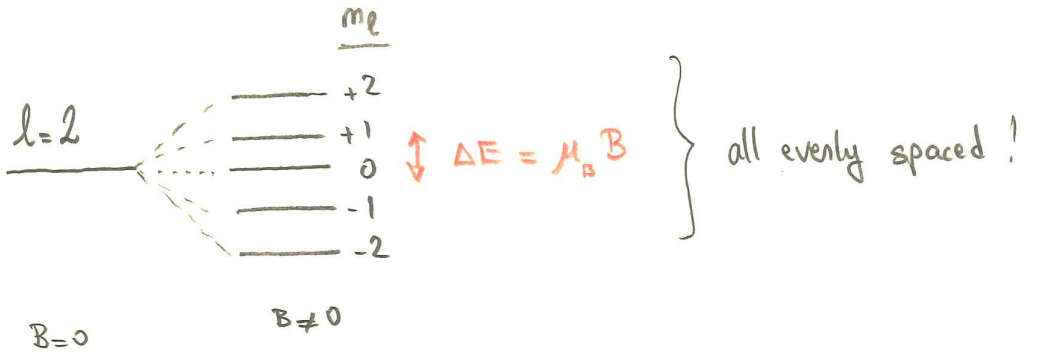
$\langle U\rangle_{\gamma l m_l}$ → expectation value of the state $\gamma l m_l$ ← all other quantum labels

$$\Rightarrow \langle \mu_{\ell,z} \rangle_{r l m_\ell} = -\mu_B \cancel{g_{e,\ell}}^{1} m_\ell$$

$$\Rightarrow \langle U \rangle_{r l m_\ell} = \mu_B m_\ell B \quad , \quad -\ell \leq m_\ell \leq \ell$$

Hence, the $(2\ell+1)$ m_ℓ states that were degenerate w/o magnetic field are now split with an energetic distance ($\vec{B}$ breaks space isotropy!)

$$\Delta E = E_{r l m_\ell} - E_{r l m_\ell - 1} = \mu_B B \quad \ldots \text{ Normal Zeeman Splitting}$$



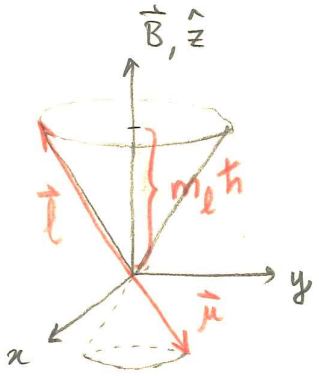
Larmor Precession

A complementary picture is to consider the dynamics of atomic magnetic moment in the presence of ext. B field. Due to torque present

$$\vec{\tau} = \vec{\mu}_\ell \times \vec{B}$$

both $\vec{l}$ and $\vec{\mu}_\ell$ will no longer be constant but precess around $\vec{B}$

(however l_z will still be const.)



Using mechanics relations

$$\vec{\tau} = \vec{\mu}_l \times \vec{B} = -\mu_B g_{e,l} \frac{\vec{l}}{\hbar} \times \vec{B}$$

$$= \frac{d\vec{l}}{dt} \leftarrow e^{-i\omega t} \vec{l}$$

$\vec{\omega}$

The Larmor precession angular frequency, $\omega = \dfrac{\mu_B g_{e,l} B}{\hbar}$

We shall leave the discussion on the EM absorption selection rules among Zeeman sub-levels to after considering coupling with radiation.

QM Treatment (Also applies to anomalous Zeeman effect w/ spin)

We consider a hydrogenic atom (with ∞ nuclear mass) in a uniform $\vec{B}$ field with vector potential $\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$ so that $\vec{B} = \vec{\nabla} \times \vec{A}$

$$\mathcal{H} = \frac{1}{2m_e}\left(\vec{p} + e\vec{A}\right)^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$\vec{p} = -i\hbar\vec{\nabla}$ and use $\vec{\nabla}\cdot\vec{A} = 0$

$$= -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{i\hbar e}{m_e}\vec{A}\cdot\vec{\nabla} + \frac{e^2}{2m_e}\vec{A}^2$$

$$\frac{e^2}{8m_e}\left|\vec{B}\times\vec{r}\right|^2 = \frac{e^2}{8m_e}\left[B^2r^2 - (\vec{B}\cdot\vec{r})^2\right]$$

$$-\frac{i\hbar e}{2m_e}(\vec{B}\times\vec{r})\cdot\vec{\nabla} = -\frac{i\hbar e}{2m_e}\vec{B}\cdot(\vec{r}\times\vec{\nabla})$$

$\vec{l} = -i\hbar\,\vec{r}\times\vec{\nabla}$

$$= \frac{e}{2m_e}\vec{B}\cdot\vec{l}$$

$$\vec{\mu}_l = -\mu_B\, g_{e,l}\,\frac{\vec{l}}{\hbar}$$

$$\mathcal{H}_1' = -\vec{\mu}_l\cdot\vec{B}$$

Linear term is same as we had in classical treatment

But, this time we also include the e^- spin, that contributes an additional intrinsic (spin) magnetic moment

$$\vec{\mu}_s = -g_{e,s}\frac{e}{2m_e}\vec{s}$$

$$= -g_{e,s}\mu_B\frac{\vec{s}}{\hbar}$$

$g_{e,s} = 2$ (Dirac Eqn. value for spin g-factor, QED-corrected value $g_{e,s} = 2.0023192\ldots$)

So, we have an additional interaction, linear in B as

$$\mathcal{H}_2' = -\vec{\mu}_s \cdot \vec{B} = \left(g_{s,e}\right) \mu_B \vec{B} \cdot \frac{\vec{s}}{\hbar}$$

($g_{s,e} = 2$)

Hence the complete Hamiltonian in the presence of $\vec{B}$ field, including the SOI (but excluding Darwin and relativistic mass correction terms)

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\vec{\nabla}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} + \zeta(r)\,\vec{l}\cdot\vec{s} + \underbrace{\frac{\mu_B}{\hbar}\left(\vec{l} + 2\vec{s}\right)\cdot\vec{B}}_{\text{paramagnetic term}} + \underbrace{\frac{e^2}{8m_e}\left|\vec{B}\times\vec{r}\right|^2}_{\text{diamagnetic term}}$$

* The linear-in-B paramagnetic term leads to the alignment of magnetic moments along $\vec{B}$ $\Rightarrow$ paramagnetism. Usually dominates over diamagnetic term

* The quadratic-in-B diamagnetic term dominates only for superhigh B fields in some astrophysical situations or in Rydberg states n: high

Now, assuming that the energy shifts due to $\vec{B}$ field are much smaller than those due to SOI, we can treat the linear-in-B terms perturbatively, assuming a z-directed field, $\vec{B} = \hat{z}B$

$$\mathcal{H}_B = \frac{\mu_B}{\hbar}\left(l_z + 2s_z\right)B$$

In the presence of SOI, the unperturbed (due to B) states are

eigenstates of J^2 and J_z labeled by j and m_j

where for a single $\bar{e}$ case $s = 1/2$, $j = \ell \pm 1/2$

$$\Delta E_{m_j} = \langle \ell \pm 1/2, m_j | \mathcal{H}_B | \ell \pm 1/2, m_j \rangle$$

Using $\ell_z + 2 s_z = j_z + s_z$ ($\ell_z + s_z$)

we have

$$\Delta E_{m_j} = \frac{eB}{2m_e} \left(m_j \hbar + \langle \ell \pm 1/2, m_j | s_z | \ell \pm 1/2, m_j \rangle \right)$$

($|j, m_j\rangle$ not an eigenstate of s_z :-(

The total ang. mom. states $|j, m_j\rangle$ can be expressed in terms of $|\ell, m_\ell; s, m_s\rangle$ states using C-G which enables the calculation of $\langle m_\ell', m_s | s_z | m_\ell, m_s \rangle$ expectations:

$$\left| \ell \pm \tfrac{1}{2}, m_j \right\rangle = \pm \sqrt{\frac{\ell \pm m_j + 1/2}{2\ell+1}} \left| m_j - 1/2, 1/2 \right\rangle + \sqrt{\frac{\ell \mp m_j + 1/2}{2\ell+1}} \left| m_j + \tfrac{1}{2}, -1/2 \right\rangle$$

$$\langle \ell \pm 1/2, m_j | s_z | \ell \pm 1/2, m_j \rangle = \frac{\hbar}{2(2\ell+1)} \left[(\ell \pm m_j + 1/2) - (\ell \mp m_j + 1/2) \right]$$

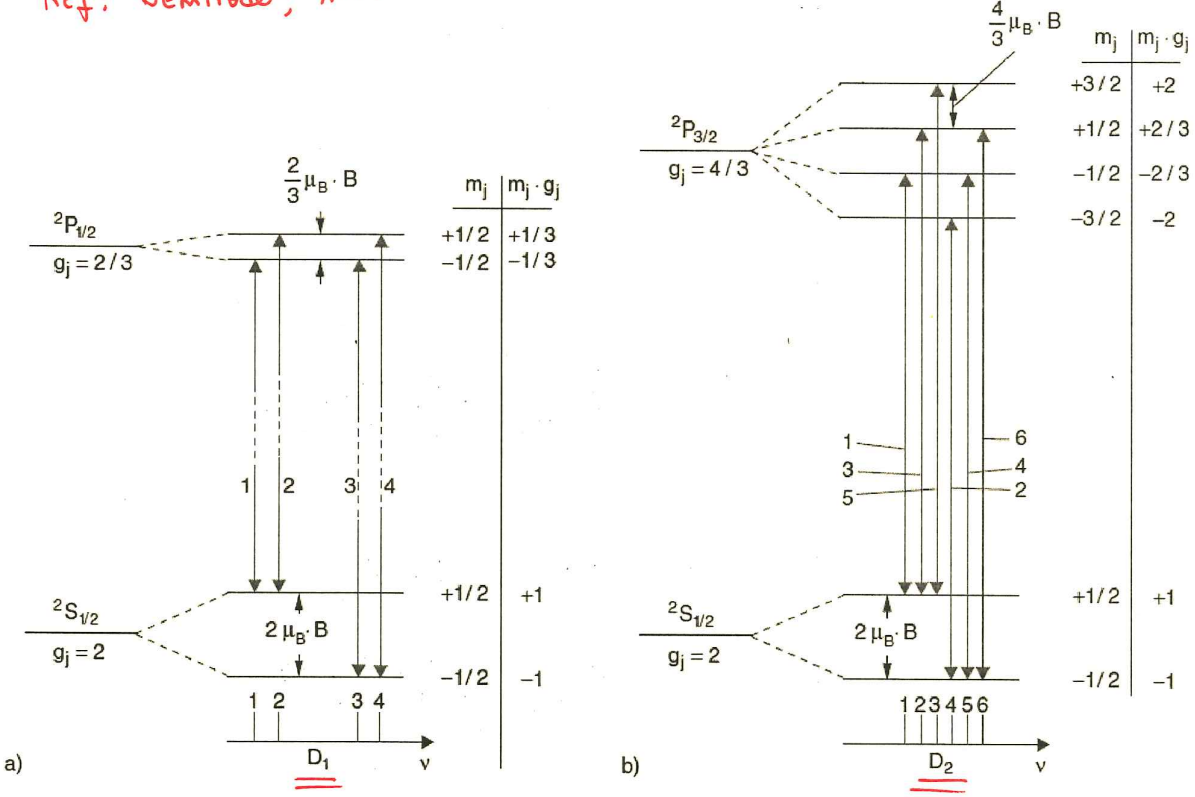
$$= \pm \frac{m_j \hbar}{2\ell+1}$$

Yielding,

$$\Delta E_{m_j} = \begin{cases} \frac{2\ell+2}{2\ell+1} \mu_B B m_j, & j = \ell + 1/2 \\ \frac{2\ell}{2\ell+1} \mu_B B m_j, & j = \ell - 1/2 \end{cases}$$

splittings are not the same for either multiplet

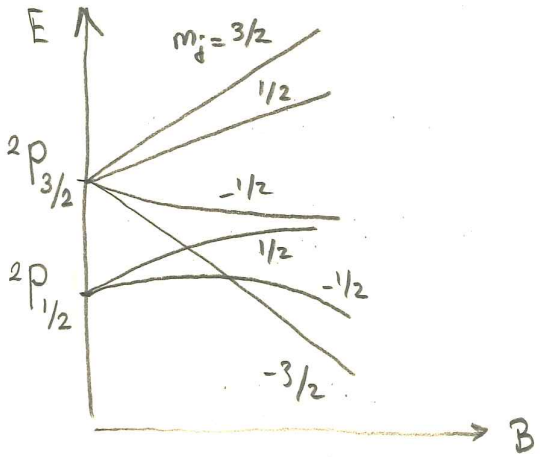
Ref: Demtröder, AMP



Zeeman pattern of the two sodium D-lines (neglecting hyperfine str.)

A historical artefact: this letter does not correspond to LS term symbol!

As the B field increases, energy levels smoothly evolve, where for large B (non-perturbative regime) the splittings becomes even (not reached below)



Zeeman Effect for Multi-electron Atom

Again neglecting the quadratic-in-B term, for the i'th $\bar{e}$ we have

$$\mathcal{H}'_i = \frac{\mu_B}{\hbar}\left(\vec{l}_i + 2\vec{s}_i\right)\cdot\vec{B}$$

Within the LS coupling regime $\vec{L} = \sum_i \vec{l}_i$, $\vec{S} = \sum_i \vec{s}_i$, we have

$$\mathcal{H}' = \sum_{i=1}^{N} \mathcal{H}'_i = \frac{\mu_B}{\hbar}\left(\vec{L} + 2\vec{S}\right)\cdot\vec{B}$$

Taking $\vec{B} = \hat{z}B$ and for weak magnetic fields (compared to SOI), the degeneracy in J is now removed by SOI $\propto \vec{L}\cdot\vec{S}$ and the atom is in an eigenstate of $\vec{J}^2$, $\vec{L}^2$, $\vec{S}^2$ and J_z. Treating Zeeman term perturbatively,

$$\Delta E = \frac{\mu_B B}{\hbar}\left\langle JLSM_J \middle| L_z + 2S_z \middle| JLSM_J \right\rangle$$

Working out the matrix element similar to one-$\bar{e}$ case we get

$$\Delta E = g_J \mu_B B M_J$$

where $g_J \equiv 1 + \dfrac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$ ... Landé factor

As in one-$\bar{e}$ case, the transition to non-perturbative B fields is smooth.

Phys 438/538, 2nd Midterm Solutions 3 May 2013

1] Multi-electron g-factor

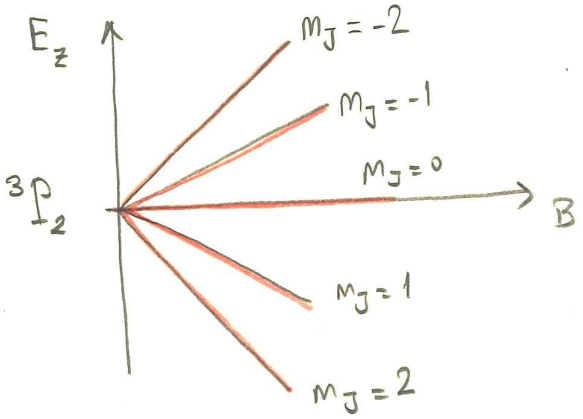
In the lecture notes you have the Landé g-factor for the multi-$\bar{e}$ case:

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$^3P_2$: $J=2$, $S=1$, $L=1$ we get $g_J = \frac{3}{2}$

Since $\hat{H}_Z = -\vec{\mu} \cdot \vec{B}$ ($B\hat{z}$), $\vec{\mu} = g_J \mu_B \vec{J}$

$$E_z = -g_J \mu_B B \langle \hat{J}_z \rangle = -g_J \mu_B B m_J \; ; \quad m_J = 0, \pm 1, \pm 2$$



Zeeman effect on hyperfine structure

The $(2F+1)$ degenerate hyperfine levels can be removed to m_F Zeeman sub-levels with an ext. B field. The nuclear magnetic moment is given by $\vec{\mu}_I = g_N \mu_N \frac{\vec{I}}{\hbar}$

g_N: nuclear g-factor

μ_N: nuclear magneton: $\frac{e\hbar}{2M_p}$ (M_p: proton mass)

$$\mathcal{H}' = \frac{\mu_B}{\hbar}(L_z + 2S_z)B - g_N \frac{\mu_I}{\hbar} I_z B$$

This sign difference is b/c nucleus has +ve charge unlike $\bar{e}$'s. But g_N can become -ve for some nuclei

1) Weak B field case (compared to Hyperfine interaction)

Within the LS coupling regime, the atom will be in an eigenstate of $\vec{F}^2$, $\vec{J}^2$, $\vec{I}^2$ and F_z and the Zeeman shift will be

$$\Delta E = \langle F J I m_F | \mathcal{H}' | F J I M_F \rangle$$

$$= g_F \mu_B B m_F$$

$$g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g'_N \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)}$$

g_F: g_J term; g'_N: $g_N \frac{\mu_N}{\mu_B}$

Since $\frac{\mu_N}{\mu_B} = \frac{m_e}{M_p} \cong \frac{1}{1836}$, g'_N can be neglected

2) Nuclear Zeeman stronger than hyperfine interaction

In this case we can start by omitting the hyperfine interaction.

So, the atom becomes an eigenstate of $\vec{J}^2$, J_z and $\vec{I}^2$, I_z

which is $\underbrace{(2J+1)}_{\text{in } m_J} \times \underbrace{(2I+1)}_{\text{in } m_I}$ - fold degenerate.

The magnetic field causes a level shift

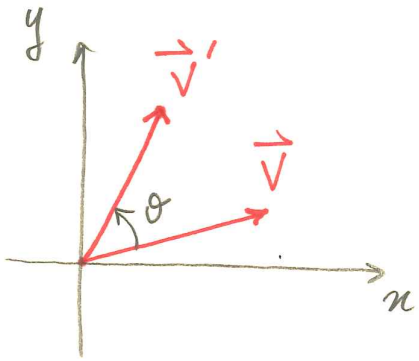
$$\Delta E = \mu_B B \left(m_J g_J - m_I g'_N \right)$$

The hyperfine interaction can then be added perturbatively.

The energy of hyperfine levels smoothly evolves as B field increases just like the electronic Zeeman case.

We shall return to Zeeman sub-levels once we introduce radiative coupling and discuss the polarization of EM transition among these sub-levels.

A Refreshment on Vectors, Tensors and Their Rotations



$$\vec{V} = \begin{bmatrix} V_x \\ V_y \\ V_z \end{bmatrix} \qquad \vec{V}' = \begin{bmatrix} V_x' \\ V_y' \\ V_z' \end{bmatrix}$$

Rotated
(say by θ around z-axis)

In general for vectors, rotation is represented by a rot. matrix

$$V_i' = \sum_j R_{ij} V_j \,, \quad \text{e.g.} \quad R_z(\theta) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Einstein sum conv. : Repeated indices summed over (x, y, z)

Vectors are also known as rank-1 tensors. The rank-0 are scalars. Unlike vectors, scalars are invariant under coordinate rotations.

The rank-2 tensors xform under rotation using two rotation matrices (one for each index) as

$$T_{ij}' = \sum_{i',j'} R_{ii'} R_{jj'} T_{i'j'}$$

We can form a Cartesian tensor of rank-2 via the outer product of two vectors $\vec{V}$ and $\vec{W}$, so that $|V\rangle\langle W|$

$$T_{ij} = V_i W_j$$

The important point is that such a Cartesian tensor is reducible to three irreducible pieces as: $T_{ij} = T_{ij}^{(0)} + T_{ij}^{(1)} + T_{ij}^{(2)}$

$$T_{ij} = \underbrace{\frac{\vec{V}\cdot\vec{W}}{3}\delta_{ij}}_{\text{scalar}} + \underbrace{\frac{V_i W_j - V_j W_i}{2}}_{\text{vector}} + \underbrace{\left(\frac{V_i W_j + V_j W_i}{2} - \frac{\vec{V}\cdot\vec{W}}{3}\delta_{ij}\right)}_{\text{symmetric, traceless rank-2 tensor}}$$

scalar: $\frac{1}{3}\mathrm{Tr}\left(\overleftrightarrow{T}\right)$

vector: $\frac{1}{2}\varepsilon_{ijk}\left(\vec{V}\times\vec{W}\right)_k$

Spherical Tensors

For AMO physics, it is the so-called spherical tensors that are important, which are defined through the following spherical basis vectors (note that they are complex vectors):

$$\hat{e}_{+1} = -\left(\frac{\hat{x}+i\hat{y}}{\sqrt{2}}\right), \quad \hat{e}_{-1} = \frac{\hat{x}-i\hat{y}}{\sqrt{2}}, \quad \hat{e}_0 = \hat{z}$$

Any vector in 3D space can be decomposed into spherical components as

$$V_q = \hat{e}_q \cdot \vec{V}$$

Using the orthonormality of spherical basis vectors:

$$\hat{e}_q^* \cdot \hat{e}_{q'} = \delta_{qq'}$$

we can express

$$\vec{V} = \sum_q V_q \hat{e}_q^*, \quad \text{so that} \quad \begin{cases} V_1 = -\frac{1}{\sqrt{2}}(V_x + iV_y) \\ V_0 = V_z \\ V_{-1} = \frac{1}{\sqrt{2}}(V_x - iV_y) \end{cases}$$

Hence, the dot product in terms of spherical components:

$$\vec{V} \cdot \vec{W} = \left(V_1 \hat{e}_1^* + V_0 \hat{e}_0^* + V_{-1} \hat{e}_{-1}^*\right) \cdot \left(W_1 \hat{e}_1^* + W_0 \hat{e}_0^* + W_{-1} \hat{e}_{-1}^*\right)$$

(use $\hat{e}_{\pm 1}^* = -\hat{e}_{\mp 1}$ and $\hat{e}_q^* \cdot \hat{e}_{q'} = \delta_{qq'}$)

$$= \sum_q (-1)^q V_q W_{-q}$$

If we generalize this to an arbitrary rank K:

$$\overrightarrow{\overrightarrow{T}}^{(K)} \cdot \vec{U}^{(K)} = \sum_q (-1)^q T_q^{(K)} U_{-q}^{(K)}$$

E.g. Spherical Harmonics can be treated as spherical tensors

$$T_q^{(K)} \longrightarrow \underbrace{Y_{lm}(\theta,\phi)}_{\langle \theta,\phi | l,m \rangle}$$ with rank $K = l$ of basis elements $q = m$

$\langle \theta,\phi | l,m \rangle$: angular momentum eigenstates

Irreducible Spherical Tensor Operators

Next, we extend to operators. A collection of $2K+1$ operators $\hat{T}^{(K)}_q$ where $q = -K, -K+1, \ldots, +K$ is defined to be an irreducible spherical tensor operator of rank-K if

$$\left.\begin{aligned} * \quad & \left[\hat{J}_z, \hat{T}^{(K)}_q\right] = \hbar q \, \hat{T}^{(K)}_q \\ * \quad & \left[\hat{J}_\pm, \hat{T}^{(K)}_q\right] = \hbar \sqrt{K(K+1) - q(q\pm 1)} \; \hat{T}^{(K)}_{q\pm 1} \end{aligned}\right\}$$

Just like $Y_{lm}(\Omega)$ being the generic spherical tensors, the operator $\vec{J}$ is the generic spherical tensor operator, with

$$\hat{J}_z |\gamma, j, m\rangle = \hbar m |\gamma, j, m\rangle$$

$$\hat{J}_\pm |\gamma, j, m\rangle = \hbar \sqrt{j(j+1) - m(m\pm 1)} \; |\gamma, j, m\pm 1\rangle$$

$$\hat{J}^2 |\gamma, j, m\rangle = \hbar^2 j(j+1) |\gamma, j, m\rangle$$

It can be shown from above that

$$\sum_i \left[\hat{J}_i, \left[\hat{J}_i, \hat{T}^{(K)}_q\right]\right] = \hbar^2 K(K+1) \hat{T}^{(K)}_q$$

Hence $\begin{cases} K \text{ is analogous to } j \\ q \text{ " " " } m \end{cases}$

Wigner-Eckart Theorem

For various matrix elements of angular momentum states $|\gamma, j, m\rangle$, an essential tool is the Wigner-Eckart theorem, which can be stated as:

$$\langle \gamma', j', m' | \hat{T}^{(k)}_q | \gamma, j, m \rangle = \frac{\langle \gamma', j' \| \hat{T}^{(k)} \| \gamma, j \rangle}{\sqrt{2j'+1}} \langle j, m' | k, q; j, m \rangle$$

Reduced matrix el. (indep. of m, m', q)

a C-G coef.

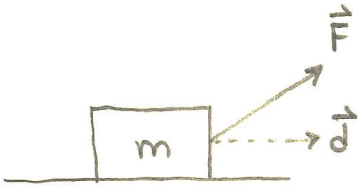
The significance of W-E theorem lies in its explicit separation of the matrix element into two factors:

1) reduced matrix element $\longrightarrow$ dynamics

2) C-G coef. $\longrightarrow$ geometry (i.e., orientation of the physical observables wrt the quantization axis)

This separation allows one to easily determine matrix elements for all values of m, m', and q (as C-G coef's) once the task has been accomplished for one particular case.

Note that the essence of W-E theorem is like the example



$$W = \vec{F}\cdot\vec{d} = \underbrace{Fd}_{\text{dynamics}}\ \underbrace{\cos\vartheta}_{\text{geometry}}$$

(reduced matrix element) (C-G coef.)

In this connection, W-E theorem is not limited to QM, nevertheless it becomes very instrumental in QM.

CAVEAT:

There are various forms of W-E, depending on phase choices, or the use of Wigner-3j symbols, and whether the $\sqrt{\ }$ part is absorbed in the reduced matrix element or not

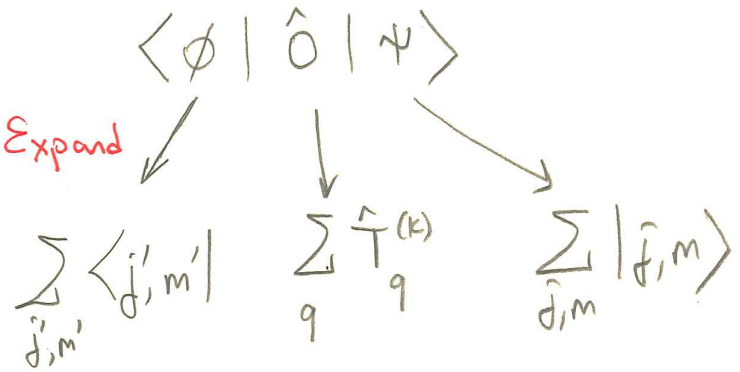
The dynamics part determines the (transition) rate of the process

The geometry part sets the selection rules " " "

$$\langle j', m' \,|\, K, q;\ j, m\rangle \quad \Rightarrow \quad \vec{J}' = \vec{K} + \vec{J}$$

That is, $m' = q + m$, $|j - j'| \le K \le j + j'$

The general procedure in employing W-E theorem is



Then for $\langle j',m' | \hat{T}^{(k)}_{q} | j,m \rangle$ use W-E theorem

Examples on the use of Wigner-Eckart Theorem

Note that in most applications we work with a physical observable which should be represented by a Hermitian operator. For the case of spherical tensor operators, this leads to

$$\hat{T}^{(k)\dagger}_{q} = (-1)^{q} \hat{T}^{(k)}_{-q}$$

* Rank-0 Case: Spin-orbit Hamiltonian

$$H_{so} = \lambda \vec{L} \cdot \vec{S}, \quad \text{using} \quad \vec{J} = \vec{L} + \vec{S}$$

$$= \frac{\lambda}{2} [J^2 - L^2 - S^2]$$

Let's extract the rank of the spherical operator H_{so}

$$[J_z, H_{so}] = \frac{\lambda}{2}\left([J_z, \vec{J}^2] - [J_z, \vec{L}^2] - [J_z, \vec{S}^2]\right)$$

$[J_z, \vec{J}^2] = 0$ (0); $[J_z, \vec{L}^2] = [J_z, L_z + S_z]$ (0); $[J_z, \vec{S}^2] = 0$ (0)

$$= 0 = \hbar q \, \hat{T}^{(K)}_q$$

Similarly, $[J_\pm, H_{so}] = 0 = \hbar\sqrt{K(K+1) - q(q\pm1)}\;\hat{T}^{(K)}_{q\pm1}$

Hence, H_{so} is indeed satisfies the irreducible tensor op. cond.

with rank $K = 0$ and $q = 0$ $\Rightarrow$ scalar operator

Plugging $K, q = 0$ in W-E theorem:

$$\langle H_{so}\rangle_{\gamma,j,m} = \frac{\langle \gamma, j \| H_{so} \| \gamma, j\rangle}{\sqrt{2j+1}} \underbrace{\langle j, m \,|\, \overset{K}{0}, \overset{q}{0}; j, m\rangle}_{1}$$

So, we immediately see that $\langle H_{so}\rangle_{\gamma,j,m}$ is indep. of m.

Since the atom w/o ext. field should be spherically symm,

the isotropy (m-independence) is expected.

* Rank-1 Case: Zeeman Hamiltonian

$$H_z = -\vec{\mu} \cdot \vec{B}$$

Even though H_z is a scalar, we shall see that it is not a scalar operator (i.e., rank-0). If it were, then just like the previous example, each Zeeman sublevel (different m's) would have the same energy $\Rightarrow$ no Zeeman splitting!

Let $\vec{B} = \hat{z} B$, $\quad \vec{\mu} = \mu_B g_J \vec{J}$

$$\Rightarrow H_z = -g_J \mu_B J_z B$$

Even though $[J_z, H_z] = 0$, $\quad [J_\pm, H_z] \neq 0$ (Zeeman)

Hence, H_z is not a rank-zero irreducible tensor operator.

As a matter of fact, $\vec{\mu} = g_J \mu_B \vec{J}$ is a vector operator, ($K=1$)

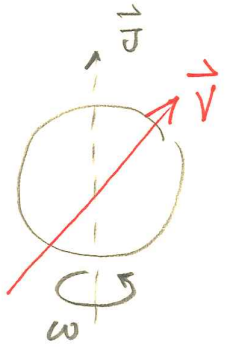
and we can use W-E theorem to find $\langle \vec{\mu} \rangle$, and forming the dot product of $\langle \vec{\mu} \rangle$ with $\vec{B}$ will yield $\langle H_z \rangle$.

For $\langle \vec{\mu} \rangle$ or rather $\langle \vec{J} \rangle$, switching to their spherical components, J_q:

$$\langle J_q \rangle_{jm} = \frac{\langle \gamma, j \| J \| \gamma, j \rangle}{\sqrt{2j+1}} \left\langle j, m \middle| \overset{K}{\downarrow} 1, q; j, m \right\rangle$$

Note that the expectation value of any vector operator is always along the dir. of the total angular momentum, $\vec{J}$.

To make this more intuitive, consider a vector $\vec{V}$ of a rotating system (could be classical as well):



Because the components of the vector which are not along the rotation axis, $\vec{J}$ are averaged out, the avg. value of the vector quantity must be along the rotation axis.

Hence,

$$\langle \mu_q \rangle_{jm} = g_J \mu_B \langle J_q \rangle_{jm}$$

$$= g_J \mu_B \frac{\langle \gamma, j \| J \| \gamma, j \rangle}{\sqrt{2j+1}} \langle j, m | k, 1 ; j, m \rangle$$

* Rank-2 Case: Electric Quadrupole Hamiltonian

The electrostatic energy of the **nuclear** charge distribution, $\rho(\vec{r})$ within the external field of the **crystal potential** $V(\vec{r})$ is given by

$$U = \int d^3r\, \rho(\vec{r})\, V(\vec{r})$$

The spatially inhomogeneous xtal potential can be expanded around the nuclear site $\vec{R}=0$ as

$$V(\vec{r}) = V(0) + \sum_\alpha x_\alpha \left.\frac{\partial V}{\partial x_\alpha}\right|_{\vec{R}=0} + \frac{1}{2!}\sum_{\alpha,\beta} x_\alpha x_\beta \left.\frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}\right|_0 + \cdots$$

Inserting into energy expression gives rise to the multipole expansion

$$U = \underbrace{q\,V(0)}_{\text{monopole}} \underbrace{- \vec{p}\cdot\vec{E}\Big|_0}_{\text{dipole}} \underbrace{- \frac{1}{6}\sum_{i,j} Q_{ij} \left.\frac{\partial E_i}{\partial x_j}\right|_0}_{\text{quadrupole}} + \cdots$$

Hence, observe that monopole couples to the (scalar) potential, dipole term couples to the (vector) electric field, quadrupole couples to the (tensor) electric field gradient (EFG).

First term is just a constant, dipole term vanishes because the nuclear ground state wf has definite parity, leaving the quadrupole term as the dominant one.

This electric quadrupole interaction is governed by the product of these rank-2 tensors

$$\mathcal{H}_Q = \overrightarrow{Q}^{(2)} \overrightarrow{U}^{(2)}$$

$\overrightarrow{Q}^{(2)}$: nuclear quadrupole moment tensor (depends on nuclear charge distr.)

$\overrightarrow{U}^{(2)}$: electric field gradient tensor (depends on electronic charge distr.)

In the previous Rank-1 example we saw that any vector obs. for the electronic part can be expressed using the total electronic angular momentum operator, $\vec{\vec{J}}$. Likewise, for the case of nuclear properties (here, quadrupole moment), we can construct a rank-2 spherical tensor operator, $\hat{\vec{\vec{T}}}^{(2)}$ using the product of nuclear angular momentum operator $\vec{\vec{I}}$ with itself, as follows:

$$T^{(2)}_{\pm 2} = I^2_{\pm 1}$$

$$T^{(2)}_{\pm 1} = \frac{1}{\sqrt{2}} \left[I_{\pm 1} I_0 + I_0 I_{\pm 1} \right]$$

$$T^{(2)}_{0} = \frac{1}{\sqrt{6}} \left[3 I_0^2 - I^2 \right]$$

This operator will act on the nuclear spin states $|I, M_I\rangle$

where $M_I = \underbrace{-I, \ldots, +I}_{2I+1}$

As mentioned previously, the W-E theorem establishes a proportionality between the matrix elements of irreducible tensor operators with same values of K and q

$$\frac{\langle \gamma j m | T_q^{(K)} | \gamma' j' m' \rangle}{\langle \gamma j m | U_q^{(K)} | \gamma' j' m' \rangle} = \frac{\langle \gamma j \| \overleftrightarrow{T}^{(K)} \| \gamma' j' \rangle}{\langle \gamma j \| \overleftrightarrow{U}^{(K)} \| \gamma' j' \rangle} \equiv A$$

a const.

Thus, applying to our case $\begin{cases} K=2, \; j \to I, \; m \to I, \; q=0 \\ U^{(2)} \to Q^{(2)} \end{cases}$

$$\langle I, m_I = I | \, Q_0^{(2)} \, | I, m_I = I \rangle = A \langle I, I | \, T_0^{(2)} \, | I, I \rangle$$

$\frac{1}{2} eQ$

this particular matrix element is chosen on purpose, as it has a physical significance in terms of so-called spectroscopic quadrupole moment, Q

$$\therefore \quad A = \sqrt{\frac{3}{2}} \frac{eQ}{I(2I-1)}$$

!! Note that for nuclei of $I = 0$ or $I = 1/2$ this term directly vanishes, which could be explained in semiclassical terms as saying that for spin-0 or spin-1/2 the "precession" of the angular mom. vector about the z-axis averages to zero quadrupole moment observed from this frame.

Hence, the so-called quadrupolar nuclei have $I \geq 1$

Having established the link bet $Q_0^{(2)}$ and $T_0^{(2)}$ we can obtain the rest as

$$Q_{\pm 2}^{(2)} = \sqrt{\frac{3}{2}} \cdot \frac{eQ}{I(2I-1)} I_{\pm 1}^2$$

$$Q_{\pm 1}^{(2)} = \frac{\sqrt{3}}{2} \frac{eQ}{I(2I-1)} \left[I_{\pm 1} I_0 + I_0 I_{\pm 1} \right]$$

$$Q_2^{(2)} = \frac{1}{2} \frac{eQ}{I(2I-1)} \left[3I_0^2 - I^2 \right]$$

Similarly, for the EFG tensor (first in terms of Cartesian components):

$$\frac{\partial^2}{\partial x_i \partial x_j} \left(\frac{-e}{4\pi\varepsilon_0 r} \right) = \frac{-e}{4\pi\varepsilon_0} \left[\frac{3x_i x_j - r^2 \delta_{ij}}{r^5} \right], \quad i,j = x,y,z$$

$$= V_{ij} = V_{ji}$$

it is possible to establish a connection bet. the spherical harmonics $l=2$ $Y_{2,m}$ and $\vec{U}^{(2)}$ as

$$\vec{U}^{(2)} = \frac{-e}{4\pi\varepsilon_0} \frac{\vec{Y}^{(2)}}{r^3} \sqrt{\frac{4\pi}{5}}$$

So, if we express quadrupole Hamiltonian in terms of spherical tensor components:

$$\mathcal{H}_Q = \vec{Q}^{(2)} \vec{U}^{(2)}$$

$$= Q^{(2)}_{+2} U^{(2)}_{-2} - Q^{(2)}_{+1} U^{(2)}_{-1} + Q^{(2)}_{0} U^{(2)}_{0} - Q^{(2)}_{-1} U^{(2)}_{+1} + Q^{(2)}_{-2} U^{(2)}_{+2}$$

If we switch to a coordinate system (EFG principal axes) where the off-diagonal Cartesian comp's $V_{ij} = 0$ for $i \neq j$, $\mathcal{H}_Q$ takes the form

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} \left[V_{zz} \left(3I_0^2 - I^2 \right) + \left(V_{xx} - V_{yy} \right) \left(I_{+1}^2 + I_{-1}^2 \right) \right]$$

Here, as $\nabla^2 V = 0$, i.e., $V_{xx} + V_{yy} + V_{zz} = 0$, only two parameters suffice to characterize EFG tensor in its principal axes frame.

The convention is to label the axes such that

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$$

$$0 \leq \eta \leq 1$$

Defining: $\langle V_{zz} \rangle \equiv eq$, $\langle V_{xx} - V_{yy} \rangle = \eta \langle V_{zz} \rangle = e\eta q$

Hence, after integrating over electronic coordinates we get

$$\mathcal{H}_Q = \frac{e^2 q Q}{4I(2I-1)} \left[3I_0^2 - I^2 + \eta \left(I_{+1}^2 + I_{-1}^2 \right) \right]$$

Part-II: **Interaction with Light**

Radiative Coupling

While considering atom-light interactions we shall treat the EM wave classically (other than for spontaneous emission case), whereas the atom quantum mechanically, hence this becomes a semi-classical approach.

Let's begin with the relation bet. EM fields and scalar/vector potentials:

$$\vec{F}(\vec{r},t) = -\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi \quad , \quad \vec{B}(\vec{r},t) = \vec{\nabla} \times \vec{A} \qquad \dots \text{ in SI}$$

Working in the Coulomb gauge:

$$\vec{\nabla}.\vec{A}(\vec{r},t) = 0 ,$$

$$\phi(\vec{r},t) = \frac{1}{4\pi\varepsilon_0} \int d^3r' \frac{\rho(\vec{r}',t)}{|\vec{r}-\vec{r}'|}$$

(ρ: (external) charge density producing the EM wave)

Hence, for an $\bar{e}$ bound to an atom (via the nuclear Coulomb field), this additional EM field will turn the electronic Hamiltonian to

$$\hat{H} = \frac{1}{2\mu}\left|\vec{p} - e\vec{A}\right|^2 - e\phi + V' \qquad \dots \text{ so-called minimal coupling Hamiltonian}$$

- μ: reduced e-nucl. mass
- V': Coulomb field of the atom (+ ext. static E-field if present)

NB: $e > 0$

Let $V \equiv -e\phi + V'$

$$\hat{H} = \hat{H}_0 + \hat{H}_{rad}$$

$$\hat{H}_0 \rightarrow \frac{-\hbar^2}{2\mu}\nabla^2 + V$$

$$\hat{H}_{rad} \rightarrow \frac{e}{2\mu}\left[2i\hbar\,\vec{A}\cdot\vec{\nabla} + i\hbar\left(\vec{\nabla}\cdot\vec{A}\right) + e\vec{A}\cdot\vec{A}\right]$$

($\vec{A}\cdot\vec{p}$; $\vec{\nabla}\cdot\vec{A} = 0$ (Coulomb Gauge))

Can we neglect $e|\vec{A}|^2$ term?

For most optical intensities (other than very intense – short wavelength lasers)

$$I(\omega) = \left|\left\langle \vec{S}(\vec{r},t)\right\rangle\right| = \left|\left\langle \frac{\vec{E}\times\vec{B}}{\mu_0}\right\rangle\right| = \frac{c\,\varepsilon_0\omega^2 A_0^2}{2}$$

($\langle\cdots\rangle$: time-avg.; $\vec{S}$: Poynting's vector)

peak amplitude of $\vec{A}$

$$eA_0 \ll |\vec{p}| \approx \frac{\hbar\pi}{a_0}$$

e.g. For a $1\,W/cm^2$ photon density of a 1eV illumination $\frac{eA_0}{p} \sim 10^{-5}$

$1\,W/cm^2$ → 26 V/cm peak electric field

Under these conditions we can neglect $e|\vec{A}|^2$ term.

Radiative Transitions in Atomic Systems

Using the time-dependent Schrödinger eqn

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(\vec{r},t)\right\rangle = \left(\hat{H}_0 + \hat{H}_{rad}\right)\left|\Psi(\vec{r},t)\right\rangle$$

At this stage we assume that the atomic part of the problem ($\hat{H}_0$) is solved $\hat{H}_0|i\rangle = \hbar\omega_i|i\rangle$, with the time evolution $e^{-i\omega_i t}$ of the eigenstate, i. So, for the perturbation $\hat{H}_{rad}$, we switch to the interaction picture to suppress the uninteresting $e^{-i\omega_i t}$ part from the states. The operators/kets in interaction picture become:

$$\hat{V}_I(t) \equiv e^{i\hat{H}_0 t/\hbar}\,\hat{H}_{rad}\,e^{-i\hat{H}_0 t/\hbar}$$

$$|\Psi(t)\rangle_I = e^{i\hat{H}_0 t/\hbar}\,e^{-i\hat{H}t/\hbar}\,|\Psi(0)\rangle_I \longrightarrow |\Psi(0)\rangle_S \equiv |\Psi(0)\rangle$$

Note that any matrix element should be invariant under S/I/H pictures

$$\langle\Psi_1(t)|\hat{V}_I(t)|\Psi_2(t)\rangle_I = \underbrace{\langle\Psi_1(0)|e^{i\hat{H}t/\hbar}}_{\langle\Psi_1(t)|}\underbrace{e^{-i\hat{H}_0 t/\hbar}\left(e^{i\hat{H}_0 t/\hbar}\hat{H}_{rad}e^{-i\hat{H}_0 t/\hbar}\right)}_{\hat{I}}\underbrace{e^{i\hat{H}_0 t/\hbar}}_{\hat{I}}\underbrace{e^{-i\hat{H}t/\hbar}|\Psi_2(0)\rangle}_{|\Psi_2(t)\rangle}$$

$$= \langle\Psi_1(t)|\hat{H}_{rad}|\Psi_2(t)\rangle \quad \checkmark$$

Let's work out time evolution in interaction picture via

$$\frac{\partial}{\partial t}|\Psi(t)\rangle_I = \frac{i}{\hbar}\,e^{i\hat{H}_0 t/\hbar}\underbrace{(\hat{H}_0 - \hat{H})}_{-\hat{H}_{rad}}e^{-i\hat{H}t/\hbar}|\psi(0)\rangle$$

$$= \frac{-i}{\hbar}\underbrace{e^{i\hat{H}_0 t/\hbar}\hat{H}_{rad}e^{-i\hat{H}_0 t/\hbar}}_{\hat{V}_I(t)}\underbrace{\left[e^{i\hat{H}_0 t/\hbar}\,e^{-i\hat{H}t/\hbar}\right]|\psi(0)\rangle}_{|\psi(t)\rangle_I}$$

($e^{-i\hat{H}_0 t/\hbar}$ inserted)

Hence, all time dependence of $|\tilde{\Psi}(t)\rangle_I$ is governed by $\hat{V}_I(t)$.

Now, we introduce the unitary time-evolution operator for the states from $t=t_0$ to t as

$$\hat{T}(t,t_0) \equiv e^{i\hat{H}_0(t-t_0)/\hbar}\, e^{-i\hat{H}(t-t_0)/\hbar}$$

so that $$|\tilde{\Psi}(t)\rangle_I = \hat{T}(t,t_0)\,|\tilde{\Psi}(t_0)\rangle_I$$

Let's work out the time evolution of this time-evolution operator

$$\frac{\partial}{\partial t}\hat{T}(t,t_0) = \frac{-i}{\hbar}\, e^{i\hat{H}_0(t-t_0)/\hbar} \underbrace{(\hat{H}_0-\hat{H})}_{-\hat{H}_{rad}} e^{-i\hat{H}(t-t_0)/\hbar}$$

$$e^{-i\hat{H}_0(t-t_0)/\hbar}\, e^{i\hat{H}_0(t-t_0)/\hbar}$$

$$\frac{\partial}{\partial t}\hat{T}(t,t_0) = \frac{-i}{\hbar}\,\hat{V}_I(t)\,\hat{T}(t,t_0)$$

Subject to $$\hat{T}(t_0,t_0) = \hat{I}$$

If we integrate both sides wrt time and use the above initial cond.

$$\hat{T}(t,t_0) = \hat{I} - \frac{i}{\hbar}\int_{t_0}^{t} \hat{V}_I(t')\,\hat{T}(t',t_0)\,dt'$$

$\hat{I}$: 1 (for ease in notation)

Formally, the solution for the time-evolution op. can be expressed as a Dyson expansion, which is simply obtained by iterative refinement procedure:

$$\hat{T}(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} \hat{V}_I(t')\,dt' + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} \hat{V}_I(t') \left(\int_{t_0}^{t'} \hat{V}_I(t'')\,dt'' \right) dt' + \cdots$$

$\hat{T}^{(1)}$: one-photon process

$\hat{T}^{(2)}$: two-photon process

Knowing $\hat{T}(t,t_0)$ amounts to knowing the transition probability amplitudes bet. the "stationary" states of the unperturbed Hamiltonian, $|i\rangle$.

Therefore, $\langle j|\hat{T}(t,t_0)|i\rangle$ gives the total transition amplitude, whereas $\langle j|\hat{T}^{(n)}(t,t_0)|i\rangle$ is the corresponding n-photon contribution to this transition.

$\vec{A}\cdot\vec{p}$ vs. $\vec{d}\cdot\vec{F}$

In the Hamiltonian, we used the radiation perturbation

$$\hat{H}_{rad} = -\frac{e}{\mu}\vec{A}\cdot\vec{p} \quad (\vec{p} \to -i\hbar\vec{\nabla}), \qquad e>0$$

There is another (and widely used) "equivalent" form within the electric dipole approximation

$$\hat{H}_{rad} = -e\vec{r}\cdot\vec{F}$$

$\vec{d}$: dipole moment of $\bar{e}$

We shall demonstrate the equivalence of both approaches in the long wavelength limit. Start with the matrix element bet. i & f : $\langle f|\vec{A}\cdot\vec{p}|i\rangle$

$$\vec{A}(\vec{r},t) = \hat{\epsilon}\,A_0\, e^{+i\frac{\omega}{c}\hat{n}\cdot\vec{r}}\, e^{-i\omega t} + c.c.$$

wave polarization vector — wave propagation dir.

$$e^{+i\frac{\omega}{c}\hat{n}\cdot\vec{r}} = 1 + i\frac{\omega}{c}\hat{n}\cdot\vec{r} + \cdots$$

1: electric dipole; $i\frac{\omega}{c}\hat{n}\cdot\vec{r}$: quadrupole

So, within the long wavelength limit $\frac{\omega}{c} \ll 1$ or $\lambda \to \infty$

$$\langle f|\, e^{-i\frac{\omega}{c}\hat{n}\cdot\vec{r}}\,\hat{\epsilon}\cdot\vec{p}\,|i\rangle \simeq \hat{\epsilon}\cdot\langle f|\vec{p}|i\rangle$$

For $H_0 = \frac{\vec{p}^2}{2\mu} + V(\vec{r})$ as we defined in the interaction picture

$$[\vec{r}, H_0] = \frac{i\hbar\vec{p}}{\mu} \longrightarrow \langle f|\vec{p}|i\rangle = -i\frac{\mu}{\hbar}\langle f|[\vec{r}, H_0]|i\rangle$$

$$= i\mu\omega_{fi}\langle f|\vec{r}|i\rangle$$

This matrix element will be multiplied by $\delta(\omega-\omega_{fi})$ term (see later), so, we can replace ω_{fi} by ω.

Also from $\vec{F} = -\frac{\partial \vec{A}}{\partial t} \Rightarrow \vec{F} = +i\omega \vec{A}$

$$\therefore \langle f | \frac{-e}{\mu} \vec{A} \cdot \vec{p} | i \rangle = \frac{e}{\mu} i\mu\omega \vec{A} \cdot \langle f | \vec{r} | i \rangle$$

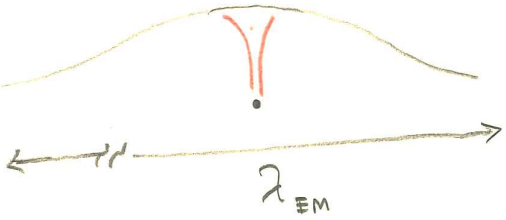
$$= \langle f | -e\vec{F} \cdot \vec{r} | i \rangle$$

Equivalent ✓ (See footnote)

So, we shall switch to $\hat{H}_{rad} = \vec{d} \cdot \vec{F}$ in the $\hat{T}(t, t_0)$ expression.

Hence, $\hat{V}_I(t) = e^{i\hat{H}_0 t/\hbar} \left[\vec{d} \cdot \vec{F}(t)\right] e^{-i\hat{H}_0 t/\hbar}$

$\frac{1}{2}\left[\vec{F}_0^* e^{i\omega t} + \vec{F}_0 e^{-i\omega t}\right]$ ... neglecting $e^{i\vec{k}\cdot\vec{r}}$ part (long wavelength limit)



If the polarization of the EM wave is along $\hat{\epsilon}$, i.e., $\vec{F} = \hat{\epsilon} F$

then $\vec{d} \cdot \vec{F} \equiv d^{\epsilon} F$

$$\hat{V}_I(t) = e^{i\hat{H}_0 t/\hbar} \left[\frac{d^{\epsilon} F_0^*}{2} e^{i\omega t} + \frac{d^{\epsilon} F_0}{2} e^{-i\omega t}\right] e^{-i\hat{H}_0 t/\hbar}$$

$\vec{A} \cdot \vec{p}$ or $\vec{d} \cdot \vec{F}$: Beyond long wavelength limit they differ!

- $\vec{d} \cdot \vec{F}$ is usually more accurate bet. two bound levels
- $\vec{A} \cdot \vec{p}$ gives better results if the transition involves a continuum of states

One-Photon Transitions

Consider two states i & f — f / i or i / f

The one-photon transition takes the form:

$\omega_0 = \frac{E_f - E_i}{\hbar}$ · from time to time we shall use ω_{fi} as well

$$T^{(1)}_{if}(t,t_0) \equiv \langle f|\hat{T}^{(1)}|i\rangle = -\frac{i}{\hbar}\int_{t_0\to-\infty}^{t\to\infty} dt' \left[e^{i(\omega_0+\omega)t'} \frac{F_0^* d^\epsilon_{if}}{2} + e^{i(\omega_0-\omega)t'} \frac{F_0 d^\epsilon_{if}}{2} \right]$$

$\langle f|d^\epsilon|i\rangle$: dipole matrix el.

NB: Radiative interaction takes place over a much longer time scale ($\sim$ ns) compared to atomic time scales $\left(1\ \text{a.u.} = \frac{m_e a_0^2}{\hbar} \sim 20\ \text{as}\right)$

Hence we can take $t_0 \to -\infty$, $t \to +\infty$ in the integral

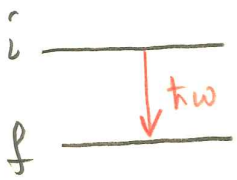
Also using: $\delta(\omega \pm \omega_0) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i(\omega\pm\omega_0)t'} dt'$

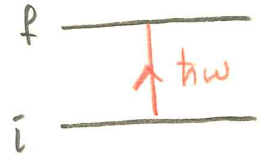
$$\Rightarrow T^{(1)}_{if}(\infty,-\infty) = -\frac{2\pi i}{\hbar} d^\epsilon_{if}\left[\frac{F_0^*}{2}\delta(\omega_0+\omega) + \frac{F_0}{2}\delta(\omega_0-\omega)\right]$$

transition freq. — laser freq.

Amplitude $\propto$ field ← Stimulated emission

Stimulated absorption





Two-Photon Transitions

Similarly for $n=2$ case, if we insert $\sum_j |j\rangle\langle j|$ bet. two $\hat{V}_I$ op's

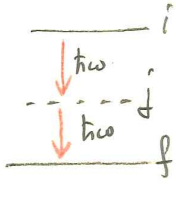
$$T_{if}^{(2)}(t,t_0) = \left(-\frac{i}{\hbar}\right)^2 \sum_j \int_{t_0\to-\infty}^{t\to+\infty} dt' \, e^{i(\omega_{fj}-\omega)t'} \left(\frac{d_{jf}^{\epsilon} F_0^{*}}{2} + \frac{d_{jf}^{\epsilon} F_0}{2} \right) \times$$

$$\times \int_{t_0\to-\infty}^{t'\to+\infty} dt'' \, e^{i(\omega_{ji}-\omega)t''} \left(\frac{d_{ij}^{\epsilon} F_0^{*}}{2} + \frac{d_{ij}^{\epsilon} F_0}{2} \right)$$

($\omega_{ji} = \omega_j - \omega_i$)

The solution, similar to $n=1$ case yields

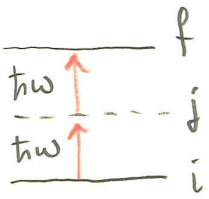
$$T_{if}^{(2)}(\infty,-\infty) = \frac{2\pi i}{\hbar^2} \sum_j \left[\delta(\omega_0+2\omega) \left(\frac{F_0^{*}}{2}\right)^2 \frac{d_{jf}^{\epsilon} d_{ij}^{\epsilon}}{\omega_{ji}+\omega} + \right.$$

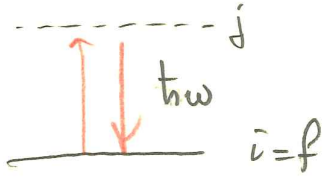


over ALL (intermediate) states — Two-photon emission (resonant)

$$\left. \delta(\omega_0-2\omega) \left(\frac{F_0}{2}\right)^2 \frac{d_{jf}^{\epsilon} d_{ij}^{\epsilon}}{\omega_{ji}-\omega} + \delta(\omega_0) \left|\frac{F_0}{2}\right|^2 \left(\frac{d_{jf}^{\epsilon} d_{ij}^{\epsilon}}{\omega_{ji}+\omega} + \frac{d_{jf}^{\epsilon} d_{ij}^{\epsilon}}{\omega_{ji}-\omega} \right) \right]$$

Two-photon absorption (resonant) — Dynamic Stark Shift





Transition Rates

The experimentally measurable quantity is the transition rate which is the transition probability per unit time as time span approaches infinity

$$R_{if}^{(n)} \equiv \lim_{t\to\infty} \frac{1}{t} \left| T_{if}^{(n)}(t/2, -t/2) \right|^2$$

(1/t: rate)

Specifically, we shall consider the one-photon ($n=1$) rate for the case of absorption:

$$R_{if,a}^{(1)} = \lim_{t\to\infty} \frac{1}{t} \left| -\frac{2\pi i}{\hbar} \left(\frac{d_{if}^{\epsilon} F_0}{2} \right) \delta(\omega_0 - \omega) \right|^2$$

Here, the square of $\delta(\cdot)$ may look weird, however one of them belongs to the line shape and the other to the period which we shall eliminate as

$$R_{if,a}^{(1)} = \frac{2\pi}{\hbar^2} \left| \frac{d_{if}^{\epsilon} F_0}{2} \right|^2 \delta(\omega_0 - \omega) \left[\lim_{t\to\infty} \frac{1}{t} \int_{-t/2}^{t/2} dt' \, e^{i(\omega_0 - \omega)t'} \right]$$

since $\omega = \omega_0$ here → set $\omega \to \omega_0$

$$\frac{1}{t} \int_{-t/2}^{t/2} dt' = 1$$

$$\Rightarrow \mathcal{R}^{(1)}_{if,a} = \frac{2\pi}{\hbar^2}\left|\frac{d^{\epsilon}_{if} F_0}{2}\right|^2 \delta(\omega-\omega_0) \; ; \quad \omega_0 \equiv \omega_f - \omega_i$$

NB: The same expression can be obtained using Fermi Golden Rule

This will be demonstrated for Einstein Coefficients.

Define, $\Omega_0 \equiv \frac{d^{\epsilon}_{if} F_0}{\hbar}$ ... Rabi frequency for the $i \leftrightarrow j$ transition

Rabi frequency is the coupling strength between the "atom" and the EM field. The frequency is controlled by the amplitude of the incident electric field and the dipole matrix element of the transition. Even though, usually an optical transition is considered ($\omega_0 \sim$ 100's THz) the Rabi freq. itself is on the order of MHz – GHz depending on laser intensity ($|F_0|^2$). It is this "slow" Rabi freq. wrt which one defines a $\pi/2$- or π- pulse, not the optical frequency, ω_0!

$$\Rightarrow R^{(1)}_{if,a} = \frac{\pi}{2}\Omega_0^2\,\delta(\omega-\omega_0)$$

We can put this expression in an alternative form using

Irradiance $I(\omega) = \underbrace{\hbar\omega}_{(J)} \Phi(\omega)$ photon flux $\left(\frac{\text{photons}}{m^2 \cdot s}\right)$

(W/m^2)

($\hbar\omega$: energy of each photon)

Using $I(\omega) = \frac{c\varepsilon_0 \omega^2 A_0^2}{2} = \frac{c\varepsilon_0 F_0^2}{2}$

$F_0 = \omega A_0$ ← $\vec{F} = -\partial\vec{A}/\partial t$

Switching to $r_{if}^{\epsilon} \equiv \frac{d_{if}^{\epsilon}}{e}$ ... length matrix element

$$\Rightarrow R_{if,a}^{(1)} = \frac{\pi}{2} \frac{e^2 F_0^2}{\hbar^2} \left|r_{if}^{\epsilon}\right|^2 \delta(\omega - \omega_0)$$

use $\alpha = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{\hbar c}$ [SI] fine-str. const.

$$= \frac{4\pi^2 \alpha}{\hbar} I(\omega) \left|r_{if}^{\epsilon}\right|^2 \delta(\omega - \omega_0)$$

$$= 4\pi^2 \alpha \, \Phi(\omega) \, \omega \left|r_{if}^{\epsilon}\right|^2 \delta(\omega - \omega_0)$$

$\tilde{r}_{if}^{\epsilon} \equiv \frac{r_{if}^{\epsilon}}{a_B}$ ... normalized to Bohr radius

$$\Rightarrow R_{if,a}^{(1)} = \underbrace{4\pi^2 a_B^2 \alpha}_{\sim 8 \cdot 10^{-18}} \Phi(\omega) \, \omega \underbrace{\left|\tilde{r}_{if}^{\epsilon}\right|^2}_{\text{of order } 1} \delta(\omega - \omega_0)$$

Line shape, in reality broadened into a Lorentzian profile

see 'resonance broadening' section

Absorption Cross-Section

This is another experimentally relevant quantity; it is defined as the ratio of absorbed EM power by the atom to the EM irradiance

$$\sigma_{abs}(\omega) = \frac{\hbar\omega R^{(1)}_{if,a}}{I(\omega)} = \frac{R^{(1)}_{if,a}}{\Phi(\omega)}$$

$$\Rightarrow \sigma_{abs}(\omega) = 4\pi^2 \alpha \omega_{fi} \left| r^{\epsilon}_{if} \right|^2 \delta(\omega - \omega_{fi})$$

This was specific for a two-level $i \to f$ transition. To generalize it for all possible final states accessible with different photon energies, ω we need $\sum_f \int d\omega$



Then, the integrated absorption cross-section becomes:

$$\int \sigma_{abs}(\omega)\, d\omega = \int \sum_f 4\pi^2 \alpha\, \omega_{fi} \left| r^{\epsilon}_{if} \right|^2 \delta(\omega - \omega_{fi})\, d\omega$$

$$= 4\pi^2 \alpha \sum_f \omega_{fi} \left| r^{\epsilon}_{fi} \right|^2$$

In connection with this expression, there is an important Sum rule.

Thomas-Reiche-Kuhn Sum Rule

Without loss of generality, let the polarization of incident field be in the x-dir., i.e., $\hat{\epsilon} = \hat{x}$.

$$\hat{H} = \hat{H}_0 + \hat{H}_{rad}(t)$$

$$= \frac{\hat{p}^2}{2\mu} + V(r) - \frac{e\vec{A}\cdot\vec{p}}{\mu}$$

Within the standard perturbative framework, the atomic states are due to H_0 part, $H_0|i\rangle = \hbar\omega_i|i\rangle$, and the time-dependent $H_{rad}(t)$ part leads to transitions among these $\{|i\rangle\}$ states.

Using H_0 we shall show that

$$\left[x, \underbrace{[x, H_0]}_{\frac{i\hbar}{\mu}p_x}\right] = -\frac{\hbar^2}{\mu},$$

Thus, $\langle i|[x,[x,H_0]]|i\rangle = \langle i|x^2 H_0 + H_0 x^2 - 2xH_0 x|i\rangle$ ($H_0 \to E_i$)

$$\langle i|-\frac{\hbar^2}{\mu}|i\rangle = 2\left[E_i\langle i|x\cdot x|i\rangle - \langle i|x\cdot H_0\cdot x|i\rangle\right]$$

($H_0 \to E_i$; $\sum_f |f\rangle\langle f|$; $\sum_f |f\rangle\langle f|$; $\sum_{f'} |f'\rangle\langle f'|$)

and $\langle f|f'\rangle = \delta_{ff'}$

$$\Rightarrow -\frac{\hbar^2}{\mu} = 2\sum_f \left[\underbrace{\langle i|x|f\rangle E_i \langle f|x|i\rangle}_{E_i|\langle i|x|f\rangle|^2} - \underbrace{\langle i|x|f\rangle E_f \langle f|x|i\rangle}_{E_f|\langle i|x|f\rangle|^2}\right]$$

$$\Rightarrow \quad \frac{2\mu}{\hbar} \sum_f \omega_{fi} \left|\langle f|x|i\rangle\right|^2 = 1 \quad \ldots \text{ Thomas - Reiche - Kuhn Sum Rule}$$

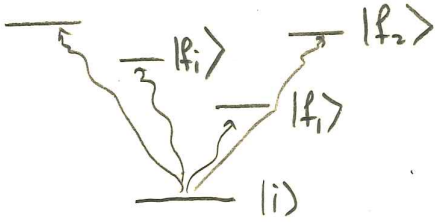
As $\left|\langle f|\vec{r}|i\rangle\right|^2 = \left|\langle f|x|i\rangle\hat{x} + \langle f|y|i\rangle\hat{y} + \langle f|z|i\rangle\hat{z}\right|^2 = \left|\langle f|x|i\rangle\right|^2 + \left|\langle f|y|i\rangle\right|^2 + e$

$\hookrightarrow + \left|\langle f|z|i\rangle\right|^2 \equiv 3\cdot\left|\langle f|x|i\rangle\right|^2$, Let $f_{fi} \equiv \omega_{fi} \dfrac{\frac{1}{3}\left|\langle f|\vec{r}|i\rangle\right|^2}{\frac{\hbar}{2\mu}}$ ... Oscillator Strength of transition $i \to f$

This is a measure of spatial overlap bet. $|i\rangle$ & $|f\rangle$

$\therefore$ we have $\sum_f f_{fi} = 1$ ... also known as f-sum rule (osc. str.)

So, from a given initial state $|i\rangle$, the dipole transitions compete with one another



Usually, it is the 1st excited dipole-allowed transition that grabs the majority of the oscillator strength (b/c spatial overlap w/ $|i\rangle$)

Applying f-sum rule to our integrated absorption cross-section

$$\int \sigma_{abs}(\omega)\, d\omega = \frac{2\pi^2 \alpha \hbar}{\mu} = \frac{\pi e^2}{2\varepsilon_0 \mu c}$$ ← does not contain $\hbar$!

Indeed, this expression can be obtained classically by treating $\bar{e}$ as an oscillator.

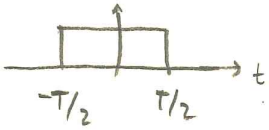
Resonance Broadening



Consider a monochromatic wave: $\cos(\omega_0 t)$, its Fourier xform is two $\delta(\cdot)$ fns:

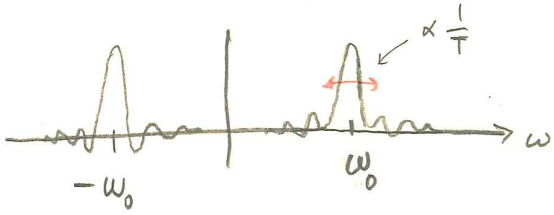


But this is for an ∞-extend fn. If we monitor the wave for a finite-duration, i.e., multiply with a time window



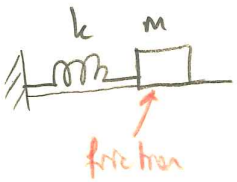
then the Fourier xform becomes the convolution of

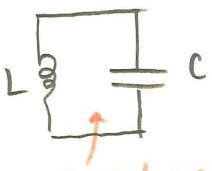
$$\delta(\omega \pm \omega_0) \circledast \mathrm{sinc}(\omega T) =$$



So, monitoring a monochromatic wave for a finite duration introduces a broadening (uncertainty) to the original wave. If this pulse duration by itself sets the linewidth, it gets called transform-limited pulse. Yet a natural source of broadening is the finite lifetime of the state(s), that give rise to a Lorentzian lineshape (next page).

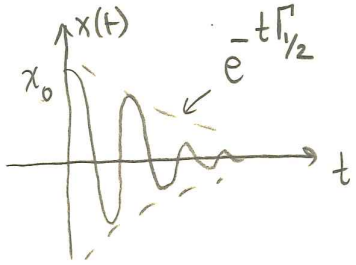
In practice, lifetime originates from coupling to environment producing loss.





$$\omega_0 = \frac{1}{\sqrt{LC}} \quad \text{or} \quad \omega_0 = \sqrt{\frac{k}{m}}$$

Therefore the oscillations will not be forever, but die out with $\Gamma_{1/2}$



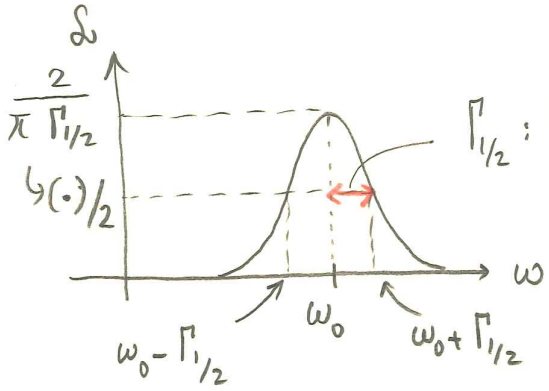
$$x(t) = x_0\, e^{-\Gamma_{1/2} t} \cos\omega_0 t$$

If we Fourier xf this fn. we get $X(\omega) = \int_{-\infty}^{+\infty} x(t)\, e^{-i\omega t}\, dt$

$$X(\omega) = \frac{x_0}{2}\left[\frac{1}{i(\omega_0-\omega)+\Gamma_{1/2}} + \frac{1}{i(\omega_0+\omega)+\Gamma_{1/2}}\right]$$

The spectral power density $X^*(\omega)X(\omega)$ becomes (in the vicinity of each resonance)

$$\mathcal{L}(\omega-\omega_0) = \frac{2}{\pi}\,\frac{\Gamma_{1/2}}{(\omega-\omega_0)^2+\Gamma_{1/2}^2} \quad \ldots \text{ Lorentzian profile}$$



with $\int_0^\infty \mathcal{L}(\omega-\omega_0)\, d\omega = 1$

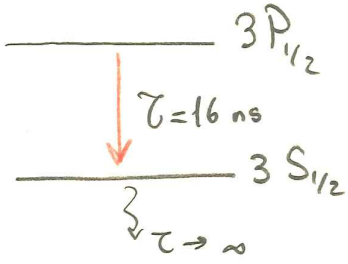
So, because of non-zero decay rate $\Gamma_{1/2}$, $\delta(\omega-\omega_0) \longrightarrow \mathcal{L}(\omega-\omega_0)$

In AMO, the physical reason of this decay (i.e., broadening) are

- spontaneous emission — natural linewidth
- collisions with other atoms (phonons in solid-state)
- doppler shift

Order of Magnitude Examples

* Natural linewidth of Na D-line:

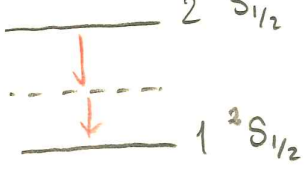


FWHM: $\delta\nu = \frac{\Gamma}{2\pi}$, lifetime: $\tau = \frac{1}{\Gamma}$

$$\Rightarrow \quad \delta\nu = \frac{1}{16.10^{-9}.2\pi} \simeq 10\,\text{MHz}$$

* Excited $2\,^2S_{1/2}$ state of H atom can only undergo 2-photon spontaneous emission to the ground state. Its lifetime is therefore long

~ 0.14 s



$\Rightarrow \delta\nu = 1.1$ Hz ← very challenging to measure

Compare with He-Ne laser linewidth of 1 MHz.

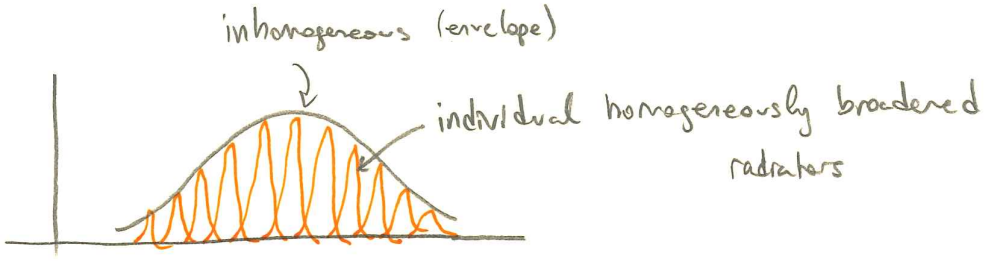
Even so that this spontaneous emission is sometimes called fundamental or natural linewidth, it can be battled by the Purcell effect. Here, the atom (or QD) is placed in a cavity with a stop-band at the spontaneous emission freq. which we want to combat.

Homogeneous vs. Inhomogeneous Broadening

If we consider (as usually the case) an ensemble of radiators (atoms, quantum dots etc.), then the issue of homogeneous vs. inhomogeneous spectral broadening arises. The former applies to processes where all radiators are affected the same way: spontaneous emission, thermal broadening. Hence, the homogeneous line width of all radiators are identical, $\Delta\omega_H$. For the case of spontaneous radiative decay, this gives us the T_1 population decay time $\Delta\omega_H = \frac{1}{T_1}$. $\Delta\omega_H$ is usually narrow (say around GHz range as $T_1 \sim$ ns)

However, in real life there are processes which affect each radiator in a distinct way. For instance Doppler effect of each gas atom will shift the resonance (emission) frequencies differently depending on individual velocities. Likewise, in quantum dots, the size of each QD as well as local strain variations or random impurities nearby cause radiator-specific shifts within the emission spectra. These give rise to inhomogeneous broadening

which broadens the overall emission spectra (collected signal).



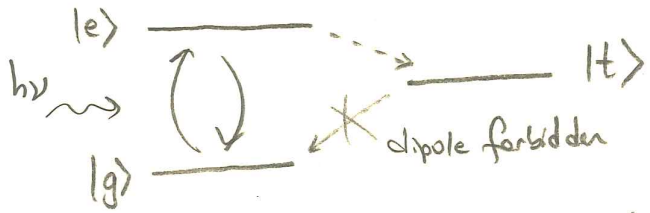
The single-atom / single-QD approaches (μ-PL) do combat this inhomogeneous broadening in special cases.

Spectral Hole Burning

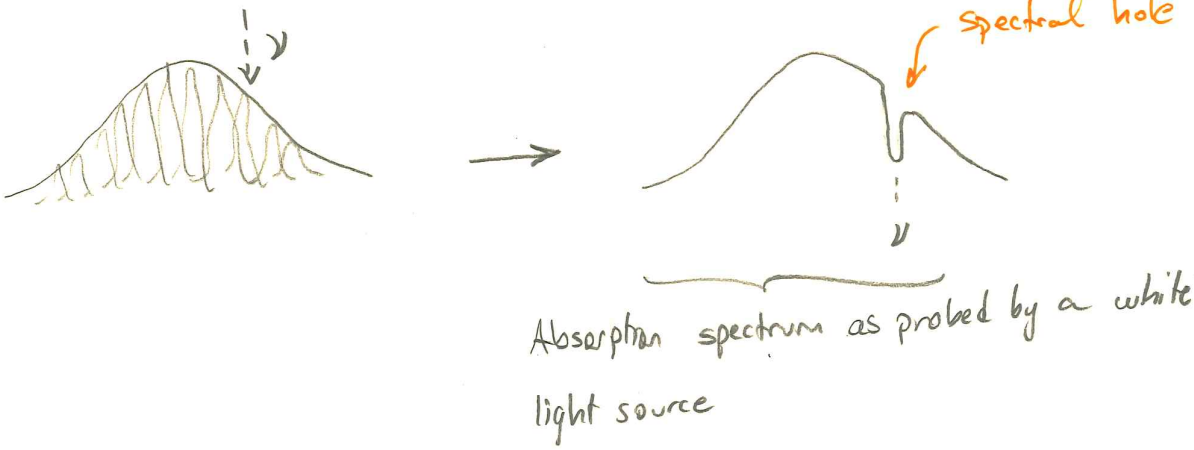
A technique that reveals the underlying homogeneous linewidth is the spectral hole burning. The ensemble of radiators are illuminated by a very narrow-linewidth laser. When the laser intensity is not too high (small Rabi frequency), only resonant radiators ($\Delta \simeq 0$) will absorb this light. The rest will not feel the laser due to their shifted transition energies (inhomogeneous broadening). Those lucky molecules excited (mostly) return back to their ground state via spontaneous emission. However, in certain cases, some excited atoms can undergo a photophysical/chemical process called intersystem crossing (more on this later)

and make a transition to a (spin triplet) state which has no dipole-allowed transition to the (spin-singlet) ground state.

As population piles in this triplet state, the ground state does



not get replenished. So that it will no longer be ready to reabsorb another photon. Hence there will be a dip formed @ ν of just the homogeneous linewidth, when probed under "white" light.



Absorption spectrum as probed by a white light source

The hole burning is used in molecular spectroscopy (determination of T_1 lifetimes, vibrational spectroscopy), in solids for studying the external perturbations (electric, magnetic fields, pressure, stress) with high sensitivity.

NB: There is also the spatial hole burning taking place in real space (say, along a waveguide)

Electric Dipole + Quadrupole and Magnetic Dipole Absorption

Returning back to $\vec{A}\cdot\vec{p}$ coupling (in the long wavelength limit)

$$\hat{\mathcal{H}}_{rad}(t) = \frac{-e}{\mu}\,\vec{A}(t)\cdot\hat{\vec{p}} \quad , \qquad e>0$$

Making use of $\frac{\partial \hat{O}}{\partial t} = \frac{i}{\hbar}[\hat{\mathcal{H}}_0, \hat{O}]$ for $\hat{O} \to \hat{p}_x = \mu v_x = \mu \frac{dx}{dt}$

$$\langle f|\hat{p}_x|i\rangle = \mu\langle f|\frac{\partial x}{\partial t}|i\rangle$$

$$= \mu\frac{i}{\hbar}\langle f|\underbrace{[\hat{\mathcal{H}}_0, \hat{x}]}_{\mathcal{H}_0 x - x\mathcal{H}_0}|i\rangle = \frac{i\mu}{\hbar}\Big[\underbrace{\langle f|\mathcal{H}_0 x|i\rangle}_{E_f\langle f|x|i\rangle} - \underbrace{\langle f|x\mathcal{H}_0|i\rangle}_{E_i\langle f|x|i\rangle}\Big]$$

$$\Rightarrow \langle f|\hat{p}_x|i\rangle = \frac{i\mu}{\hbar}(E_f - E_i)\langle f|x|i\rangle \quad \leftarrow \text{We shall make use of this result...}$$

ω_{fi}

Considering a plane wave form for the vector potential (radiation)

$$\vec{A}(t) = \hat{\varepsilon}\left[A_0\, e^{-i(\omega t - kx)} + c.c.\right]$$

In the long wavelength limit (but with one more term wrt electric dipole)

$$e^{ikx} \simeq 1 + ikx$$

This is a plane wave propagating in $+x$ dir. Choosing the polarization (TEM) as $\hat{\varepsilon} = \hat{z}$, the matrix element for radiative coupling becomes

$$\frac{-e}{\mu} \langle f | A_0 (1+ikx)\, e^{-i\omega t}\, \hat{z}\cdot\vec{p} + A_0^* (1-ikx)\, e^{i\omega t}\, \hat{z}\cdot\vec{p} \,| i \rangle$$

$e^{-i\omega t}$: Absorption; $e^{i\omega t}$: Emission

Near resonance (where transitions are effective) $\omega \sim \omega_{fi}$, if we consider the absorption term (emission is almost identical)

$$M_A \equiv -\frac{A_0 e}{\mu}\, e^{-i\omega t} \left[\langle f | \hat{p}_z | i \rangle + ik \langle f | x \hat{p}_z | i \rangle \right]$$

$\langle f | \hat{p}_z | i \rangle$: as we obtained above $\rightarrow i\mu\omega_{fi} \langle f | z | i \rangle$

$x\hat{p}_z = \frac{1}{2}\left[(x\hat{p}_z + z\hat{p}_x) + (x\hat{p}_z - z\hat{p}_x) \right]$

$-(\vec{r}\times\hat{\vec{p}})_y = -\hat{L}_y$

using $\mu \frac{d}{dt}(xz) = x\hat{p}_z + \hat{p}_x z = x\hat{p}_z + z\hat{p}_x$ ($\hat{p}_x$ commute)

Also from $\frac{\partial \hat{O}}{\partial t} = \frac{i}{\hbar}[\hat{H}_0, \hat{O}]$; $\mu \frac{d(xz)}{dt} = \frac{i\mu}{\hbar}\left(\hat{H}_0 xz - xz \hat{H}_0 \right)$

Hence $\langle f | x\hat{p}_z + z\hat{p}_x | i \rangle = \frac{i\mu}{\hbar}(E_f - E_i) \langle f | xz | i \rangle$, $E_f - E_i = \omega_{fi}$

Combining the pieces together

$$M_A = -A_0\, e^{-i\omega t}\left[\underbrace{i\omega_{fi}\langle f|ez|i\rangle}_{\text{electric dipole}\atop E1} - \underbrace{\frac{ik}{2}\frac{e}{\mu}\langle f|\hat{L}_y|i\rangle}_{\text{magnetic dipole}\atop M1} + \underbrace{\frac{ik}{2}\omega_{fi}\langle f|exz|i\rangle}_{\text{electric quadrupole}\atop E2}\right]$$

Let's now compare their relative intensities (i.e., $|M_{A_i}|^2$).

For a rough estimation we shall take

$$\langle f|x|i\rangle \sim a_B\,, \qquad \langle f|xz|i\rangle \sim a_B^2$$

$$\langle f|\vec{L}|i\rangle \sim \hbar\,, \qquad \text{and} \quad \lambda \sim 500\,\text{nm}$$

If we set the intensity for electric dipole $\longrightarrow$ 1

" " magnetic dipole $\longrightarrow \dfrac{\hbar^2}{4\mu^2 c^2 a_B^2} \sim 10^{-5}$

" " electric quadrupole $\longrightarrow \dfrac{(2\pi)^2 a_B^2}{4\lambda^2} \sim 10^{-7}$

So, we observe that E1 is by far stronger than M1 which is still much stronger than E2. We include M1 or E2 whenever the stronger one(s) vanish because of selection rules.

Selection Rules

We shall consider a transition (E1, M1 or E2) among atomic states

$|\gamma, L, S, J, M_J\rangle$

- γ: other quantum labels, say n (principal quantum number)
- L: total orbital ang. mom.
- S: total spin ang. mom.
- J: total electronic ang. mom.
- M_J: z-projection of $\vec{J}$

NB: If we also include the hyperfine interaction, then the defining quantum labels for the full atom (inc. nucleus) become

$|\gamma, L, S, J, F, M_F\rangle$

$\vec{F} = \vec{I} + \vec{J}$: atomic ang. mom. and its z-prj.

Selection rules tell us which transitions will be allowed, i.e., with non-vanishing matrix elements $\langle i | E1, M1, E2 | f \rangle$ based on the conservation of angular momentum.

The photon carries a spin angular momentum of $\pm\hbar$ or 0 (linear pol. (later)) and in special cases can have an orbital angular momentum as well. More on this later.

Let's first give a more "physical" reasoning behind the selection rules considering the E1 transitions. Here, the point is the non-vanishing of the matrix element

$$\langle f | \hat{r} | i \rangle = \int \psi_f^* \, \hat{r} \, \psi_i \, d^3r$$

* **magnetic quantum number** selection rule derives from the conservation of electron/atom + photon angular momentum along the quantization axis (z) wrt which 'm' is defined

$$\Delta m = \left\{ \begin{array}{ll} 0 : & \text{linearly pol'd light} \\ \pm 1 : & \text{circularly " "} \end{array} \right\} \quad \text{More on these later}$$

* **Parity selection**

$$\int_{-\infty}^{+\infty} \psi_f^* \, \hat{r} \, \psi_i \, d^3r$$

overall integrand must be of even parity to non vanish

$\hat{r}$: odd parity

$\Rightarrow$ ψ_i and ψ_f must be of opposite parity

Together with the fact that in E1 transitions photon can at most provide $\pm\hbar$ angular momentum

$$\Rightarrow \quad \Delta l = \pm 1$$

* spin quantum number selection rule

E1 transition $(-e\vec{r}\cdot\vec{\mathcal{E}})$ does not act on the spin state, even indirectly in the absence of spin-orbit interaction!

$\therefore \quad \Delta S = 0$

i.e., transitions bet. singlet $(S=0)$ and triplet $(S=1)$ are forbidden.

NB: For heavier atoms SOI cannot be neglected, so $\Delta S = \pm 1$ becomes possible, though still much weaker than $\Delta S = 0$ lines.

A rigorous way to derive selection rules is to use Wigner-Eckart theorem:

$$\langle \gamma', j', m' | \hat{T}^{(K)}_q | \gamma, j, m \rangle = \underbrace{\langle j', m' | K, q; j, m \rangle}_{\text{C-G coef}} \frac{\langle \gamma', j' \| \hat{\vec{T}}^{(K)} \| \gamma, j \rangle}{\sqrt{2j'+1}}$$

Selection rules derive from C-G coef part: $\vec{J}' = \vec{K} + \vec{J}$

$m' = q + m, \quad |j - j'| \leq K \leq j + j'$, where $q = \overbrace{-K, -K+1, \ldots, +K}^{2K+1}$

* For E1 transitions: $K=1$ } with the exceptions: $j=0 \not\to j'=0$
$\Delta j = 0, \pm 1, \quad \Delta m = 0, \pm 1$ } $m'=0 \not\to m=0$ when $\Delta j = 0$

* For E2 transitions $K=2 \to 2^{nd}$-rank tensors due to $\langle f | x z | i \rangle$ matrix el's

Therefore, for E2 transitions $\Delta j = 0, \pm 1, \pm 2$

E1 : Electric Dipole Selection Rules (for allowed transitions)

$$|\gamma\, L, S, J, m_J\rangle \longrightarrow |\gamma', L', S', J', m_J'\rangle$$

- $\Delta J = J - J' = 0, \pm 1$, excluding $J = J' = 0$ case
- $\Delta m_J = m_J - m_J' = 0, \pm 1$,
- $\Delta L = L - L' = \pm 1$,
- $\Delta S = S - S' = 0$

If we further include the hyperfine coupling then m_J will no longer be conserved (ignore it, in the above list) and take into account these additional rules:

- $\Delta F = F - F' = 0, \pm 1$
- $\Delta m_F = m_F - m_F' = 0, \pm 1$

NB: In these selection rules we did not include the constraints coming from $\hat{\varepsilon}.\hat{r}$ part of the dipole matrix elements:

$$\langle f|\vec{d}.\vec{F}|i\rangle = \langle \hat{r}.\hat{\varepsilon}\rangle \langle f|d^e F_0|i\rangle$$

This will be separately considered in 'polarization selection rules' →

M1 : Magnetic Dipole Selection Rules

- $\Delta J = 0, \pm 1$
- $\Delta L = 0$
- $\Delta m_J = 0, \pm 1$
- $\Delta S = 0$

E2 : Electric Quadrupole Selection Rules

- $\Delta J = 0, \pm 1, \pm 2$
- $\Delta S = 0$
- $\Delta m_J = 0, \pm 1, \pm 2$
- $\Delta L = 0, \pm 2$

Polarization Selections

The selections rules stated are for a general EM polarization. Depending on the particular polarization some of these allowed transitions will be favored or rejected, i.e., we have polarization selection rules which are practically very important. They originate from the $\hat{r}\cdot\hat{\varepsilon}$ term in the $\vec{J}\cdot\vec{F}$ dipole coupling term.

$$\hat{r} = \frac{1}{r}\left(\hat{x}\,x + \hat{y}\,y + \hat{z}\,z\right)$$

$$= \sin\theta\cos\phi\,\hat{x} + \sin\theta\sin\phi\,\hat{y} + \cos\theta\,\hat{z}$$

$\sin\theta\cos\phi \rightarrow \sqrt{\frac{2\pi}{3}}\left(Y_{1,-1} - Y_{1,1}\right)$

$\sin\theta\sin\phi \rightarrow i\sqrt{\frac{2\pi}{3}}\left(Y_{1,1} + Y_{1,-1}\right)$

$\cos\theta \rightarrow \sqrt{\frac{4\pi}{3}}\,Y_{1,0}$

Note that these $Y_{l,m}$ spherical harmonics are wrt to "z-axis", which we choose as the angular momentum "quantization" axis $\xrightarrow{\text{defining}}$ 'm' quantum label

$$\Rightarrow \hat{r} = \left[\, Y_{1,-1}\underbrace{\left(\frac{\hat{x}+i\hat{y}}{\sqrt{2}}\right)}_{-\hat{e}_{+1}} + Y_{1,0}\underbrace{\left(\hat{z}\right)}_{\hat{e}_0} + Y_{1,1}\underbrace{\left(\frac{-\hat{x}+i\hat{y}}{\sqrt{2}}\right)}_{-\hat{e}_{-1}}\right]\sqrt{\frac{4\pi}{3}}$$

$\hat{e}_{\pm 1,0}$ are the spherical basis vectors that we defined in spherical tensors.

Similarly, we can express the EM polarization vector $\hat{\varepsilon}$ as σ^+, σ^- circular polarizations as well as linear polarization π along the same quantization axis as:

$$\hat{\varepsilon} = \varepsilon_{\sigma^-}\underbrace{\left(\frac{\hat{x}-i\hat{y}}{\sqrt{2}}\right)}_{\hat{e}_{-1}} + \varepsilon_{\pi}\underbrace{\left(\hat{z}\right)}_{\hat{e}_0} + \varepsilon_{\sigma^+}\underbrace{\left(-\frac{\hat{x}+i\hat{y}}{\sqrt{2}}\right)}_{\hat{e}_{+1}}$$

COMPLEX unit vectors !

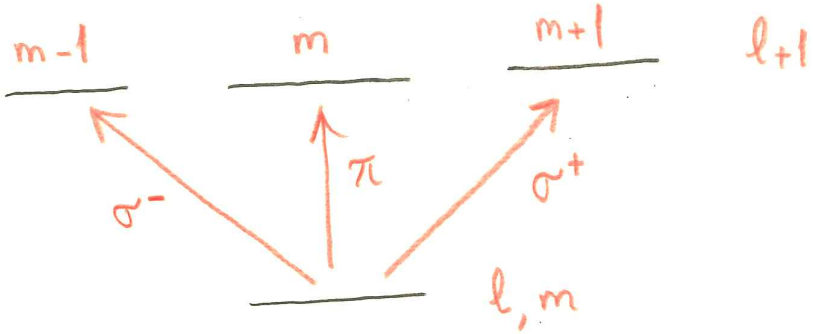
Observe that: $\hat{e}_{+1}\cdot\hat{e}_{+1} \equiv 0$, $\hat{e}_{+1}\cdot\hat{e}_{-1} = -1$

$$\therefore\ \hat{r}\cdot\hat{\varepsilon} = \sqrt{\frac{4\pi}{3}}\left[-\varepsilon_{\sigma^-}Y_{1,-1} + \varepsilon_{\pi}Y_{1,0} - \varepsilon_{\sigma^+}Y_{1,1}\right]$$

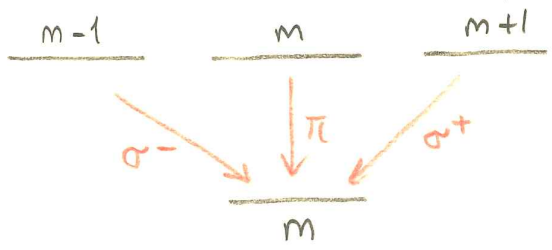
In practice an EM wave will have only one of these polarizations $\sigma^{\pm}/\pi$.

But note that $\sigma^{\pm}$ is associated with $Y_{1\,\pm1}$ and $\pi \longrightarrow Y_{1,0}$

Therefore, we have the following polarization-selected transitions



For emission we have exactly the same polarization selection



This is basically a conservation of angular momentum (along "quantization" axis)

σ^+ carries a $+\hbar$ angular momentum along this axis

σ^- " " $-\hbar$ " " " "

π " 0

Hence polarization selection rules can be implemented by just matching

$$m_f = m_i \pm m_{photon} \quad \begin{cases} +1 & (\sigma^+) \\ 0 & (\pi) \\ -1 & (\sigma^-) \end{cases}$$

(abs. ↑ / em. ↓)

Ex: Consider an EM wave at $\vec{r}=0$ as

$$\vec{F} = -\frac{F_0}{\sqrt{2}}\left[\hat{x}\cos(\omega t+\varphi) + \hat{y}\sin(\omega t+\varphi)\right]$$

use $\sin\theta = \cos(\theta - \frac{\pi}{2})$

$$\Rightarrow \vec{F} = \mathrm{Re}\left\{\hat{\mathcal{E}}\, F_0\, e^{-i(\omega t+\varphi)}\right\} \quad \text{where} \quad \hat{\mathcal{E}} = \hat{e}_{+1} = -\frac{\hat{x}+i\hat{y}}{\sqrt{2}}$$

So, this is a σ^+ pol. wrt $0z$ axis.

Note that we did not mention anything about the dir. of propagation of the wave, i.e. $\hat{k} = \pm \hat{z}$. Now, if we let

* $\hat{k} = +\hat{z}$ (wave $\rightsquigarrow +z$) the Electric field describes RH helicity
* $\hat{k} = -\hat{z}$ (wave $-z \leftsquigarrow$) " " " LH helicity

Whatever the sense of propagation along the z-axis, the EM wave is σ^+ circularly polarized wrt z-axis.

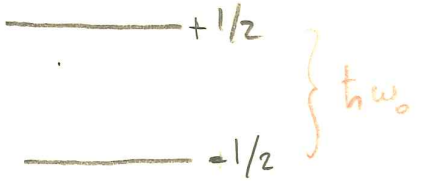
Likewise, the E-field of σ^- pol'd light is obtained by replacing

$$\hat{\mathcal{E}} \rightarrow \hat{e}_{-1} = \frac{\hat{x} - i\hat{y}}{\sqrt{2}}$$

The end result of a physical calculation will not depend on the chosen "quantization axis" if the space is isotropic. But if there is a say magnetic field applied, which is usually chosen to be the quantization axis, then the result will depend on it.

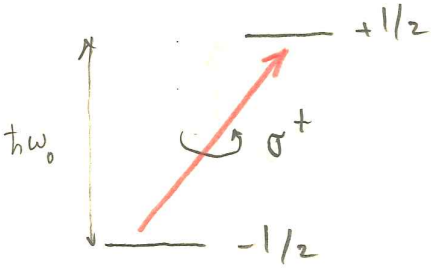
The σ^+/σ^- nomenclature is the preferred choice for radiative transitions as opposed to RH/LH helicity specification, because σ^+/σ^- are labeled wrt a quantization axis (or $\vec{B}_{dc}$ when it exists) which forms the basis for magnetic quantum labels, m and selection rules.

As a nice illustration, consider $J = 1/2$ level split by a static magnetic field, $\vec{B}_{dc} = \hat{z} B$ into two Zeeman sublevels $m = \pm 1/2$ by an energy say $\hbar\omega_0$ proportional to B_0



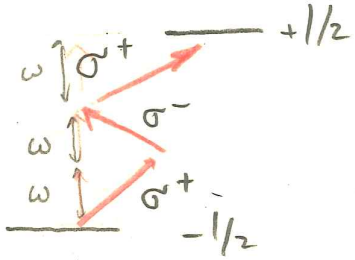
NB: Here, we assume $g < 0$ (or $\gamma < 0$) so that $m_s = -1/2$ is the ground st.

For a transition from $m = -1/2$ to $m = +1/2$, the $\bar{e}$ needs to increase its angular momentum along $\hat{z}$ by $+\hbar$. It can do this in general by absorbing $(n+1) \to \sigma^+$ and $n \to \bar{\sigma}$ photons of energy



One-photon abs.

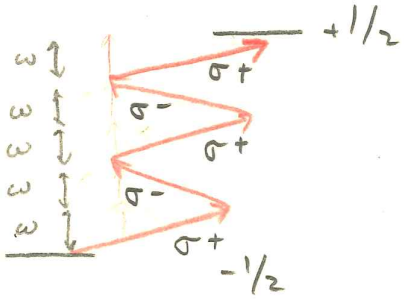
$\omega_0 = \omega$



Three-photon abs.

$\omega_0 = 3\omega$

(very weak)



Five-photon abs.

$\omega_0 = 5\omega$

(much more weaker)

Wigner-Eckart theorem for electric dipole transitions

Stating the theorem:

$$\langle \gamma' j' m' | \hat{T}^{(K)}_q | \gamma, j, m \rangle = \frac{\langle \gamma' j' \| \hat{\vec{T}}^{(K)} \| \gamma, j \rangle}{\sqrt{2j'+1}} \underbrace{\langle j', m' | K, q; j, m \rangle}_{\text{C-G part det's the branching ratios}}$$

For our case $\hat{T}^{(K)}_q \xrightarrow[K=1,\ q=0,\pm1]{\vec{r}\cdot\hat{\varepsilon}} \sum_{q=-1}^{1} r_{-q} \varepsilon_q$ → det's light pol.

For d states, $l=2 \Rightarrow j'=2$,

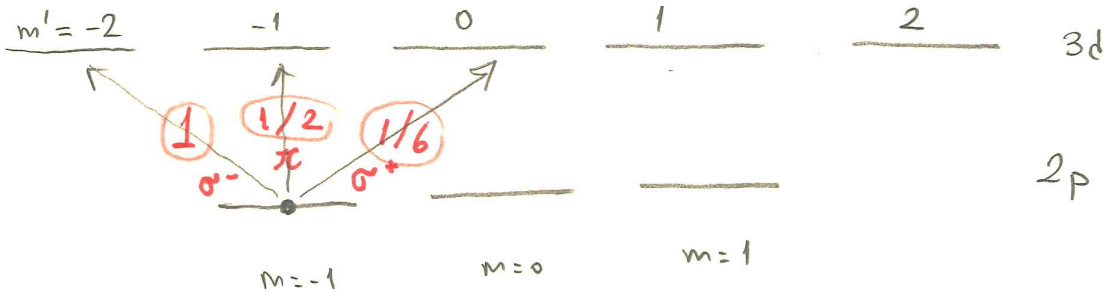
p " $l=1 \Rightarrow j=1$

Relative Branching Ratios: $\left| \langle j'=2, m' | 1, q; j=1, m=-1 \rangle \right|^2$

According to addition of angular momenta (C-G) only possibilities:

Use 1x1 sector in C-G table: $\langle 2,-2 | 1,-1; 1,-1 \rangle = 1$

$\langle 2,-1 | 1,0; 1,-1 \rangle = 1/\sqrt{2}$, $\langle 2,0 | 1,1; 1,-1 \rangle = 1/\sqrt{6}$



Spontaneous vs. Stimulated Emission

Usually spontaneous emission process is introduced ad-hoc into semi-classical treatments. To see how it naturally appears, we need to switch to a second-quantized EM field formalism.

In this case the amplitude of the vector potential, A_0 which was a poor complex number, now becomes a bosonic operator

$$\hat{A}_0 = \sqrt{\frac{\hbar}{2\omega \varepsilon_0 V}} \left(\hat{b}^\dagger + \hat{b}\right)$$

- ω: monochromatic angular freq.
- ε_0: permittivity
- V: normalization volume
- $\hat{b}^\dagger$: photon creation op.
- $\hat{b}$: annihilation op.

Obey bosonic commutation relation:

$$\left[\hat{b}, \hat{b}^\dagger\right]_- = 1$$

$$\hat{b}\hat{b}^\dagger - \hat{b}^\dagger\hat{b} = 1 \neq 0$$

Here, we consider a single-mode EM field so that we suppress the indices for photon mode $\hat{b}_j \rightarrow \hat{b}$. They behave as the standard harmonic oscillator raising/lowering operators

$$\hat{b}^\dagger |n_{ph}\rangle = \sqrt{n_{ph}+1}\, |n_{ph}+1\rangle, \quad \hat{b}\,|n_{ph}\rangle = \sqrt{n_{ph}}\, |n_{ph}-1\rangle$$

So, when we consider atom-photon interaction in 2nd-quantized formalism the states will become:

$$|i_{atom}\rangle \otimes |n_{ph}\rangle \text{ or } |i_{atom}, n_{ph}\rangle$$

Absorption matrix element modulus square will become

$$\left| \langle f | \hat{\vec{A}} \cdot \vec{\nabla} | i \rangle \right|^2 = \frac{\hbar}{2\omega V \varepsilon_0} \left| \langle f_{atom}, n_{ph}-1 | \left(\hat{b}^+ + \hat{b}\right) \hat{\varepsilon} \cdot \vec{\nabla} | i_{atom}, n_{ph} \rangle \right|^2$$

EM polarization

only this op. is operational in absorption

$$= \frac{\hbar n_{ph}}{2\omega \varepsilon_0} \left| \langle f_{atom} | \hat{\varepsilon} \cdot \vec{\nabla} | i_{atom} \rangle \right|^2$$

Absorption rate is proportional to the # density of photons present; for this reason it is called stimulated absorption. In semi-classical treatment it was proportional to electric field amplitude square

Emission rate coefficient similarly becomes:

$$\left| \langle f | \hat{\vec{A}} \cdot \vec{\nabla} | i \rangle \right|^2 = \frac{\hbar}{2\omega \varepsilon_0 V} \left| \langle f_{atom}, n_{ph}+1 | \left(\hat{b}^+ + \hat{b}\right) \hat{\varepsilon} \cdot \vec{\nabla} | i_{atom}, n_{ph} \rangle \right|^2$$

now this op. will be effective

stimulated + spontaneous

$$= \frac{\hbar \left(n_{ph} + 1\right)}{2\omega \varepsilon_0} \left| \langle f_{atom} | \hat{\varepsilon} \cdot \vec{\nabla} | i_{atom} \rangle \right|^2$$

Remarks:

* Photons (bosons) favor to be in the same final state – final state stimulation

as $\hat{b}^+ |n_{ph}\rangle = \sqrt{n_{ph}+1}\ |n_{ph}+1\rangle$

for fermions this stops at 1, for bosons this process becomes even more probable as n_{ph} increases!

This is the basis of Lasers! In the case of fermions, Pauli Exclusion Principle avoids such a stimulated process!

* The very existance of spontaneous emission can be traced to the zero point oscillations (as in harmonic oscillators) of the photon field or rather called the vacuum fluctuations. In this vacuum state, even though the expectation value of the electric field vanishes, its fluctuations (proportional to $\langle (\hat{b}^\dagger + \hat{b})^2 \rangle_{vac}$), do not!

It is these vacuum fluctuations that induce the atom in an excited state to undergo spontaneous emission. However, the reverse does not happen. That is, these fluctuations do not cause a ground-state e^- to be excited (i.e., spontaneous absorption). This is a direct consequence of the fact that the operators $\hat{b}$ and $\hat{b}^\dagger$ do not commute!

Dirac's ~~Fermi's~~ Golden Rule and Einstein B Coefficients

We can obtain the same stimulated emission and absorption expressions via FGR using the electric dipole radiative perturbation

$$\mathcal{H}_{rad}(t) = \vec{d}\cdot\hat{\epsilon}\left(\frac{F_0}{2}e^{-i\omega t} + \frac{F_0^*}{2}e^{i\omega t}\right)$$

$\frac{F_0}{2}e^{-i\omega t}$ → absorption; $\frac{F_0^*}{2}e^{i\omega t}$ → emission

{ Recall $e^{-iEt/\hbar}$ time evolution

$$W_{i\to f}^{abs/em} = \frac{2\pi}{\hbar}\left|\langle f|\vec{d}\cdot\hat{\epsilon}\,\frac{F_0}{2}|i\rangle\right|^2 \underbrace{\delta(E_f - E_i \mp \hbar\omega)}_{\frac{1}{\hbar}\delta(\omega_{fi}\mp\omega)}$$

In general we can assume that atom is not immersed in a monochromatic light but a general field described by density of modes $D_{field}(\omega)$

In this case the rate of transition requires $\int d\omega\, D_{field}(\omega)$

$$\therefore W_{i\to f}^{abs} = \int d\omega\, D_{field}(\omega)\,\frac{2\pi}{\hbar^2}\left|\langle f|d^{\epsilon}|i\rangle\right|^2\frac{|F_0|^2}{4}\,\delta(\omega-\omega_{fi})$$

$$= \frac{2\pi}{\hbar^2}\left|d_{fi}^{\epsilon}\right|^2\frac{|F_0|^2}{4}D_{field}(\omega_{fi})$$

For an unpolarized light (as in black body radiation) $\left|d_{fi}^{\epsilon}\right|^2 = \frac{1}{3}\left|\vec{d}_{fi}\right|^2$

$$\left(d_{fi}^x\right)^2 + \left(d_{fi}^y\right)^2 + \left(d_{fi}^z\right)^2$$

Also recalling the time-averaged EM energy density as

$$u_{avg} = \frac{1}{2}\varepsilon_0 |E_0|^2$$

$$W^{abs}_{i\to f} = \underbrace{\frac{\pi}{3\hbar^2\varepsilon_0}|\vec{d}_{fi}|^2}_{B_{i\to f}} \underbrace{u_{avg}\, D_{field}(\omega_{fi})}_{\rho(\omega_{fi})\ \cdots \text{ spectral energy density}}$$

$B_{i\to f}$ Einstein B coefficient

In his 1917 paper "Zur Quantentheorie der Strahlung" Physikalische Zeitschrift 18, 121 (1917), Einstein introduced his A- and B-coefficients to describe how a 2-level atom attains detailed balance in the presence of radiation.

Einstein Rate Equations

Let's switch from i, f labels to 1, 2, 3, 4 etc for the atomic states. Considering an ensemble of (for the time-being) two-level atoms interacting with EM field governed by the spectral radiance,

$$I(\nu) \xrightarrow{[SI]} \frac{W}{sr \cdot m^2 \cdot Hz}; \qquad \rho(\nu) = \frac{4\pi}{c} I(\nu)$$

sr → steradian; $\rho(\nu)$ ↓ spectral energy density

Do not mix it with irradiance which is also denoted by I :-(

For generality assume that states $i = 1, 2$ are degenerate with $g_i = 2J_i + 1$ with the number density of atoms being N_i

g_2, N_2 ——— E_2

Einstein wrote the rate eqn. for the excited state $i = 2$ as

g_1, N_1 ——— E_1

$$\frac{dN_2}{dt} = \underbrace{-N_2 A_{2\to1}}_{\text{spontaneous emission}} \underbrace{- N_2 B_{2\to1} I(\omega)}_{\text{stimulated emission}} \underbrace{+ N_1 B_{1\to2} I(\omega)}_{\text{(stimulated) absorption}}$$

(out-going: $N_2 A_{2\to1}$, $N_2 B_{2\to1} I(\omega)$; in-coming: $N_1 B_{1\to2} I(\omega)$)

For a closed system $N_1(t) + N_2(t) = N$ must be constant,

i.e., $\frac{dN_2}{dt} = -\frac{dN_1}{dt}$

$$\therefore \quad \frac{dN_1}{dt} = N_2 A_{2\to1} + N_2 B_{2\to1} I(\omega) - N_1 B_{1\to2} I(\omega)$$

When the system reaches steady state, $\frac{dN_i}{dt} \to 0$, $N_i(t) \to N_{i,ss}$

But still denote it by $N_{i,ss} \to N_i$

$$\therefore \quad \frac{N_2}{N_1} = \frac{B_{1\to2} I(\omega)}{A_{2\to1} + B_{2\to1} I(\omega)}$$

Now, let $g_1 = g_2 = 1$. In this case we can drop the indices of A & B, because $B_{1\to 2} = B_{2\to 1}$ (see, $g_2 B_{21} = g_1 B_{12}$ next page)

$$\frac{N_2}{N_1} = \frac{1}{\frac{A}{BI(\omega)} + 1}$$

Since A, B, $I(\omega)$ are all +ve, we have $N_2 < N_1$ for a two-level system in the steady state: no population inversion!

Hence, we have no net gain of light as it passes through a 2-level system. Note that $\frac{N_2}{N_1}$ ratio also corresponds to stimulated versus total emission from the excited state

$$\frac{W_{\text{stim. emission}}}{W_{\text{tot. emission}}} = \frac{B\,I(\omega)\,N_2}{A N_2 + B I(\omega) N_2} = \frac{1}{\frac{A}{BI(\omega)} + 1} = \frac{N_2}{N_1}$$

Hence, for a system w/o population inversion, spontaneous emission process dominates over the stimulated emission.

One needs to put the system to population inversion $N_2 > N_1$ to reveal the stimulated emission. This requires a configuration more than 2-states and it was first achieved rather late in 1953 using an ammonia maser.
↖ microwave laser

But, from statistical mechanics we know that occupancy of (excited) states in thermal equilibrium is given by the Boltzmann statistics as

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\hbar\omega\beta} \quad ; \quad \beta = \frac{1}{k_B T}$$

Equating this to the Einstein rate eq. and solving for $I(\omega)$

$$I(\omega) = \frac{A_{2\to1}}{B_{2\to1}} \frac{1}{\frac{g_1 B_{1\to2}}{g_2 B_{2\to1}} e^{\beta\hbar\omega} - 1}$$

On the other hand from Plank's blackbody distribution we have

$$I(\omega) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\beta\hbar\omega} - 1}$$

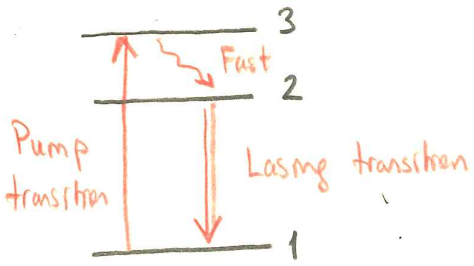
$$\Rightarrow \quad g_2 B_{2\to1} = g_1 B_{1\to2}$$

$$\frac{A_{2\to1}}{B_{2\to1}} = \frac{2h\nu^3}{c^2}$$

Before we discuss 3-level and 4-level schemes, we should point out that there is a good reason why stimulated emission was first demonstrated at a rather low frequency (microwave as opposed to IR or visible). This is because the Einstein relation $\frac{A}{B} = \frac{2h}{c^2}\nu^3$, the spontaneous/stimulated emission ratio increases by the cube of frequency!

Three and Four Level Systems

To have gain, we need population inversion bet. the radiative transition states. We have seen that this is not possible for a two-level scheme.



If we introduce another high-lying metastable state (3) into which we pump the ground state (1), then the population in 3 will not build up (hence saturate) as it is chosen to be rapidly decaying state (non-radiatively) into state 2 which then radiatively recombines to state 1

Notation:

We shall drop state indices from Einstein A & B coef's.

total # atoms

$N = N_1(t) + N_2(t) + \cancel{N_3(t)}^{\,0}$ (fast decay, no population accumulation)

we ignore stimulated emission (safe, unless system is highly inverted)

$$\frac{dN_2}{dt} = BIN_1 - AN_2 \quad , \quad \frac{dN_1}{dt} = -\frac{dN_2}{dt} = -BIN_1 + AN_2$$

Introduce population difference $\Delta N(t) \equiv N_1(t) - N_2(t)$

In terms of ΔN we get:

$$\frac{d\Delta N}{dt} = \frac{dN_1}{dt} - \frac{dN_2}{dt} = -2BIN_1 + 2AN_2$$

$$\begin{cases} N_1 = (N + \Delta N)/2 \\ N_2 = (N - \Delta N)/2 \end{cases}$$

$$\Rightarrow \quad \frac{d\Delta N}{dt} = -BIN - BI\Delta N + AN - A\Delta N$$

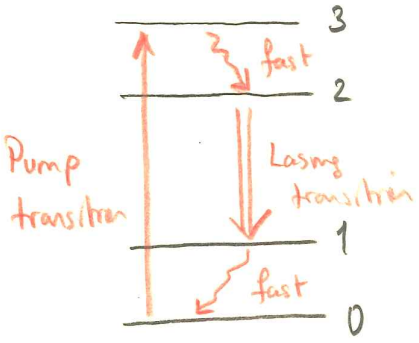
In steady state $\frac{d}{dt} \to 0$, we get

$$(A + BI)\,\Delta N = (A - BI)\,N$$

$$\Rightarrow \Delta N = N\,\frac{A - BI}{A + BI} \quad \text{or} \quad \Delta N = N\,\frac{1 - I/I_{sat}}{1 + I/I_{sat}} \quad \text{where } I_{sat} \equiv \frac{A}{B}$$

So, when $I > I_{sat}$, $\Delta N < 0$ i.e., population inverted!

Note that there is a threshold to be exceeded to achieve population inversion in a 3-level case. This can be relaxed if we go to a 4-level scheme. Here, we introduce another level below state 1



Since level 1 rapidly decays to 0

$N_1 \approx 0$ so that $\Delta N = N_1 - N_2 \simeq -N_2$

$N(t) = N_0(t) + N_2(t)$ ← total # atoms

or $N_0(t) = N - N_2(t)$

$$\frac{dN_2}{dt} = BIN_0 - AN_2 \quad \Rightarrow \quad \frac{dN_2}{dt} = BI(N - N_2) - AN_2$$

$$\Delta N \equiv N_1 - N_2 \approx -N_2, \quad -\frac{d\Delta N}{dt} = BIN + BI\Delta N + A\Delta N$$

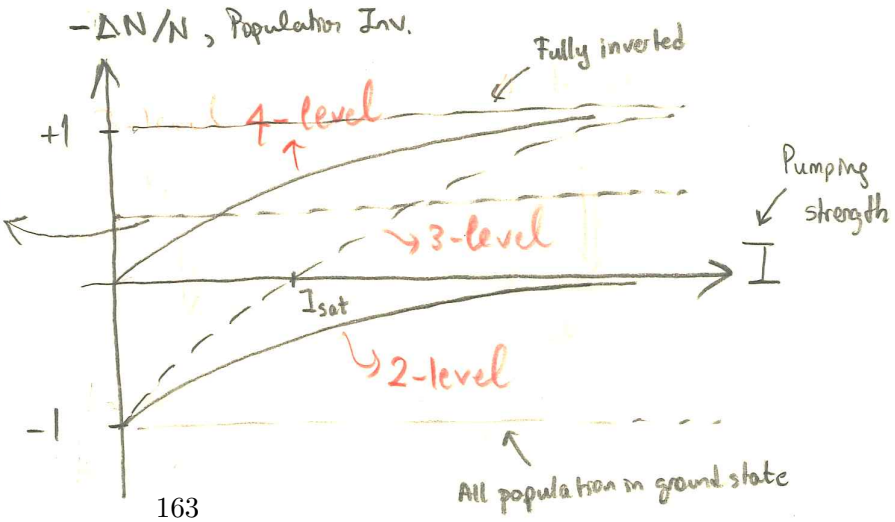
Steady state: $0 = BIN + BI\Delta N + A\Delta N$

$$\Rightarrow \quad \Delta N = -\frac{BIN/A}{1 + BI/A} \qquad I_{sat} \equiv \frac{A}{B}$$

$$\Delta N = -N \frac{I/I_{sat}}{1 + I/I_{sat}}$$

For a 4-level $\Delta N < 0$, population inversion is unconditionally obtained!

So, in summary:



(Due to additional losses it is somewhat above inversion limit)

Don't be upset, when you see people only considering spontaneous emission term (i.e., ignoring stimulated emission) in the discussions of radiative recombination. As we have seen above, for the stimulated emission term to dominate, special precautions need to be taken such as population inversion with a 4-level scheme and embedding within a resonant cavity etc. Furthermore, spontaneous emission rate increases with f^3, so at optical frequencies and beyond it is very effective! Therefore, in the above rate equations where we looked for inversion thresholds, we neglected the stimulated emission wrt spontaneous term. Obviously in operation regime of a laser (well above inversion threshold) one should definitely include the stimulated emission term.

When is the Rate Equation Approach Applicable?

This formalism only keeps track of state populations, so it is convenient for extracting the T_1 time so-called population decay time. One uses it for incoherent processes where phase information is not needed.

For coherent processes one should use time-dependent Schrödinger equation, or some Master Equation based on density matrix time evolution.

Er^{3+} ion Rate Equations

Er is a rare earth metal, $Z = 68$ with $[Xe]\,4f^{12}\,6s^2$ → $^1S_0$

vacancies: f^2

$L = 5,\ S = 1,\ J = 6, 5, 4$

$\sum_i m_{l_i} = 2 + 3 \rightsquigarrow H$

$m_l = -3\ -2\ -1\ 0\ 1\ 2\ 3$ (2 and 3 occupied)

$\Rightarrow$ $^3H_6$, $^3H_5$, $^3H_4$

↳ ground term

Er^{3+} is the technologically important ion configuration with $[Xe]\,4f^{11}$

Again considering vacancies: $f^{11} \longrightarrow f^3$ ... 1 2 3

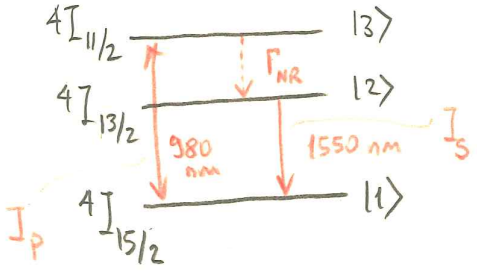
$L = \sum_i m_{l_i} = 6 \rightsquigarrow I$, $S = \sum_i m_{s_i} = 3/2$

$\Rightarrow$ $\vec{J} = \vec{L} + \vec{S}$; $J = 15/2,\ 13/2,\ 11/2,\ 9/2$

$^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$

↳ Ground term

The most frequently used three-level scheme for Er^{3+} is



The rate eq's involving Einstein A-B coefs:

$$\dot{n}_3 = -\Gamma_{NR} n_3 - A n_3 - A n_3 + B I_p n_1 - B I_p n_3$$

- $-\Gamma_{NR} n_3$: non-rad. decay from 3 → 2
- $-A n_3$: spontaneous decay to 2 & 1
- $-A n_3$: spontaneous decay from 3
- $B I_p n_1$: stim. abs. from 1
- $-B I_p n_3$: stim. em. to 1

I_s, I_p: spectral radiances for the signal and pump fields

Similarly for populations of 2 and 1 we have

$$\dot{n}_2 = +(A+\Gamma_{NR})\,n_3 - A\,n_2 - B\,I_s\,n_2 + B\,I_s\,n_1$$

$$\dot{n}_1 = (A+I_p B)\,n_3 - B\,I_p\,n_1 - B\,I_s\,n_1 + (A+I_s B)\,n_2$$

For the case of Γ_{NR} dominating, so that $n_3(t) \simeq 0$, we get

$$\dot{n}_2 = -A\,n_2 - B\,I_s\,n_2 + B\,I_s\,n_1 + \underbrace{B\,I_p\,n_1}_{\text{from 1 (via 3)}}$$

In this case $n_1(t) + n_2(t) = 1$, so that $\dot{n}_1 = -\dot{n}_2$

For the steady state, we set $\dot{n}_i = 0$

$$\Rightarrow \quad 0 = -(A+B I_s)\,n_2 + B(I_s+I_p)\,\underbrace{n_1}_{1-n_2}$$

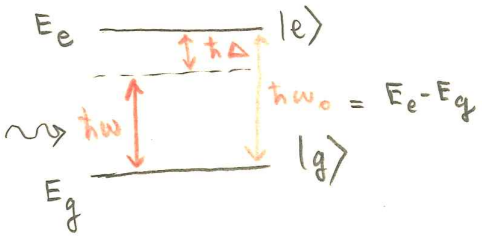
$$\Rightarrow \quad n_2 = \frac{B(I_s+I_p)}{A+B(I_p+2I_s)}$$

NB: A curious thing is that $1 \leftrightarrow 2$, $1 \leftrightarrow 3$ transitions should be dipole forbidden as $\Delta L = 0$ ($^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$)

How come this becomes an efficient pumping and emission route for EDFA's?

The reason is that these LS symbols are for a free Er^{3+} ion. When embedded into a solid-state environment (like silica) the crystal field breaks inversion symm. and selection rules hence cause the so-called induced electric dipole transitions.

Rabi Oscillations (in semiclassical level)



Starting with a general solution

$$|\Psi(t)\rangle = C_g(t)\, e^{-iE_g t/\hbar}|g\rangle + C_e(t)\, e^{-iE_e t/\hbar}|e\rangle$$

Inserting into time-dependent Schrödinger eqn.

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(t)\,|\Psi(t)\rangle$$

$\hat{H}(t) = \hat{H}_0 + \hat{V}_0 \cos\omega t$

$\hat{V}_0 \cos\omega t \to -\vec{d}_{eg}\cdot\vec{F}_0$

$\hat{H}_0 \to E_g|g\rangle\langle g| + E_e|e\rangle\langle e|$

$$\Rightarrow i\hbar\left(\dot{C}_g - i\frac{E_g}{\hbar}C_g\right)e^{-iE_g t/\hbar}|g\rangle + i\hbar\left(\dot{C}_e - i\frac{E_e}{\hbar}C_e\right)e^{-iE_e t/\hbar}|e\rangle =$$

$$\hookrightarrow C_g\, e^{-iE_g t/\hbar}E_g|g\rangle + C_e\, e^{-iE_e t/\hbar}E_e|e\rangle + C_g\, e^{-iE_g t/\hbar}\hat{V}_0|g\rangle + C_e\, e^{-iE_e t/\hbar}\hat{V}_0|e\rangle$$

Now project the above eqn. into $|g\rangle$ & $|e\rangle$ using

$$\begin{cases} \langle e|e\rangle = \langle g|g\rangle = 1 \\ \langle e|g\rangle = \underbrace{\langle e|\vec{d}|e\rangle = \langle g|\vec{d}|g\rangle = 0}_{\text{of definite parity}} \end{cases}$$

$$\dot{C}_g = \frac{-i}{\hbar}\langle g|\hat{V}_0|e\rangle \cos\omega t\; e^{-i\omega_0 t}\, C_e(t)$$

$\omega_0 = (E_e - E_g)/\hbar$

$\langle g|\hat{V}_0|e\rangle = V$ (can be taken as real)

$$\dot{C}_e = -\frac{i}{\hbar}V\cos\omega t\; e^{i\omega_0 t}\, C_g(t)$$

To simplify our analytical task, invoke the rotating wave approximation (RWA):

$$\cos\omega t\; e^{\pm i\omega_0 t} = \frac{1}{2}\left[e^{i(\omega\pm\omega_0)t} + e^{-i(\omega\mp\omega_0)t}\right]$$

Discard the rapidly oscillating terms: $e^{\pm i(\omega+\omega_0)t}$

This leaves us with

$$\dot{C}_g = -\frac{i\nu}{2\hbar}\, e^{i(\omega-\omega_0)t}\, C_e(t) \quad , \quad \dot{C}_e = -\frac{i\nu}{2\hbar}\, e^{-i(\omega-\omega_0)t}\, C_g(t)$$

($-\Delta$ in the exponent of the first; Δ in the exponent of the second)

We can uncouple these coupled 1st order d.e. by d/dt

$$\Rightarrow \dot{C}_g = i\frac{2\hbar}{\nu}\, e^{-i\Delta t}\left[-i\Delta\, \dot{C}_e + \ddot{C}_e\right]$$

$$\frac{-i\nu}{2\hbar}\, e^{-i\Delta t}\, C_e$$

$$\Rightarrow \frac{\nu^2}{4\hbar^2} C_e - i\Delta\, \dot{C}_e + \ddot{C}_e = 0 \quad \leftarrow \text{A homogeneous } 2^{nd} \text{ o.d.e}$$

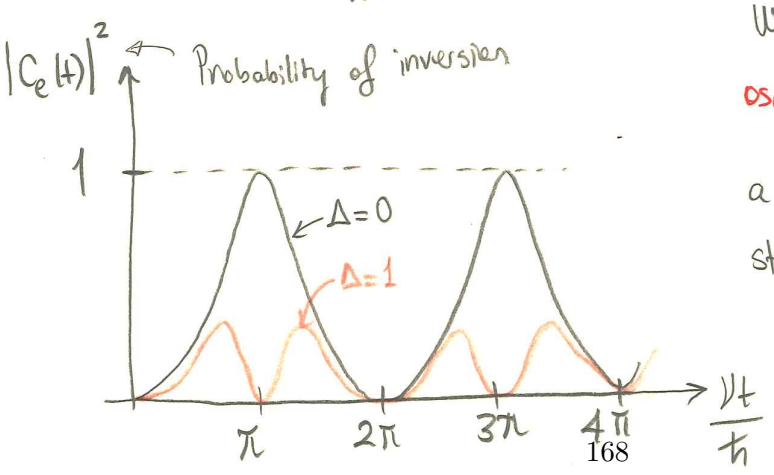
Try $C_e(t) = A\, e^{i\lambda t}$

$$\Rightarrow \lambda_{\pm} = \frac{1}{2}\left(\Delta \pm \sqrt{\Delta^2 + \frac{\nu^2}{\hbar^2}}\right) \rightarrow \Omega_R : \text{Generalized Rabi Freq.}$$

Invoking the initial conditions: $C_e(0)=0$ and $C_g(0)=1 \Rightarrow \dot{C}_e(0) = -\frac{i\nu}{2\hbar}$

we get:

$$C_e(t) = i\frac{\nu}{\hbar\Omega_R}\, e^{i\Delta t/2} \sin\frac{\Omega_R}{2} t$$

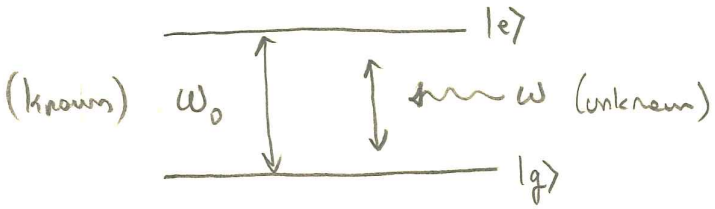


We observe the so-called Rabi oscillations bet. $|g\rangle$ and $|e\rangle$:

a bi-stable oscillator out of stimulated absorption and emission

Ramsey Interferometry

Historically the first application for this was in the precision measurement of an oscillator frequency. The setting is like an unknown incoming frequency, ω which is compared with a known transition freq. (2-level sys.

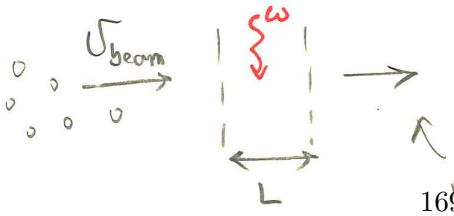


$$\Delta = \omega - \omega_0$$

As we have seen from the Rabi oscillations discussion, this will give rise to a probability of excitation from $|g\rangle$ to $|e\rangle$ which is a fn. of Δ, $V/\hbar$ and interaction time, τ with the 2-level sys.

$$P(\Delta, V, \tau) = |C_e(\tau)|^2 = \frac{1}{1+\left(\frac{\Delta}{\hbar V}\right)^2} \sin^2\left(\frac{\tau}{2}\sqrt{\frac{V^2}{\hbar^2}+\Delta^2}\right)$$

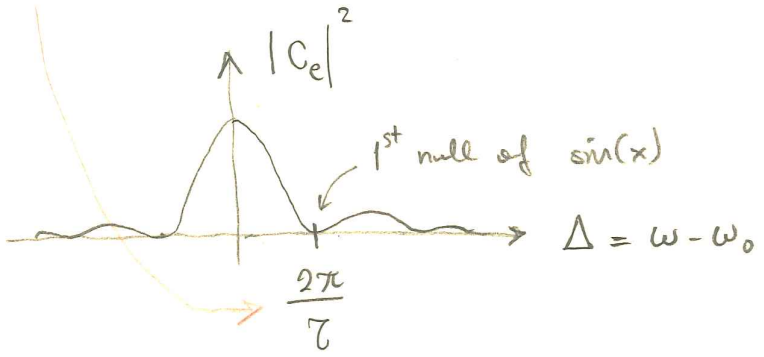
A common set-up is such that an atomic beam (2-level sys) is sent through an (unknown) osc. field zone



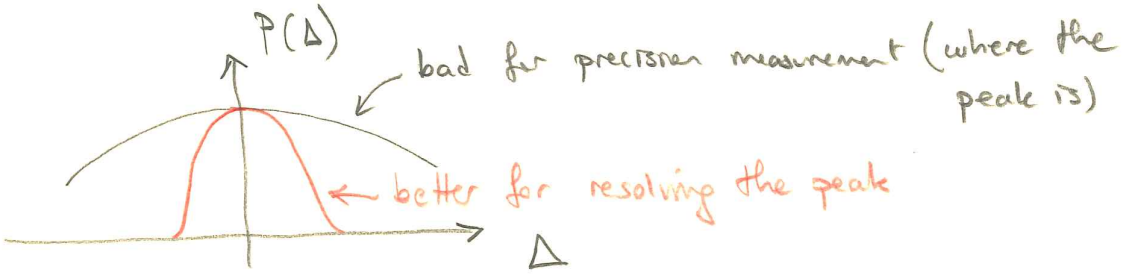
$$\tau = \frac{L}{v_{beam}}$$

measure the probability of excitation on the atomic beam

To better resolve the detuning bet. ω & ω_0, i.e., Δ, we need to increase the interaction time, τ within the oscillator zone.

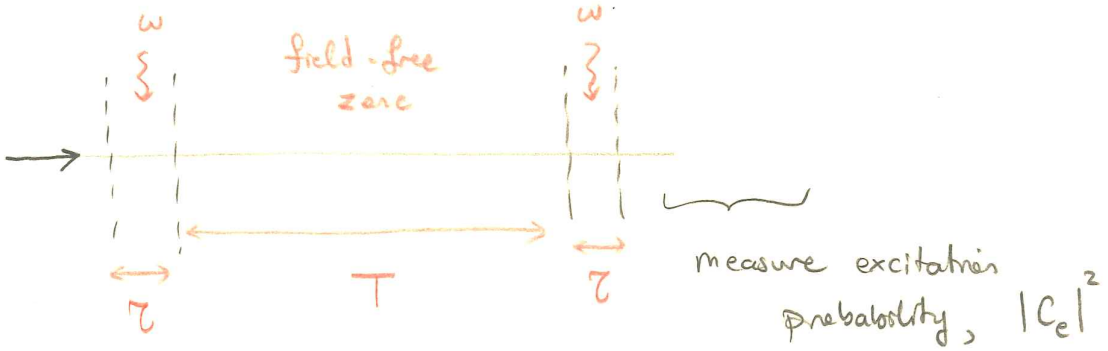


This is because, for discriminating a deviation we need more sensitivity to that variation

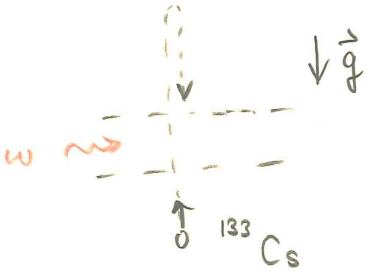


It is not surprising that we need large τ for better frequency resolution — Fourier xform relation.

However, if the atomic beam stays for longer within the interaction zone, it will be prone to line broadening mech. due to inhomogeneous atomic velocity distr. etc. This dilemma is alleviated by the Ramsey interferometry scheme.



In fountain clocks usually the atomic beam passes from the same RF cavity twice: on the way up and down



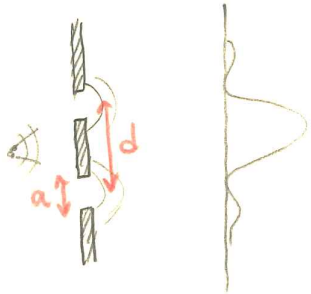
In this case $|C_e(t)|^2$ after exit from the 2nd cavity becomes

$$C_e(t) = \frac{V^*}{2\hbar}\left[\underbrace{\frac{1-e^{i\Delta\cdot\tau}}{\Delta}}_{1^{st}\text{ pulse}} + \underbrace{e^{i\Delta\cdot T}}_{\substack{\text{additional}\\ \text{phasing}\\ \text{bet. pulses}}}\underbrace{\frac{1-e^{i\Delta\cdot\tau}}{\Delta}}_{2^{nd}\text{ pulse}}\right]$$

$$\Rightarrow |C_e(t)|^2 = \left|\frac{V\tau}{2\hbar}\right|^2\left[\frac{\sin(\Delta\cdot\tau/2)}{\Delta\cdot\tau/2}\right]^2\cos^2\left(\frac{\Delta\cdot T}{2}\right)$$

NB: This is reminiscent of Young's double-slit interferometry for intensity

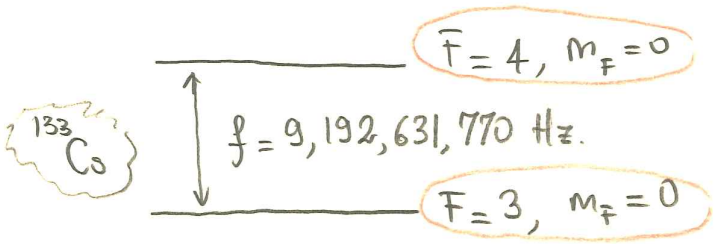
$$I = I_0\,\underbrace{\operatorname{sinc}^2\left(\tfrac{1}{2}ka\sin\theta\right)}_{\text{diffraction of a single slit}}\underbrace{\cos^2\left(\tfrac{1}{2}kd\sin\theta\right)}_{\text{interference}}$$



Note that in this case the central lobe width is controlled by the $\cos^2(\cdot)$ term as $T \gg \tau$, governed by frequency width $\delta f = \frac{1}{2T}$

Atomic Clocks

In the metrology lab's around the world Cs or Rb fountain clocks are in use. Since all ^{133}Cs isotopes are identical, precise measurements would agree with each other, within experimental uncertainties. The chosen clock transition is between two hyperfine states of $m_F = 0$ so that they have no first-order Zeeman shifts.



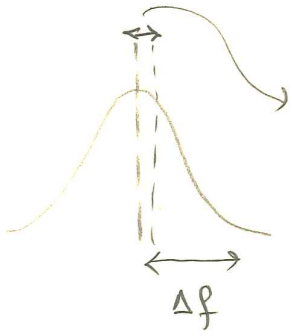
Here, the dominant contribution to linewidth comes from the finite interaction time τ as atoms pass through the field zone of length L.

$$\Delta f \sim \frac{1}{\tau} = \frac{v_{beam}}{L}$$

For $L = 2m$, $v_{beam} = v_{Cs} = \left(3k_B T / M_{Cs}\right)^{1/2} \Big|_{T=360K} = 210\ m/s$

$$\Delta f \simeq 100\ Hz$$

$$\frac{f}{\Delta f} \sim 10^8$$



peak can be located up to $\frac{1}{100}$ of Δf

$\Rightarrow$ precision $\sim$ 1 part in 10^{10}

This feedback info on the deviation from the reference signal (^{133}Cs transition) is used to lock the tunable RF oscillator to fractional stabilities smaller than 10^{-16}.

Optical Clocks

As opposed to μw transitions (having RF oscillators), optical clocks are based on optical transitions (having a laser as the oscillator). The main obstacle was to directly measure

the very high optical freq. which has been overcome by femtosecond frequency combs (Hall & Hänch Nobel Prize 2005).

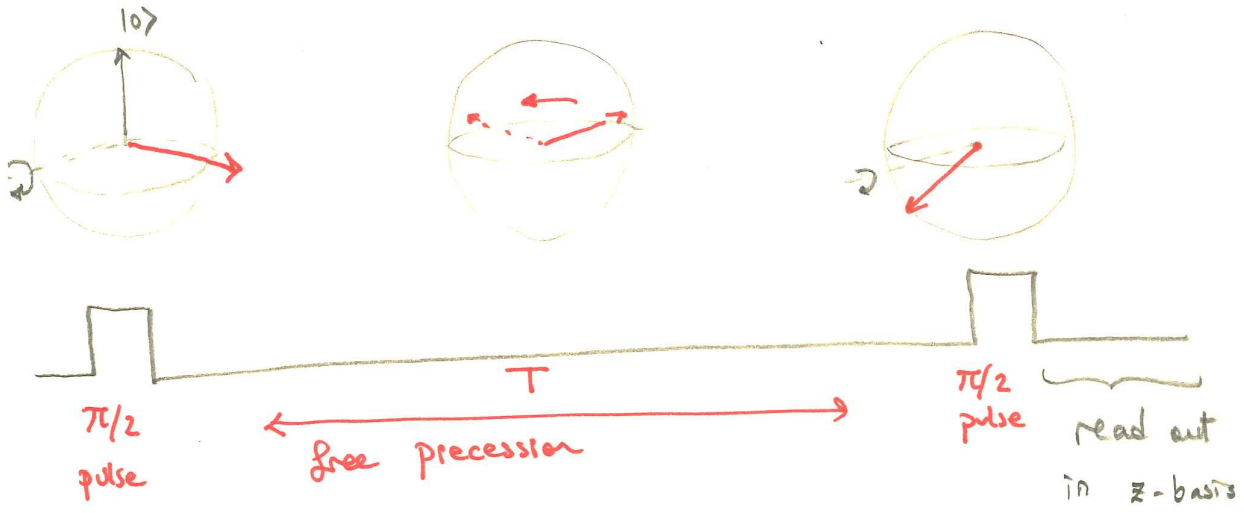
Here, optical freq. is divided down to directly measurable RF.

Although the laser phase noise is generally greater than stable μw sources, after division it becomes less.

Best experimental optical clocks have absolute freq. uncertainties $< 10^{-17}$

Phase Qubit/Gate

Ramsey interferometry scheme is also used in the context of quantum logic gates, as the Pauli Z-gate (phase-shift gate)

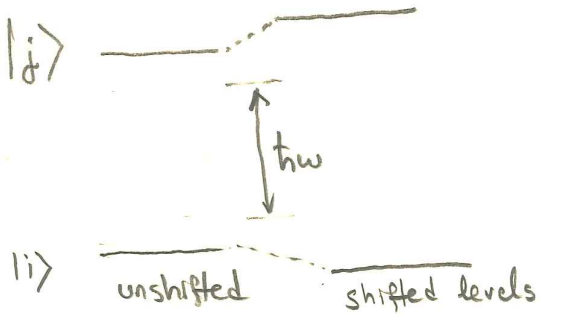


In this case, the π/2 pulses are definite, that is we do not have any variation/drift in their values, unlike the case in metrology.

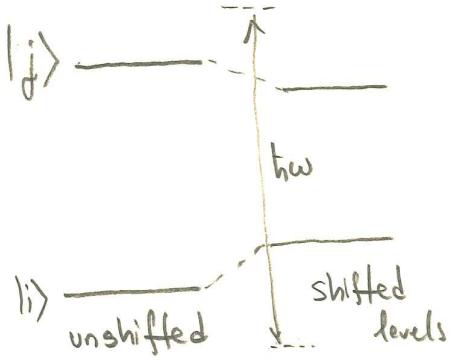
Dynamic Stark Effect

A.K.A. AC Stark effect, light-shift or lamp shift :-)

This light-shift is proportional to the intensity of the incident field and inversely proportional to the detuning from the intermediate states. The previous case demonstrates the two-photon transitions. They also occur in other cases, such as one-photon transition bet. two atomic energy levels.



Red detuned case

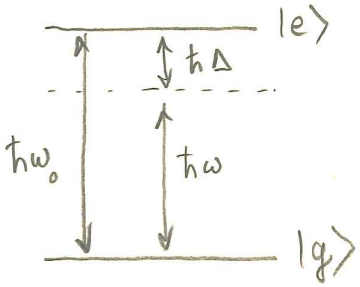


Blue detuned case

This concept is very useful for laser cooling and trapping of atoms. Depending on the laser intensity, light-shifts of MHz and even GHz are routinely attained. In the following section we give some technical details on how this effect comes about.

Light Shift (AC Stark Effect)

Here, we consider the coupling bet. a 2-level atom $\{|g\rangle, |e\rangle\}$ with the photonic states $\{|n+1\rangle, |n\rangle\}$. Due to coupling bet. them a so-called **dressed-atom** emerges with different energies.



bare atom under red-detuned light

$\Delta = \omega_0 - \omega$

For this definition, $\Delta > 0 \Rightarrow$ red detuned radiation

Considering also the photon energies, under no coupling ($\gamma = 0$)

$$|e\rangle|n\rangle \longrightarrow E_e + n\hbar\omega$$

$$|g\rangle|n+1\rangle \longrightarrow E_g + (n+1)\hbar\omega$$

$$\underbrace{(E_e - E_g)}_{\hbar\omega_0} - \hbar\omega = \hbar\Delta$$

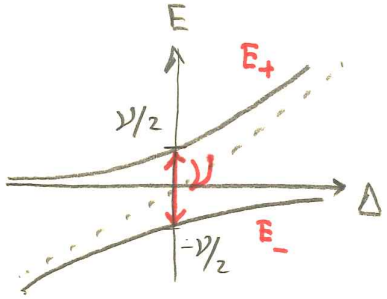
Under light-atom coupling the atomic subspace (i.e., suppressing photonic part) ($\hbar \to 1$)

$$\begin{bmatrix} \Delta & -\gamma/2 \\ -\gamma/2 & 0 \end{bmatrix} \begin{bmatrix} C_e \\ C_g \end{bmatrix}$$

a) Eigenvalues:

$$\begin{vmatrix} \Delta - E & -\nu/2 \\ -\nu/2 & -E \end{vmatrix} = 0$$

$$E^2 - \Delta E - \frac{\nu^2}{4} = 0 \quad , \qquad E_\pm = \frac{\Delta \pm \sqrt{\Delta^2+\nu^2}}{2}$$



b) Eigenvectors: $|+\rangle$, $|-\rangle$

$$|+\rangle = C_{e+}|e\rangle + C_{g+}|g\rangle \qquad \begin{bmatrix} \Delta - E_+ & -\nu/2 \\ -\nu/2 & -E_+ \end{bmatrix} \begin{bmatrix} C_{e+} \\ C_{g+} \end{bmatrix} = 0$$

$$\Rightarrow \frac{\Delta - \sqrt{\Delta^2+\nu^2}}{2} C_{e+} = \frac{\nu}{2} C_{g+} \quad \& \quad |C_{e+}|^2 + |C_{g+}|^2 = 1 \ \text{(Normalization)}$$

Let $\tan\vartheta \equiv \frac{\nu}{\Delta}$, $\Rightarrow \left(1 - \underbrace{\sqrt{1+\tan^2\vartheta}}_{\sec\vartheta}\right) C_{e+} = \tan\vartheta \, C_{g+}$

$$\Rightarrow \frac{\cos\vartheta - 1}{\sin\vartheta} C_{e+} = C_{g+}, \quad \text{combine with normalization} \Rightarrow |C_{e+}| = \frac{1}{\sqrt{1+\left(\frac{\cos\vartheta-1}{\sin\vartheta}\right)^2}}$$

Taking C_{e+} as purely real,

$$C_{e+} = \frac{\sin\vartheta}{\sqrt{2-2\cos\vartheta}} = \frac{2\sin\frac{\vartheta}{2}\cdot\cos\frac{\vartheta}{2}}{2\cdot\sin\frac{\vartheta}{2}} = \cos\frac{\vartheta}{2}$$

$$\Rightarrow C_{g+} = -\cos\frac{\vartheta}{2}\cdot\frac{1-\cos\vartheta}{\sin\vartheta} = -\sin\frac{\vartheta}{2}$$

half ϑ's

$$\boxed{|+\rangle = \cos\frac{\vartheta}{2}|e\rangle - \sin\frac{\vartheta}{2}|g\rangle}$$

$$|-\rangle = C_{e-}|e\rangle + C_{g-}|g\rangle$$

$$\begin{bmatrix} \Delta - E_- & -\nu/2 \\ -\nu/2 & -E_- \end{bmatrix} \begin{bmatrix} C_{e-} \\ C_{g-} \end{bmatrix} = 0 \qquad \begin{cases} \dfrac{\Delta + \sqrt{\Delta^2+\nu^2}}{2} C_{e-} = \dfrac{\nu}{2} C_{g-} \\ |C_{e-}|^2 + |C_{g-}|^2 = 1 \end{cases}$$

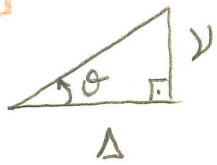
$$\left(1 + \sqrt{1+\tan^2\vartheta}\right) C_{e-} = \tan\vartheta \, C_{g-} \quad \Rightarrow \quad |C_{e-}| = \frac{1}{\sqrt{1+\left(\frac{\cos\vartheta+1}{\sin\vartheta}\right)^2}} = \frac{2\sin\frac{\vartheta}{2}\cos\frac{\vartheta}{2}}{2\cos\frac{\vartheta}{2}}$$

Taking C_{e-} as real

$$C_{e-} = \sin\frac{\vartheta}{2} \; ; \qquad C_{g-} = \sin\frac{\vartheta}{2} \cdot \frac{1+\cos\vartheta}{\sin\vartheta} = \sin\frac{\vartheta}{2} \cdot \frac{2\cos^2\frac{\vartheta}{2}}{2\sin\frac{\vartheta}{2}\cos\frac{\vartheta}{2}} = \cos\frac{\vartheta}{2}$$

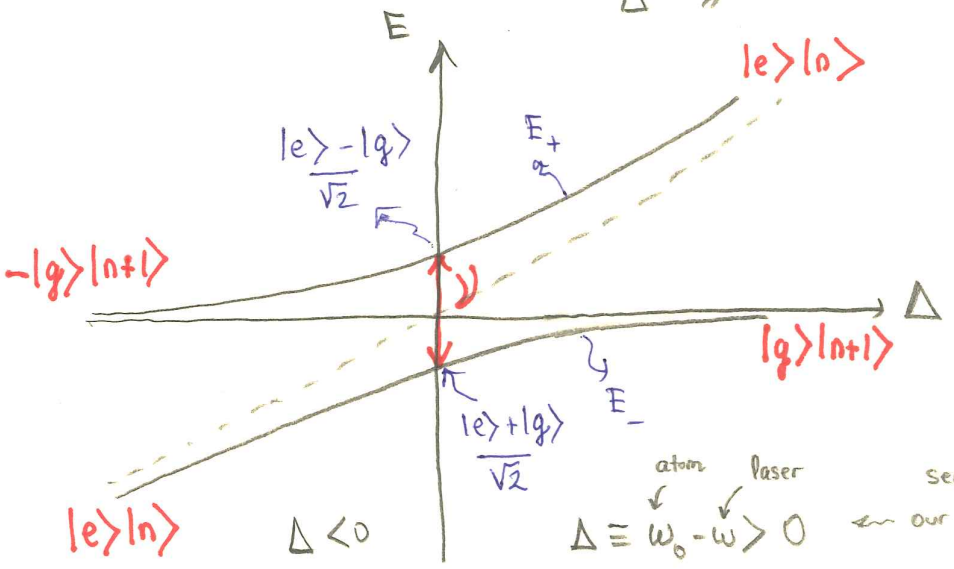
$$\Rightarrow \boxed{|-\rangle = \sin\frac{\vartheta}{2}|e\rangle + \cos\frac{\vartheta}{2}|g\rangle} \; ; \quad \text{Check that } \langle +|-\rangle = 0 \; \checkmark$$

Since $\tan\vartheta \equiv \dfrac{\nu}{\Delta}$

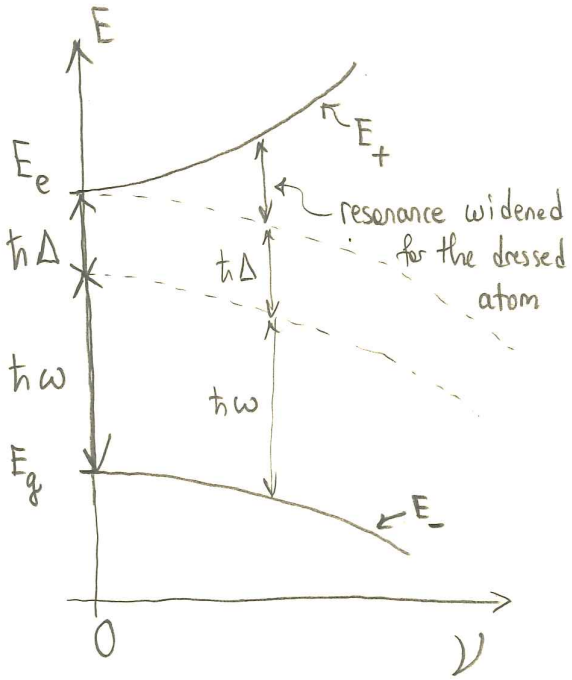


For a given ν value, as ϑ runs from $0 \to \frac{\pi}{2} \to \pi$

Δ " " $+\infty \to 0 \to -\infty$

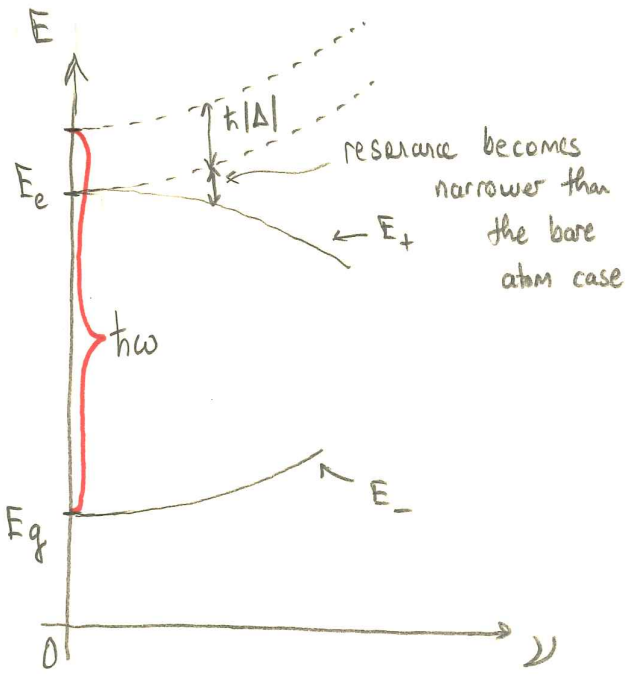


Physical Consequences of AC Stark Effect



red-detuned laser

$\Delta > 0$ (in our case)



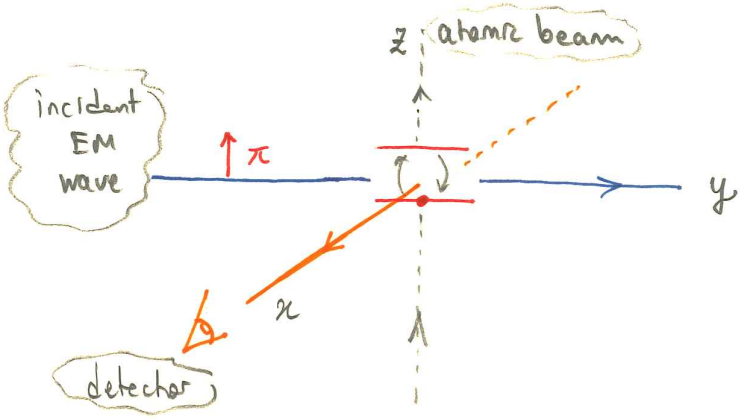
blue-detuned laser

$\Delta < 0$

So, strong light coupling redresses the atom (a non-perturbative phenomenon) such that resonance becomes wider (narrower) than that wrt bare atom case under light-coupling ($\gamma \neq 0$) for the case of red-detuned (blue-detuned) cases.

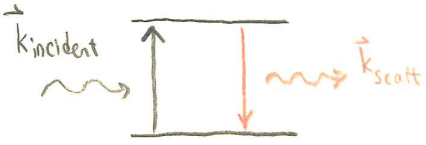
Resonance Fluorescence

Resonance fluorescence is usually measured in a mutually $\perp$ arrangement of an atomic beam, optical beam and detection as shown below.



When the incoming light freq. is resonant with the atomic transition (represented by a 2-level system), and if this driving EM field is at a low intensity (Rabi freq. much less than linewidth of the atomic levels involved, i.e., $\nu_R \ll \Delta\omega \sim \Gamma_{sp}$), then the atom absorbs a photon at the excitation freq. and re-emits it at the same freq.

spontaneous emission

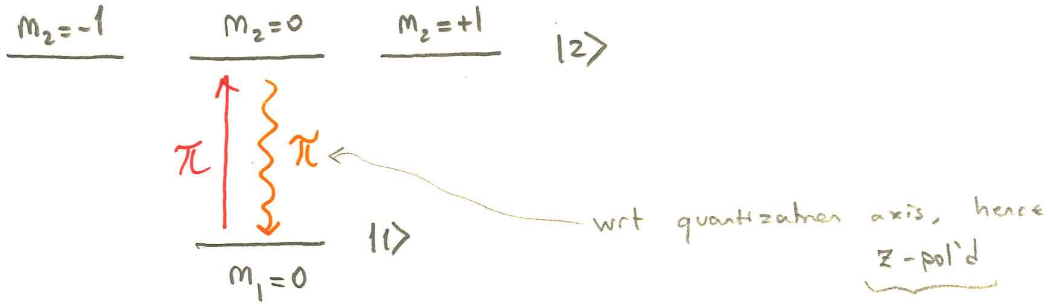


However, the emitted light is not along the $\vec{k}_{incident}$ but random in "all" directions.

↳ see later

The "scattered" light is extremely bright and even a single atom (or a quantum dot) interacting with the incident light can be resolved provided that it has a significant spontaneous decay rate, $\Gamma_{sp} \equiv A_{2\to 1}$

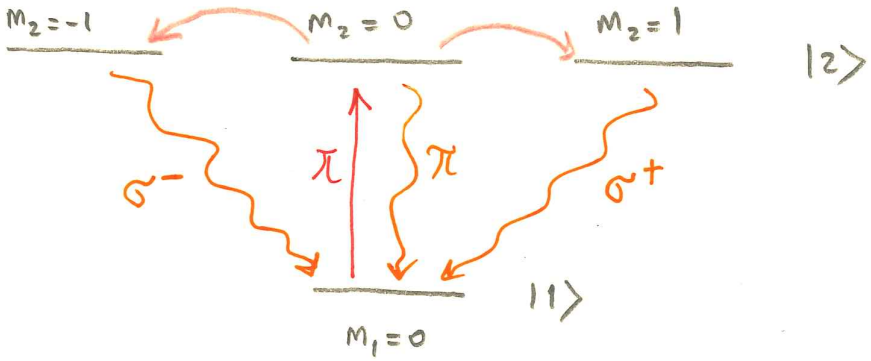
Let's assume that $\vec{k}_{incident} = \hat{y}$ with a linear polarization along $\hat{z}$ (i.e., $\vec{E}_{incident} \parallel \hat{z}$). Due to polarization selection rule, the absorption will be for $\Delta m = 0$ transition. If we assume that ground state is $J_1 = 0$ and the excited state with $J_2 = 1$, then



Consequently the detector placed in $\hat{x}$ direction will receive a $\hat{z}$-pol'd light. Note that $\vec{k}_{scattered}$ fluorescent light can be in "all" directions, but compatible with this specific polarization. Here, $\vec{k}_{scattered}$ cannot be along $\hat{z}$, as for a TEM wave $\vec{k}_{scatt} \perp \left(\vec{E} \parallel \hat{z}\right)$.

How can we alter the polarization of the emitted light?

→ Via population xfer in the excited state. After $\bar{e}$ is pumped to $m_2 = 0$ state, it can be redistributed among all m_2 sub-levels by collisions or non-collinear magnetic field (Hanle effect).



So, the existence of population xfer mechanisms are easily detected via a loss (deviation) in the definite polarization due to the appearing of (here) $\sigma^{+/-}$ polarizations.

Hanle Effect

This effect was reported (not surprisingly) by Wilhelm Hanle in 1924 which was instrumental in solving the quantum puzzle of that era.

Any DC magnetic field $\perp$ to the "quantization axis" (here $\hat{z}$ as defined by the $\Delta m = 0$, π polarization) will induce transitions among $m_z = 0, \pm 1$ states if the magnetic field is weak, and mixing of these levels if it is strong. In practice this is always a weak DC magnetic field.

For $\vec{B} = \hat{x} B_0$, $\hat{\mathcal{H}}^x_z = -\hat{\vec{\mu}} \cdot \hat{x} B_0 = -g_J \frac{e}{2m_e} B_0 \hat{J}_x$

(g_J: Landé factor (includes orbital + spin contributions))

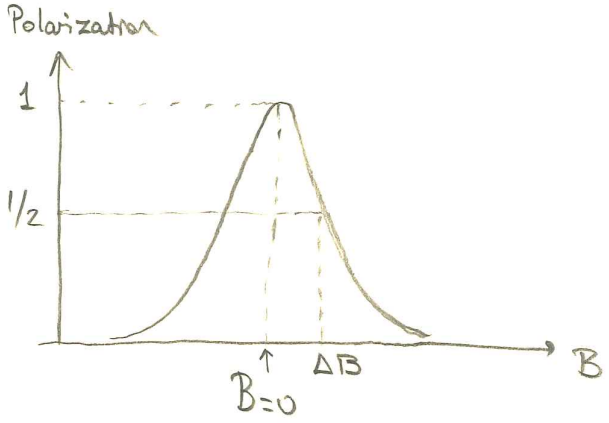
This perturbation enables non-diagonal matrix elements among m_z sub-levels

$\frac{1}{2}(\hat{J}_+ + \hat{J}_-) = \hat{J}_x$; use $\hat{J}_+ |1,0\rangle = \sqrt{2}\hbar |1,1\rangle$

$$\left\langle J_z, m_z = 1 \right| \hat{\mathcal{H}}_z^x \left| J_z, m_z = 0 \right\rangle = \frac{\hbar \omega_0}{\sqrt{2}}$$

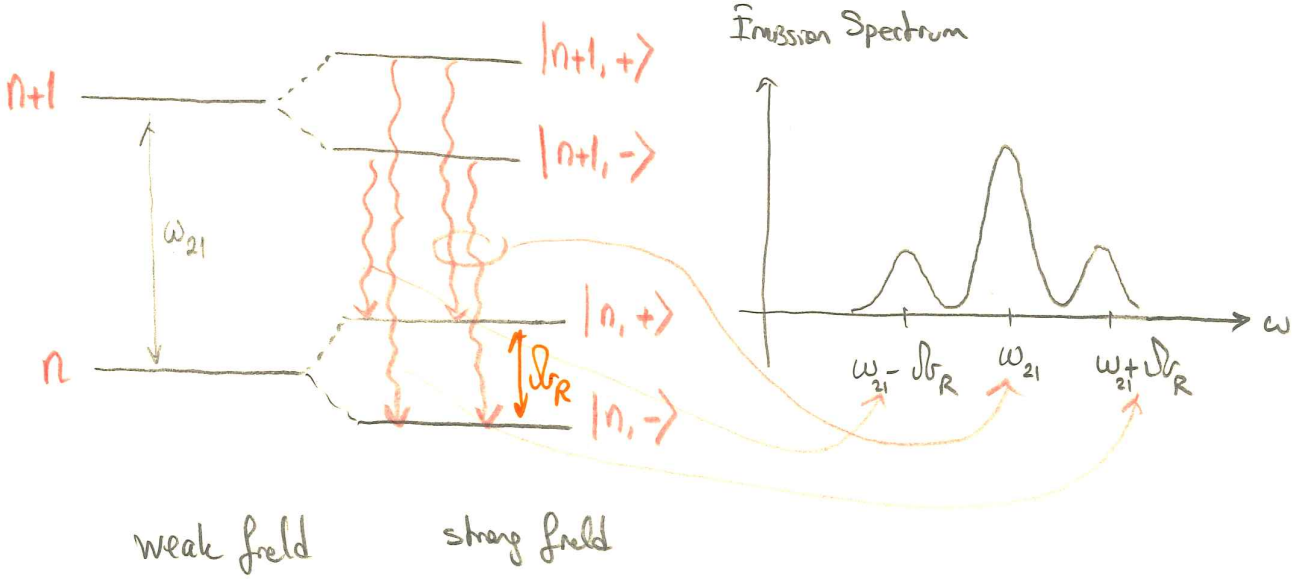
where $\omega_0 = -g_J \frac{e}{2m_e} B_0$ ... Larmor frequency

So, due to B_x field excited level population oscillates among the $m_z = 0, \pm 1$ sub-levels. Subsequently $\hat{y}$-polarization component can be present if decays via $\sigma^{+/-}$ emission. On the other hand if spontaneous decay occurs much more rapidly before population $\times$fer takes place, the emitted light remains π-pol'd (i.e., $\hat{z}$ only) Therefore, there is a race bet. these two processes, governed by the ratio ω_0 / Γ_{sp} which is easily controlled by B_0; increasing B_0 increases the degree of depolarization.



Resonance Fluorescence under Strong Field

An interesting thing happens to the emission spectrum when driving field becomes very strong $\Omega_R > \Gamma_{sp}$. The single peak splits by Ω_R into a triplet with separation being a fn. of field intensity



This is because in the strong coupling [atom + photon] states make-up new <u>dressed states</u> with the 'normal mode splittings' within the n & (n+1) excitation manifolds being roughly same, Ω_R. This is also known as Mollow's triplet.

Optical Pumping

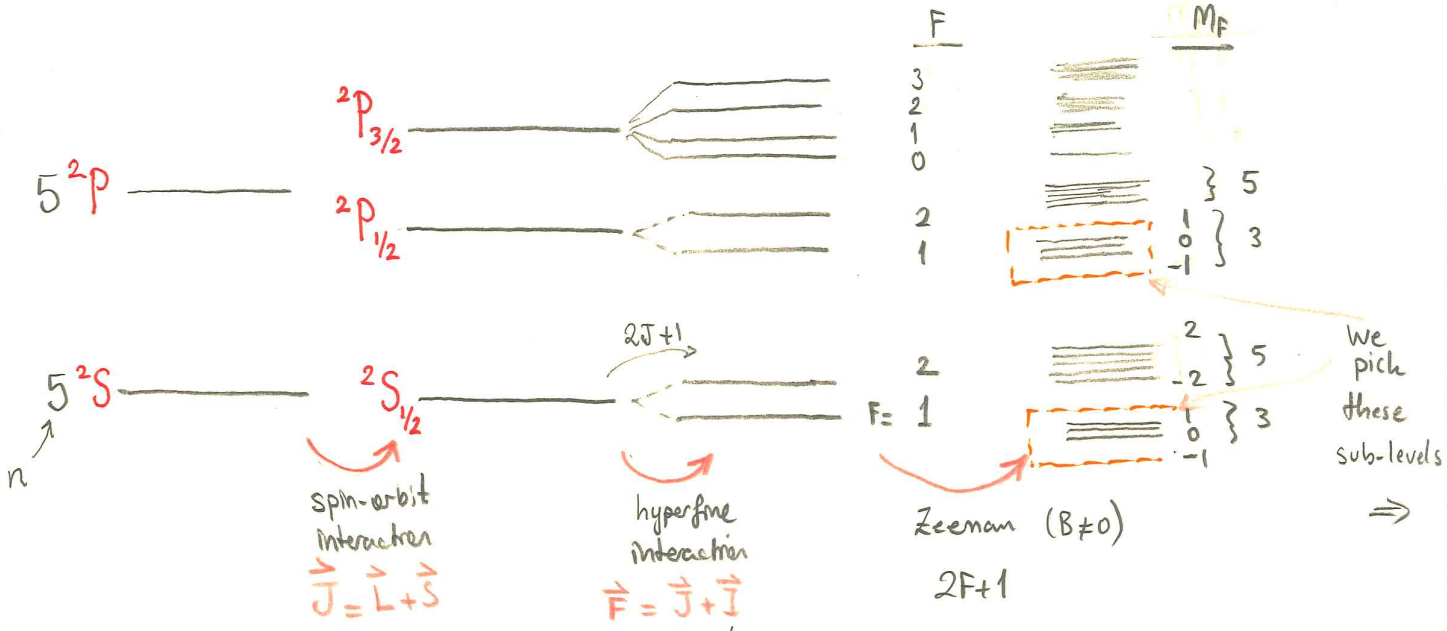
We now extend the sub-level manifold to the ground state as well. A technique utilizing this was invented by A. Kastler in 1949 based on selection rules governing the interaction of an atom with pol'd light that gives rise to a non-equilibrium distribution of population amongst the sub-levels of the ground state. This got him a Nobel prize in 1966. We shall demonstrate optical pumping over the beloved element of AMO physicists, rubidium. It has a single valence $\bar{e}$: $[Kr]\,5s^1$

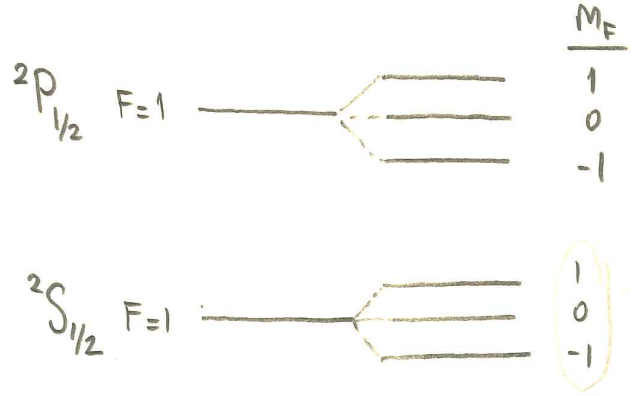
often called optical $\bar{e}$

Rubidium has two "stable" isotopes:

^{85}Rb (72 %) with $I = 5/2$

^{87}Rb (28 %) with $I = 3/2$ ← we shall consider this isotope





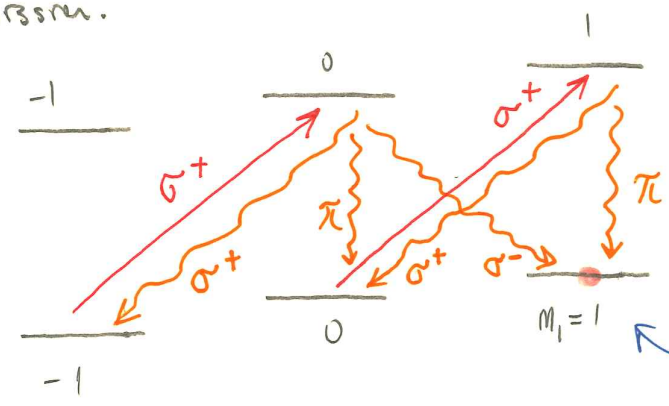
$\Delta L = \pm 1$, $\Delta S = 0$, $\Delta F = 0, \pm 1$

* Observe that according to E1 selection rules all transitions are allowed bet.

$^2S_{1/2}$ F=1, M_F $\xleftrightarrow{E1}$ $^2P_{1/2}$ F=1, M_F

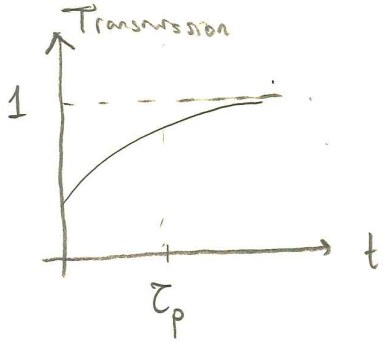
* Ground states equally-populated in equilibrium: Zeeman splittings are much smaller than $k_B T$

If we illuminate ^{87}Rb atoms continuously with a σ^+ pol'd light, we shall have $\Delta m_F = +1$ in absorption, but $\Delta m_F = 0, \pm 1$ in emission.



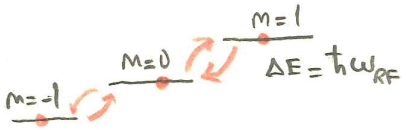
Since at each cycle only part of the $\bar{e}$'s return to their original states from where they were excited, eventually all atoms in the ensemble are (optically) pumped to $m_1 = 1$ state which cannot absorb σ^+ radiation to initiate a transition, therefore it is called a dark (trapping) state. By this means we end up with a non-equilibrium population among otherwise equally-populated states.

If we plot the transmission of σ^+ light through the ^{87}Rb cell, we start with very high absorption, which gradually disappears over a timescale of a few times the optical pumping period $\sim \tau_p$.



However, any relaxation process will tend to equalize the populations of the ground-state sub-levels back to thermal eql. $\Rightarrow$ absorption will reappear.

For instance applying an RF magnetic field $\perp$ to $\vec{B}_0$ resonant with Zeeman sub-levels will unpump $m_1 = 1$ state!



Upon optical pumping, the atom is said to be oriented in a particular m_F sublevel. Hence, starting from oriented initial sublevels, if an external DC $\perp$ magnetic field is further considered, through the Hanle effect this will enable the measurement of such magnetic fields to an accuracy of 10^{-13} T.

Part-III: **Molecules**

Molecular Systems: Interaction with EM Field

Unlike atoms, molecules have additional degrees of freedom and their "optical" spectra is more involved. We can include molecular solids into this discussion as well. Some examples are: aromatic hydrocarbons, conjugated polymers, defect (color) centers (like NV centers). These molecular solids behave more like molecules than say, semiconductors (like Si, Ge, GaAs etc.) Mainly because

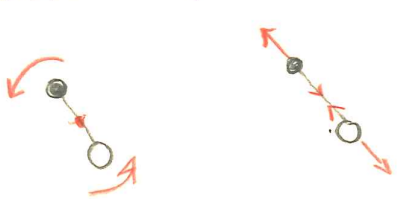
(*) Electronic & vibrational states are localized near individual molecules, even though they are embedded in a solid-state environment, called matrix. This matrix is usually amorphous as in spin-coated thin films on glass substrates ⇒ soft condensed matter. As these are mainly organic molecules, they are covalently bound within, but only via vdW to the host lattice

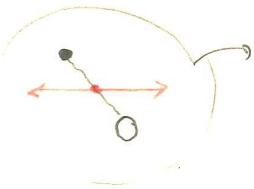
(*) Optical transitions are vibronic in character, that is, a transition simultaneously changes the electronic + vibrational (+rotational) state of the molecule.

Obviously there are some differences bet. isolated molecules and the molecular solids. We shall mainly treat the former as a cleaner system.

Molecules: New degrees of freedom

In contrast to atoms, molecules have two more degrees of freedom: rotational & vibrational, further inflated by dimensionality





as in atoms, translational d.o.f. of c.m. (not relevant/interesting)

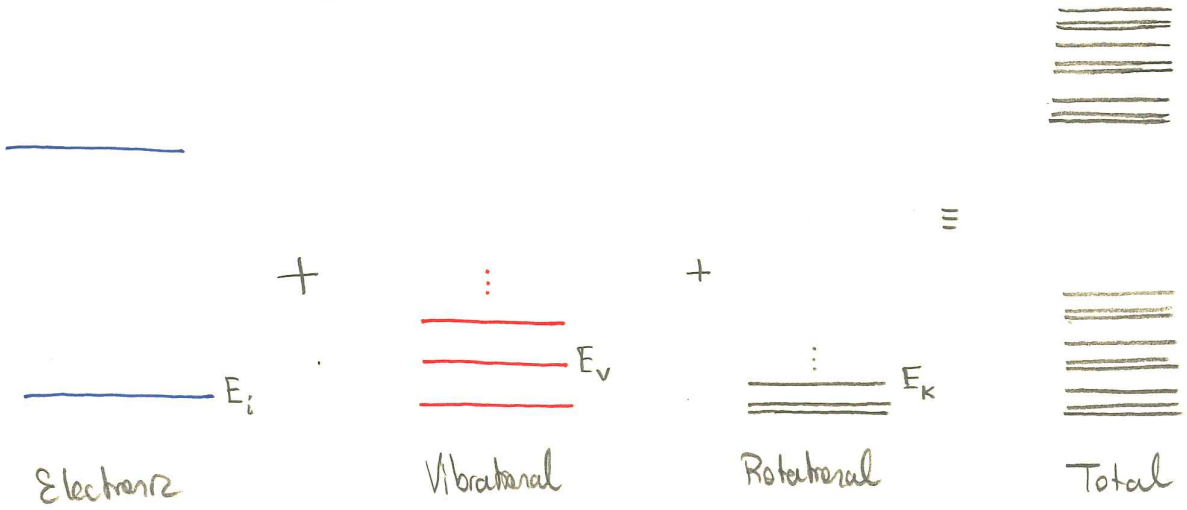
If we also recall the electronic degrees of freedom, there are three main features in the molecular spectra. Each of these motions are governed by QM, hence quantized.

→ How do we deal with all of these?

We make use of the so-called Born-Oppenheimer approximation which treats them not simultaneously but separately by freezing the other degrees of freedom (if slow) or incorporating their mean field contribution (if much faster) compared to the process under investigation. This is possible as each of these has different characteristic time (energy):

	time	mass / I	spectrum
rotations:	$\sim 10^{-11}$ s	(large moment of inertia, I)	μwaves – mm waves
vibrations:	$\sim 10^{-13}$ s	(relative ionic mass, m_{eff})	far IR – IR
electronic:	$\sim 10^{-15}$ s	(electronic mass, m_e)	visible – UV

Within the Born-Oppenheimer framework:

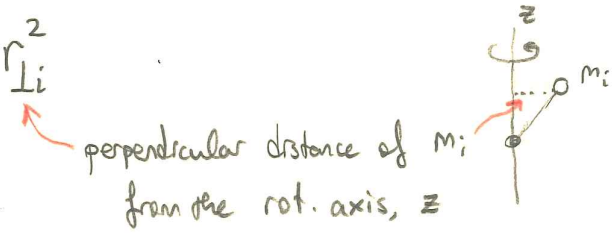


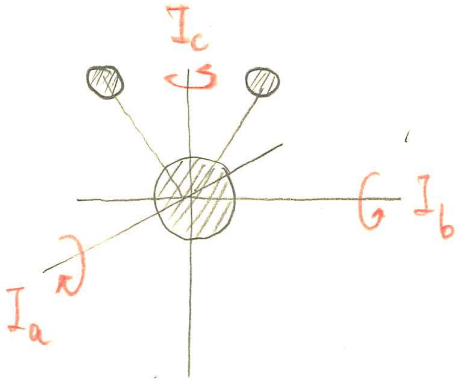
The rotational & vibrational spectra contains the fingerprint of the molecule; their analysis leads to bond strengths, lengths, and angles, as well as dipole moments.

Rotational Motion

The central molecular parameter is the moment of inertia, I of the molecule,

$$I_z = \sum_i m_i r_{\perp i}^2$$





There are three moments of inertia, I_a, I_b, I_c around the three orthogonal axes.

Convention: Label them as a, b, c based on

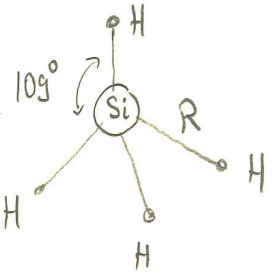
$$I_c \geq I_b \geq I_a$$

We shall initially consider rigid rotors: bodies that do not distort under the stress of rotation.

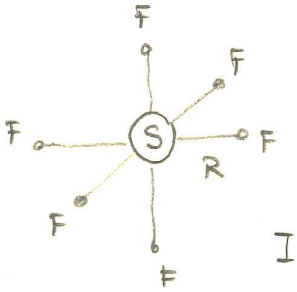
We classify rotors in 4 types based on I relations

1) Spherical Rotors: $I_a = I_b = I_c$

Eg: CH_4, SiH_4, SF_6



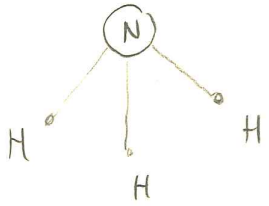
$I = \frac{8}{3} m_H R^2$



$I = 4 m_F R^2$

2) Symmetric Rotors: two equal I's

Eg: NH_3, CH_3Cl, CH_3CN



3) Linear Rotors: $I_a \equiv 0$

Eg: CO_2, HCl, OCS, $HC \equiv CH$



$I = 2 m_o R^2$

4) Asymmetric Rotors: $I_a \neq I_b \neq I_c$

Eg: H_2O, H_2CO, CH_3OH

Rotational Energy Levels

Ideally we need to solve the Schrödinger eqn right away for the rotational dynamics of the rotor. But there is a short cut: use the classical expression for the energy of the rotor expressed in terms of its angular momentum $\vec{J}$, then incorporate the quantization of $\vec{J}$.

The classical mechanics KE expression for rotation is:

$$E = \frac{1}{2} I_a \omega_a^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2 \quad , \quad \omega_{a,b,c}: \text{angular velocities around three axes}$$

The classical angular momentum about an axis i:

$$J_i = I_i \omega_i$$

I_i: not the nuclear spin! (moment of inertia)

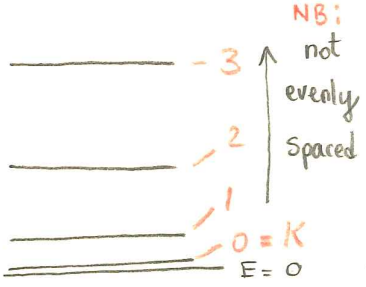
Hence $$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

(a) Spherical Rotor $(I_a = I_b = I_c \equiv I)$

$$E = \frac{J_a^2 + J_b^2 + J_c^2}{2I} = \frac{J^2}{2I}$$ (still in classical mechanics)

$$J^2 \xrightarrow{QM} K(K+1)\hbar^2 \quad , \quad K = 0, 1, 2, \ldots$$

$$E_K = K(K+1)\frac{\hbar^2}{2I} \quad , \quad K = 0, 1, 2, \ldots$$



NB: Large molecules (large I) have closely spaced rotational energy levels.

Define the rotational constant, B

$$hcB \equiv \frac{\hbar^2}{2I}$$

$$\Rightarrow E_K = hcB\,K(K+1), \quad K = 0, 1, 2, \ldots$$

or in terms of wavenumbers we use $F(K) \equiv B\,K(K+1)$

(b) Symmetric Rotors $I_{\parallel}, I_{\perp}, I_{\perp}$

Benzene



If $I_{\parallel} > I_{\perp}$ → oblate (eg. C_6H_6)

If $I_{\parallel} < I_{\perp}$ → prolate (eg. CH_3Cl)

$$E = \frac{J_{\perp}^2}{2I_{\perp}} + \frac{J_{\parallel}^2}{2I_{\parallel}} \; ; \qquad J^2 = J_{\perp}^2 + J_{\parallel}^2 \; ; \quad \text{Quantization axis} \parallel J_{\parallel}$$

$$J^2 \xrightarrow{QM} K(K+1)\hbar^2, \quad K = 0, 1, 2, \ldots$$

$$J_{\parallel} \xrightarrow{QM} m_K \hbar \; ; \qquad m_K = 0, \pm 1, \pm 2, \ldots \pm K \quad (\text{magnetic q. \#})$$

Hence $J_{\parallel}^2 \rightarrow m_K^2 \hbar^2$

$$\Rightarrow F(K, m_K) = B\,K(K+1) + (A-B)\,m_K^2$$

$B \rightarrow \frac{\hbar}{4\pi c I_{\perp}}$ $\qquad$ $(A-B) \rightarrow \frac{\hbar}{4\pi c I_{\parallel}}$

(c) Linear Rotors

$$F(K) = B\,K(K+1), \quad K = 0, 1, 2 \ldots$$

Degeneracy of the rotational states

For a linear rotor since the component of angular momentum along linear axis is quantized in the form $M_K \hbar$; $M_K = 0, \pm 1, \ldots, \pm K$, there are $2K+1$ degenerate states (which corresponds to the quantization wrt overall rotation of the molecule).

For a spherical rotor in addition to M_K quantum number with $2K+1$ degeneracy, we have the other $2K+1$ degeneracy from the axis wrt which other directions are defined (as in the linear rotor). Therefore, altogether there are $(2K+1)^2$ degeneracy; this increases very rapidly with K.

For $K=10$, there are $(21)^2 = 441$ states of the same energy.

Stark Effect

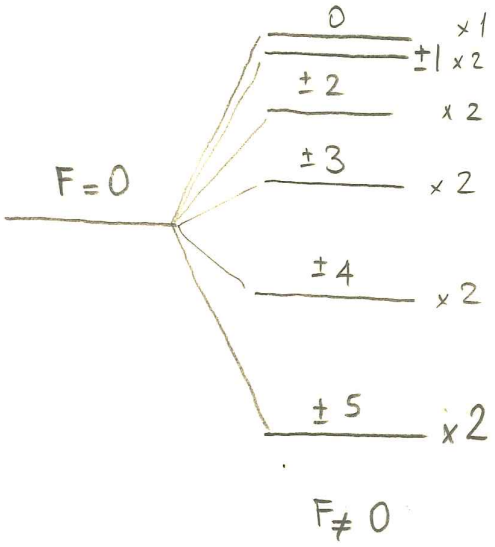
The overall rotation of the molecule giving rise to M_K quantum number degeneracy can be removed by an external electric field provided that the molecule is polar, with a dipole moment $\vec{d}$.

For a linear rotor in an electric field, $\vec{F}$, the energy of the state $|K, M_K\rangle$ is modified as

$$E(K, M_K) = hcBK(K+1) + a(K, M_K)\, d^2 F^2$$

d → dipole moment of the molecule

$$a(K, M_K) = \frac{K(K+1) - 3M_K^2}{2hcBK(K+1)(2K-1)(2K+3)}$$

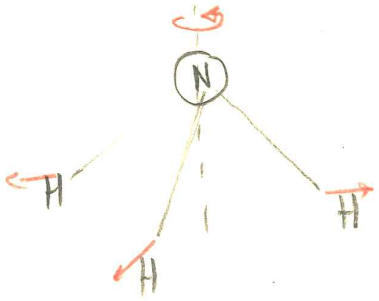


Stark splitting of the (polar) rotational state $K = 5$

$\pm m_K$ deg. remains (Kramers doublet)

Centrifugal Distortion

We now relax the rigid rotor restriction. In reality the atoms experience tidal forces that tend to distort the molecular geometry and modify the moments of inertia (just like the shape of Earth being distorted around the equatorial zone due to its spin).

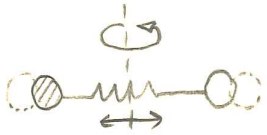


The net effect is $I \rightarrow I(\omega)$. This is taken into account empirically as:

$$F(K) = BK(K+1) - D_K K^2 (K+1)^2$$

D_K: centrifugal distortion constant

D_K of a diatomic molecule is related to the vibrational wavenumber $\tilde{\nu}$ (to be introduced later) of the band as

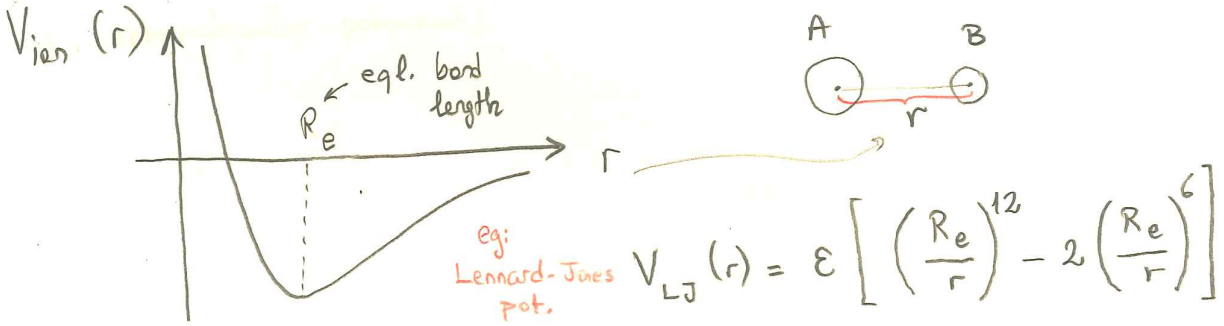


$$D_K = \frac{4B^3}{\tilde{\nu}^2}$$

In other words, this effect shows the coupling of the rotational and vibrational degrees of freedom which was neglected within the Born-Oppenheimer framework.

Vibrational Motion

Consider a diatomic molecule, say AB with the ionic potential, $V_{ion}(r)$



eg: Lennard-Jones pot.

$$V_{LJ}(r) = \varepsilon\left[\left(\frac{R_e}{r}\right)^{12} - 2\left(\frac{R_e}{r}\right)^{6}\right]$$

If we expand $V_{ion}(r)$ around R_e, the equilibrium molecular separation

$$V_{ion}(r) = V_{ion}(R_e) + \left.\frac{dV_{ion}}{dr}\right|_{R_e}(r-R_e) + \frac{1}{2}\left.\frac{d^2V_{ion}}{dr^2}\right|_{R_e}(r-R_e)^2 + \dots$$

$\left.\frac{dV_{ion}}{dr}\right|_{R_e} = 0$ (equilibrium, no force)

higher-orders (anharmonicity)

So, up to 2nd order we can approximate $V_{ion}(x)$; $x \equiv r - R_e$ as

$$V_{ion}(x) \simeq \frac{1}{2}\left.\frac{d^2V_{ion}}{dx^2}\right|_e \cdot x^2$$

$\left.\frac{d^2V_{ion}}{dx^2}\right|_e$: curvature of $V_{ion}(r)$

$\rightarrow$ k: force constant

large k $\rightarrow$ stiff bond

small k $\rightarrow$ weak bond



The Schrödinger eqn. for relative motion of A-B with a quadratic potential energy is

$$-\frac{\hbar^2}{2m_{eff}}\frac{d^2\psi_v}{dx^2} + \frac{1}{2}kx^2\psi_v = E_v\psi_v \quad \dots \text{SHO}$$

$$m_{eff} \equiv \frac{m_A m_B}{m_A + m_B}$$

The solution for SHO is the well-known Hermite poly × Gaussian wfs, with the vibrational energy levels:

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega ;$$

v = # vibrational quanta

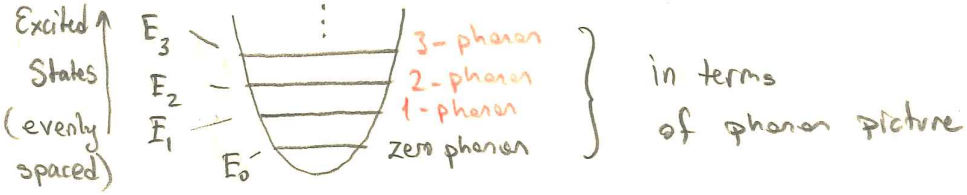
$v = 0, 1, 2, \ldots$

even for $v=0$, $E_0 = \frac{\hbar\omega}{2} \neq 0$

Due to zero-point energy uncertainty principle

where $\omega \equiv \sqrt{\frac{k}{m_{eff}}}$.

No frozen limit in QM



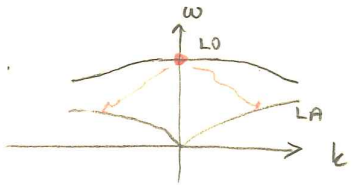
in terms of phonon picture

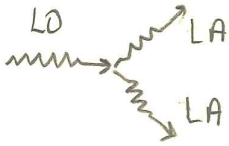
OR in terms of wavenumbers, we have vibrational terms, $G(v)$

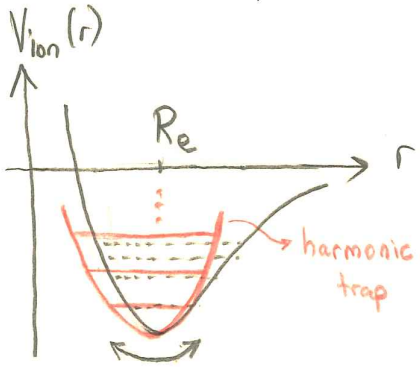
$$G(v) = \left(v + \frac{1}{2}\right)\tilde{\nu}, \quad \text{where} \quad \tilde{\nu} \equiv \frac{1}{2\pi c}\sqrt{\frac{k}{m_{eff}}}$$

Anharmonicity

The deviation of the interatomic potential from a parabola gives rise to important physical effects like 2^{nd}-order NLO, thermal expansion, finite phonon lifetime etc.







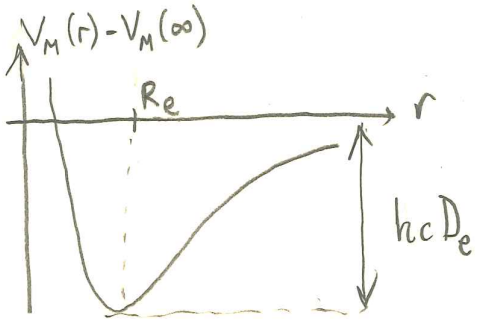
For large amplitude vibrations around R_e, the motion becomes anharmonic in the sense that the restoring force is no longer proportional to displacement $F \neq -kx$.

Because the actual curve is less confining than a parabola, we can anticipate that the energy levels become closely-spaced at high excitations.

Morse Potential

An analytical interatomic potential that resembles the true potential having a closed-form solution is the Morse potential.

$$V_M(r) = hc\, D_e \left[1 - e^{-a(r-R_o)}\right]^2 \quad , \quad a = \sqrt{\frac{m_{eff}\,\omega^2}{2hcD_e}}$$



with the energies (as in SHO)

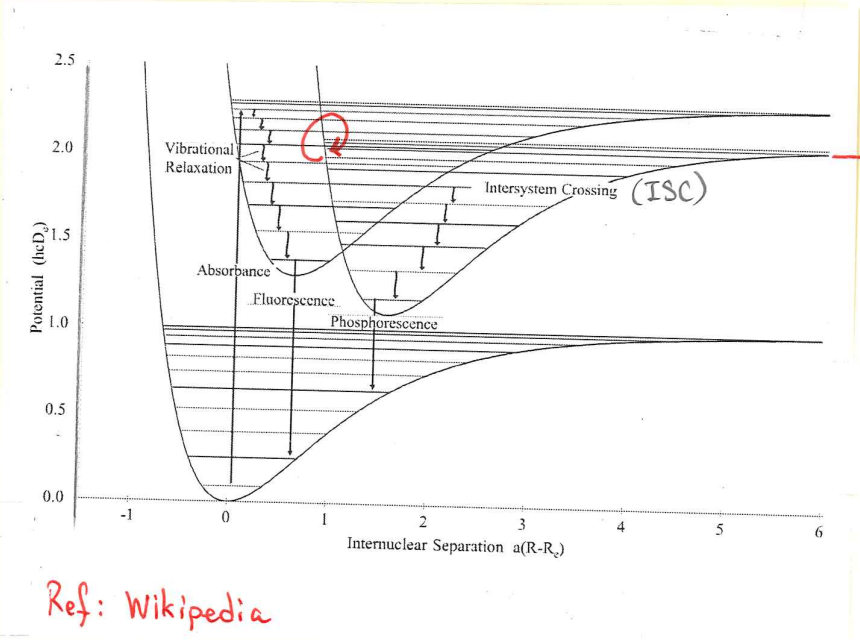
$$G(v) = \left(v+\tfrac{1}{2}\right)\tilde{\nu} - \left(v+\tfrac{1}{2}\right)^2 \chi_e \tilde{\nu}$$

(anharmonicity)

where $\chi_e \equiv \dfrac{\tilde{\nu}}{4D_e}$

This overall slow process $S_1 \rightarrow T_1 \rightarrow S_0$ happens typically in a few ms duration and known as phosphorescence { Fluorescent lamps are actually phosphorescent!

A more realistic illustration would be to include the actual vibrational levels for the singlet and triplet electronic levels.



Ref: Wikipedia

→ When the vibrational levels of S_1 and T_1 coincide ISC can take place with the relaxation continuing through the T_1 levels which goes to lower energies as $E_{T_1} < E_{S_1}$ (usually)

Configuration Diagram – Diatomic Molecule

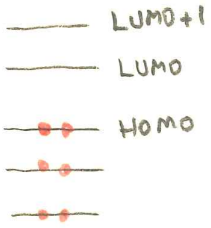
Let's investigate the details of the configuration diagram a bit more closely. For this purpose we shall leave out the ISC process.

In a diatomic molecule there is only one vibrational mode (stretching), the vibrational configuration of the molecule can be given a direct physical interpretation as the intermolecular separation.

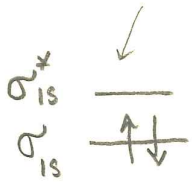
Nomenclature for Molecular Electronic Structure: Photochemistry

HOMO: Highest occupied molecular orbital

LUMO: Lowest unoccupied " "



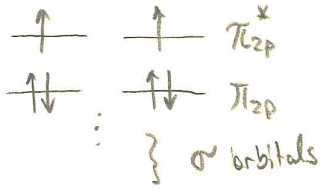
The ground states of most organic molecules are spin singlet ($S=0$ hence diamagnetic) Eg: H_2, He_2, CO



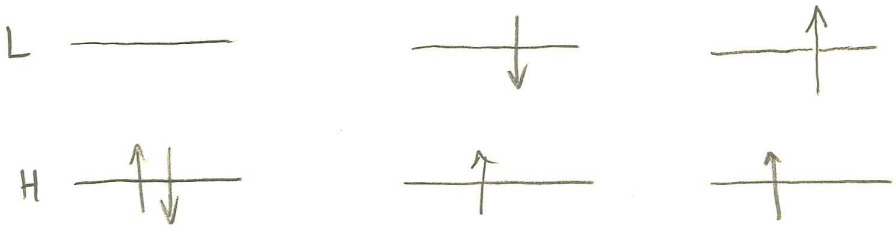
Not very common as the ground state, since they are free radicals ⇒ prone to further reactions...

NB: There are few cases of ground-state paramagnetic molecules with $S>0$, like NO, B_2, O_2

NO: $S=1/2$; B_2, O_2: $S=1$



The excited states of $S=0$ molecules can have $S=0$ or $S=1$



Ground state: usually singlet ($S=0$) S_0

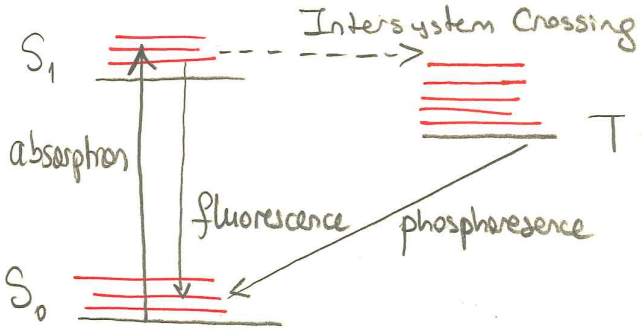
1st excited: singlet S_1

1st excited: triplet T_1

CAVEAT: Do not mix this notation with LS term symbols. This is mainly chemists notation: $S_0, S_1, S_2, \ldots$, $T_1, T_2, \ldots$ for singlet-triplet states.

NB: Recall from our exchange energy discussions that the triplet excited state T_1 tends to have lower energy compared to S_1.

Since the electric dipole (E1) transitions have $\Delta S = 0$ selection rule, the most common optical absorption – emission cycles are:



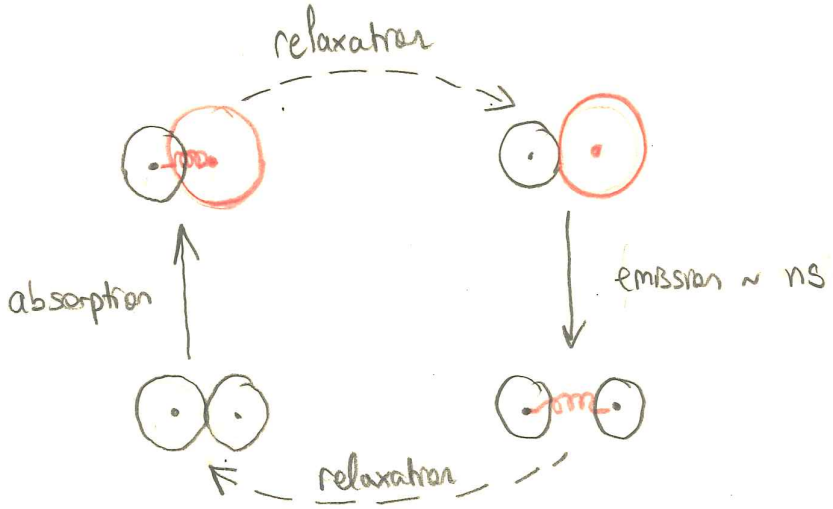
$S=0$ $S=1$

* The $S_1 \rightarrow S_0$ radiative transition is called fluorescence which is dipole-allowed, hence quite fast $\sim 10^{-10} - 10^{-9}$ s { more on this with Franck-Condon discussion ...

* The other path, intersystem crossing (ISC) is a radiationless process involving a transition bet. two states with different electronic spin multiplicity, say $S_1 \rightarrow T_1$. This happens in the presence of spin-orbit interaction which allows for spin flips, but this is usually a weak process, so that time scale of ISC $\sim 10^{-8} - 10^{-3}$ s. The radiative decay from $T_1 \rightarrow S_0$ is also possible due to spin-orbit interaction.

Franck-Condon Principle

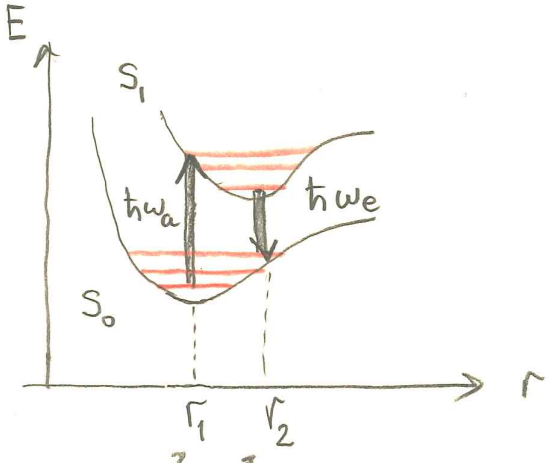
The FC model of electronic-vibrational coupling in the photon absorption and fluorescence cycle can be illustrated as follows:



FC principle relies on the following assumptions:

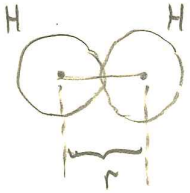
- The radiative transitions are vertical in configuration diagram (i.e., at the same nuclear coordinate): The electronic excitation cannot be followed instantly by the heavy nuclei
- Lattice vibrations are well des'd by quantum harmon osc. → i.e., parabolic confinement (hence equally-spaced level) assumption
- The initial excitation is from the lowest ($n_i = 0$) lattice vibrational state (a "low"-temperature assumption)
- Interaction bet. molecule and the lattice is the same in both the ground- & excited-states (i.e., both equally-shaped parabolas)

Based on Born-Oppenheimer approximation we can plot the energy level diagram for the ground and first excited state as a function of mean interatomic separation, r.

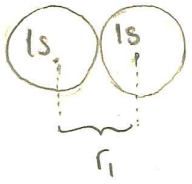


Why do minima occur at different r (ground state vs. excited st.)?

To explain this point consider the H_2 molecule

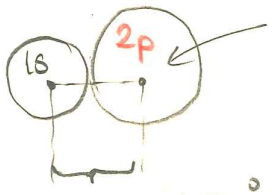


→ Ground-state equilibrium separation of the nuclei



$r_1 = 0.74\ \text{Å}$

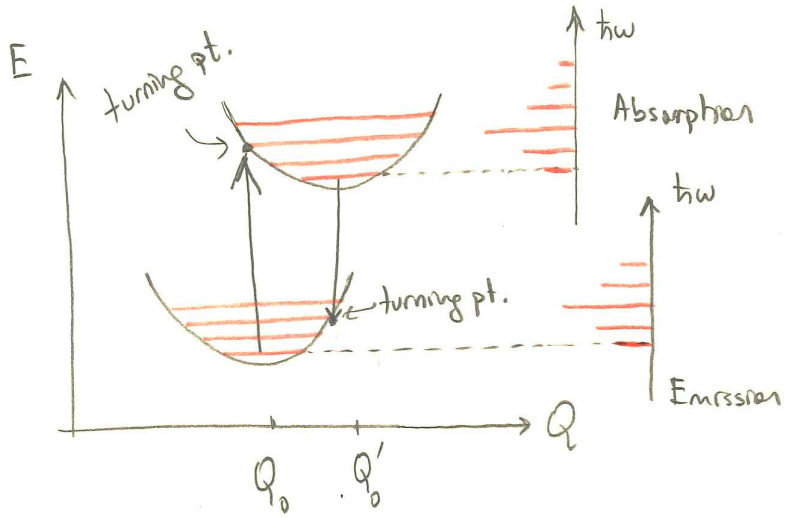
→ Excited-state



one $\bar{e}$ in excited 2p state (larger atomic radius)

$r_2 = 1.3\ \text{Å}$

So, on atomic radii considerations we can explain the interatomic dilation from $r_1 \rightarrow r_2$



According to FC principle the most probable transitions are from $n=0$ to turning pt. of the other electron-vibrational "parabola". This can be demonstrated by considering the matrix element for E1 transition in either emission or absorption.

The dipole operator for electron-ionic composite (molecular) system is

$$\vec{d} = -e\sum_i \vec{r}_i + e\sum_I Z_I \vec{R}_I$$

$$M_{12} = \langle 2_e, 2_v | \vec{d}\cdot\hat{\varepsilon} F | 1_e, 1_v \rangle \quad \text{or} \quad |1_e\rangle \otimes |1_v\rangle$$

$$= -eF\langle 2_e | \sum_i \vec{r}_i\cdot\hat{\varepsilon} | 1_e\rangle \langle 2_v | 1_v\rangle + eF\langle 2_e | 1_e\rangle \langle 2_v | \sum Z_I \vec{R}_I\cdot\hat{\varepsilon} | 1_v\rangle$$

$\langle 2_e | 1_e\rangle = 0$ orthogonal

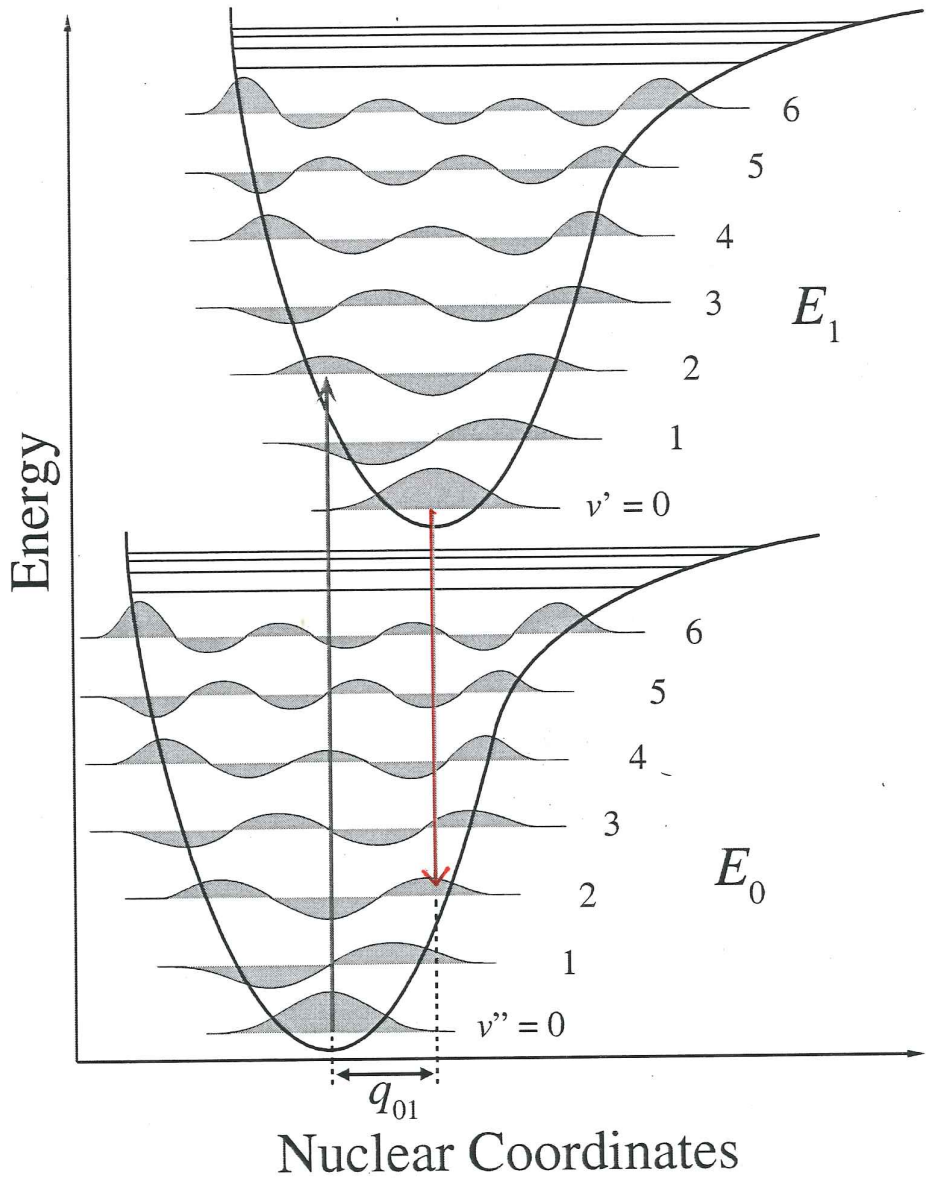
d_{12}^{ε} ↓ electron dipole matrix el.

$\langle 2_v | 1_v\rangle$ Vibrational wf overlap: I_{n_1,n_2}

The E1 transition rate is det'd by the Franck-Condon factor

$$I_{n_1,n_2} = \left| \langle 2_v | 1_v \rangle \right|^2 = \left| \int_0^\infty \varphi^*_{n_2}(Q - Q_0') \, \varphi_{n_1}(Q - Q_0) \, dQ \right|^2$$

displaced HO wf's

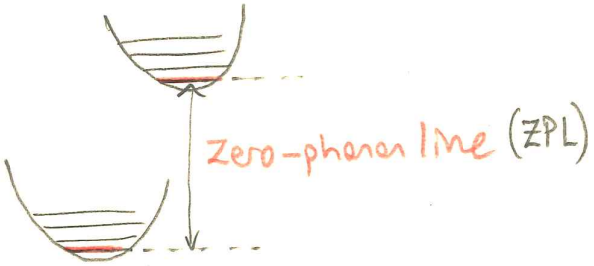


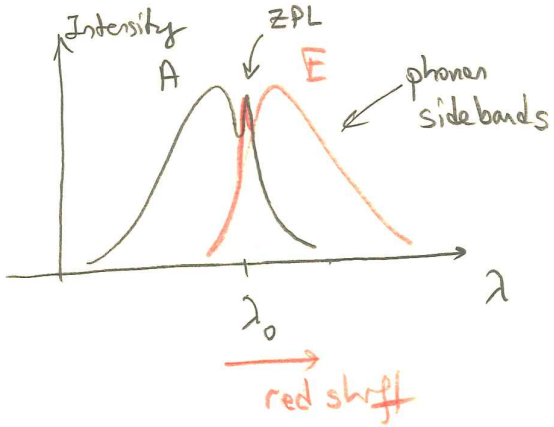
Ref: Wikipedia

There is an approximate rule of thumb: Franck-Condon factor will be largest for levels with the edge of their classical potential well close to Q_0.

↖ turning point

In this simple model, the emission spectrum becomes the 'mirror' of the absorption. The energy that goes to vibrational excitations bet. absorption and emission paths gives rise to an overall Stokes shift (i.e., red shift) of the emitted signal





The transition that involves no vibrational quanta in both absorption and emission is called the zero-phonon line which is nevertheless broadened due to radiative lifetime of the states involved. The other transitions involving a number of vibrational quanta are termed as phonon sidebands. The most probable # of phonons involved as determined by the FC principle is a measure of the electron-phonon coupling in this system. The number of vibrational quanta emitted is also called the Huang-Rhys factor named after inventors of this theoretical framework.

NV Centers

Absorption and Fluorescence Spectra: Phonon Sideband

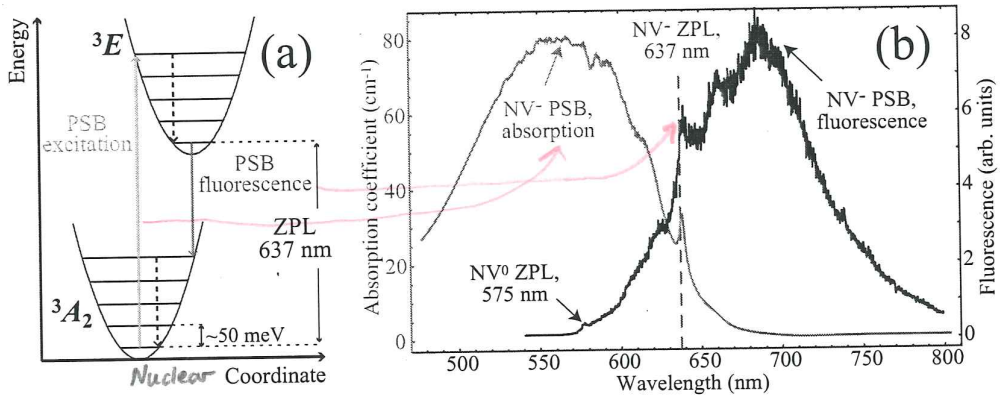


Figure 1.4: (a) Schematic illustrating the Franck-Condon principle for excitation and fluorescence of the main optical transition, $^3A_2 \leftrightarrow {}^3E$. Non-radiative decay is shown with dashed lines. (b) Room-temperature optical absorption and fluorescence (excited at 532 nm) spectra for an HPHT diamond with $[NV^-] \approx 15$ ppm. Besides the spectral features attributed to the NV^- center discussed in the text, the weak line at 575 nm is present from the NV^0 ZPL. PSB–Phonon sideband, ZPL–zero-phonon line.

Ref. Acosta PhD Thesis

We need to remember that there are also vibrational levels, as illustrated above. In thermal eql. at RT, about 90% of NV centers will be in the lowest vibrational level, corresponding to an effective vibrational spacing of ~ 50 meV. According to the Franck-Condon principle, the most probable vertical transitions are to the turning point in the ^3E harmonic well, which corresponds to about 4 vibrational quanta (~ 0.2 eV) ↔ such a large shift occurs because e^2 and a_1e configurations have significantly different nuclear coordinates ⇒ broad peaks in the absorption & fluorescence spectra known as phonon sideband (PSB).

The sharp resonant transition $^3A_2 \longrightarrow {}^3E$ at 637 nm between ground vibrational levels in both states is called zero-phonon line (ZPL).

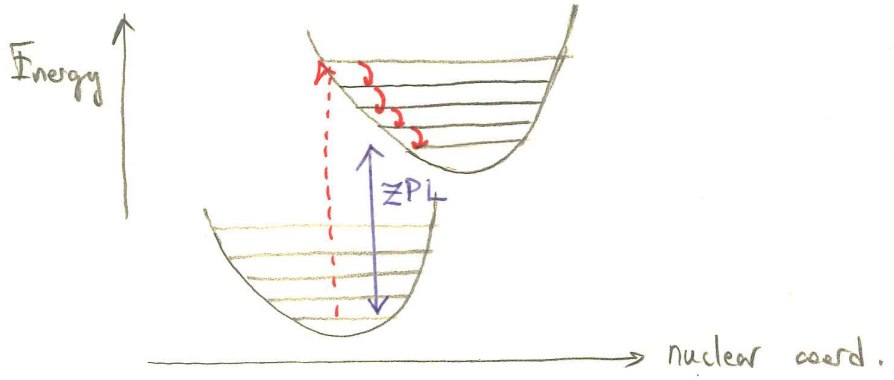
Based on the absorption spectrum, it is possible to estimate the electron-phonon coupling parameter, also known as the Huang-Rhys factor

$$S = -\ln \frac{I_{ZPL}}{I_{tot}}$$

integrated absorption intensities (after normalization to light freq.)

When applied to data on the previous page, it yields $S = 3.9$

The Huang-Rhys parameter basically corresponds to mean # vibrational quanta involved in the absorption (or emission) process

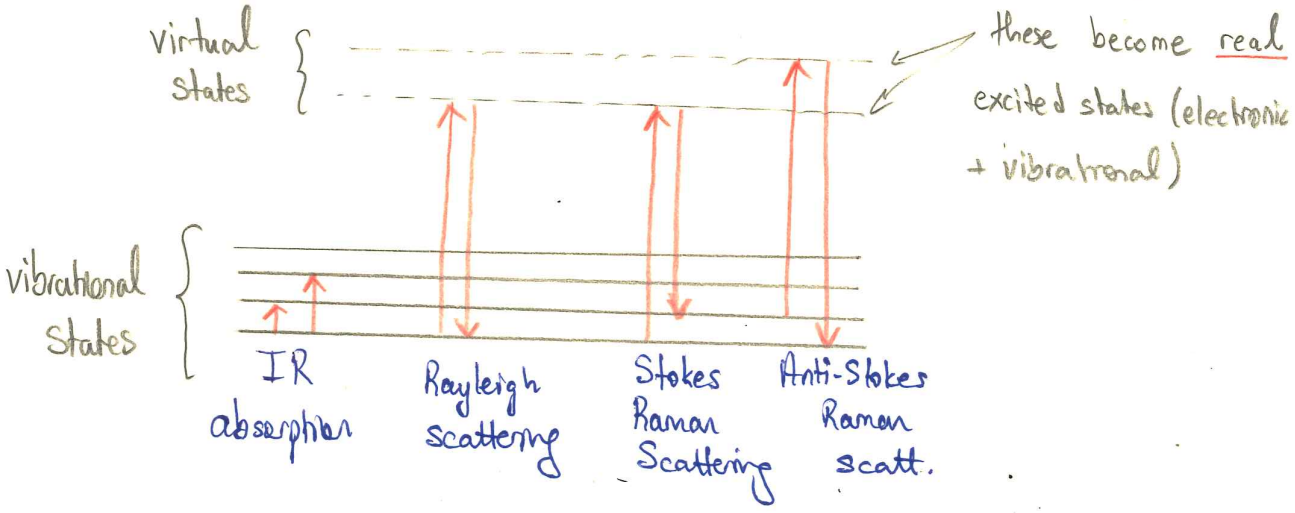


IR - Raman Spectroscopies

These techniques are widely used to probe the **local chemical environment** within a sample. The energy scale involved usually matches with the vibrational (and sometimes with the rotational) modes. The physics of IR vs. Raman spectra are markedly different!

IR → one-photon process

Raman → two-photon process



in resonance Raman, these become real excited states (electronic + vibrational)

IR spectrum is divided into three bands:

Near-IR: 4000 - 14000 cm^{-1} (2.5 - 0.8 μm) → Energetic to excite overtones (multiple phonos)

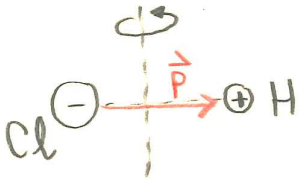
Mid-IR: 400 - 4000 cm^{-1} (25 - 2.5 μm) → For fundamental rotational-vibrational str.

Far-IR: 10 - 400 cm^{-1} (1000 μm - 25 μm) → Adjacent to μwave used for rotational spectroscopy

IR Absorption Spectra

Rotational Spectra

For the pure rotational mode of a molecule to be probed by IR spectroscopy, it must be polar (i.e., have a permenant electric dipole moment). The reason is that a polar molecule appears to possess an oscillating dipole when rotating, but a nonpolar does not!



... Hydrogen cloride

For polar molecules, the specific rotational selection rules are just the same for E1 dipole transitions, i.e.,

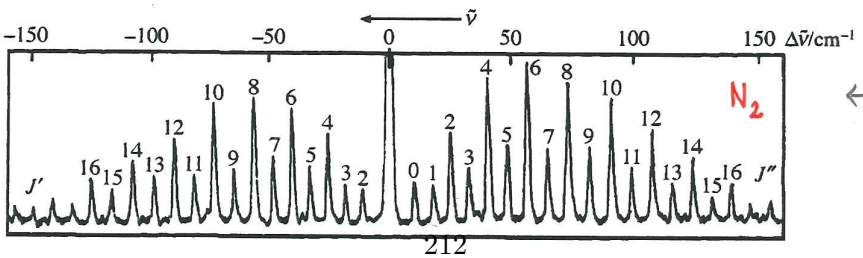
For IR activity:

$$\Delta K = \pm 1$$ ← photon abs. / photon em.

$$\Delta M_K = 0, \pm 1$$ ← Cons. angular momentum (along quantization axis)

$+\sigma$, $-\sigma$, π polarization selections

NB: The rotational spectra of non-polar molecules can be measured by Raman spectroscopy.



Eg. Nitrogen molecule

Ref: Kroto, Molecular Rotation Spectra

Vibrational Spectra

Similarly, the underlying selection rule for EM (IR) coupling to vibrational dynamics is that the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. Such vibrations are said to be infrared active.

Homonuclear diatomic molecules are IR inactive because their dipole moments remain zero as they vibrate (eg. H_2)

For IR active molecules, the specific vibrational selection rules follow from dipole matrix elements bet. the harmonic oscillator states:

$$\langle f|x|i\rangle = \text{const.} \underbrace{\int_{-\infty}^{+\infty} H_f \; x \, H_i \; e^{-y^2} \, dx}_{\int_{-\infty}^{+\infty} H_f \; y \, H_i \; e^{-y^2} \, dy} ; \quad x = \alpha y , \quad \alpha = \left(\frac{\hbar^2}{m_{eff} k}\right)^{1/4}$$

(Hermite polyn.)

Using recursion relation: $y H_n = n H_{n-1} + \frac{1}{2} H_{n+1}$

$$i \underbrace{\int_{-\infty}^{+\infty} H_f \, H_{i-1} \, e^{-y^2} \, dy}_{\delta_{f,i-1}} + \frac{1}{2} \underbrace{\int_{-\infty}^{+\infty} H_f \, H_{i+1} \, e^{-y^2} \, dy}_{\delta_{f,i+1}}$$

Hence, the selection rule is: $\Delta v = \pm 1$ (+1: photon abs.; −1: photon emission)

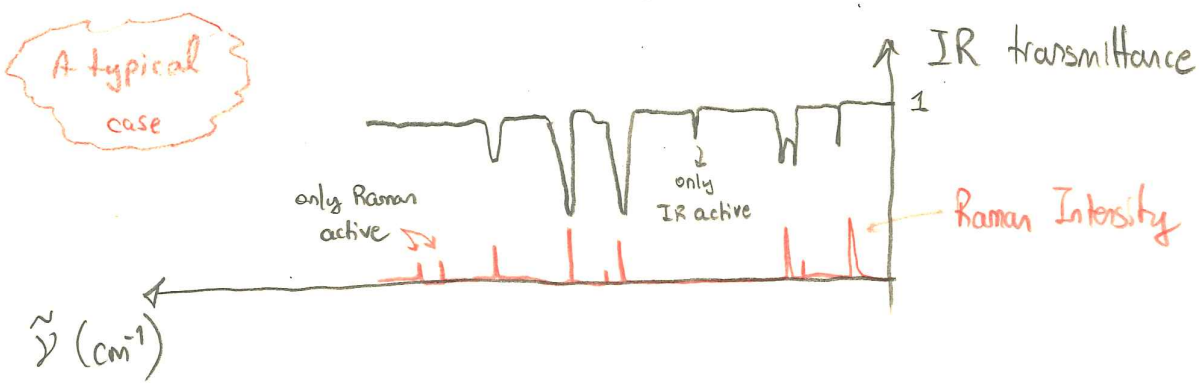
Population of the vibrational levels

At room temperature, $k_B T / hc \approx 200\ cm^{-1}$, and most vibrational wavenumbers are significantly greater than $200\ cm^{-1}$! Hence according to Boltzmann distribution, $e^{-E_v / k_B T}$

almost all molecules will be in their vibrational ground states (initially). Hence, the dominant transition will be the fundamental transition $v_i = 0 \rightarrow v_f = 1$. As a result, the vibrational spectrum is expected to consist of a single absorption line.

A somewhat complementary technique is the Raman spectroscopy. A certain vibrational mode can be more readily captured by IR, Raman or neither.

next section...



For instance, molecules with a center of symmetry, IR inactive transitions are Raman active and vice versa. An example is CO_2 molecule

$\underset{\text{Raman active (IR inactive)}}{\underbrace{O \overset{\leftarrow}{=} C \overset{\rightarrow}{=} O}}$ $\qquad$ $\underset{\text{IR active (Raman inactive)}}{\underbrace{O \overset{\leftarrow}{=} C \overset{\leftarrow}{=} O}}$

next section...

Raman Spectra *

1 Introduction

When a monochromatic electromagnetic wave is incident on a surface, we get the well-known reflected, and refracted beams as governed by Snell's law. Even though this picture is quantitatively quite accurate, qualitatively it misses some important phenomena. Real materials also contain static and dynamic scatterers. The former cause an elastic scattering (i.e., at the same wavelength as the incoming wave) in all directions, which is about 1/10,000 of the incident intensity, and is known as *Rayleigh scattering*. Moreover, about 1/1000 of the scattered wave gets inelastically scattered (i.e., at a shifted wavelength with respect to incident wave) that arises from dynamic processes which is known as the *Raman scattering*. This Raman signal, though usually a tiny fraction ($\sim 1/10^7$) of the incident intensity, plays a vital role in identifying the atomic constituents of the sample through their vibrational and rotational fingerprints.

Hence, both Raman and IR spectroscopy are tools primarily for vibrational properties of molecules, surfaces and solids (crystalline or amorphous). They usually act as complementary techniques, as some vibrational modes are only IR-active, and some are only Raman-active. There are also cases where a particular mode can be active or silent for either one. Among the other differences between the two techniques, Raman has a simpler spectrum than IR as often only the fundamental (lowest-order) processes are visible. Furthermore, in the Raman a monochromatic (usually a laser) source is used, whereas IR utilizes broadband sources.

2 A classical consideration for the Raman process

First, we shall see that some essential features of the Raman scattering can be captured by a basic classical treatment [1, 2, 3].

2.1 An isolated molecule

We start with a single molecule that may in general have a *permanent* dipole moment $\vec{d}$, and an *induced* dipole moment through a polarizability tensor α_{ij}, where i, j are the Cartesian indices, so that under an incident monochromatic electromagnetic field $\vec{E} = \vec{E}_0 \cos(\omega t)$, the resultant dipole moment becomes

$$p_i = d_i + \alpha_{ij} E_j \,,$$

with the convention that repeated Cartesian indices are implicitly summed over. Note that both $\vec{d}$ and $\overleftrightarrow{\alpha}$ are functions of the coordinates of the nuclei and electrons. We shall assume that electronic cloud can instantly respond to any change in the nuclear vibrations. Therefore, essentially these quantities are controlled by the nuclear displacements, for which we shall use their so-called normal coordinates as denoted by $\vec{Q}_k$, where k labels any one of the vibrational degrees of freedom. Note that for an N-atom molecule, these are in total $3N - 6$. If we further assume that the incident light is off-resonant with both electronic and vibrational transitions,

*This is based on a section I prepared as an infinitesimal contribution to Prof. Mehmet Erbudak's lectures on Physics and Chemistry at Surfaces.

then such small-amplitude oscillations for the nuclear normal modes can be governed by the first two terms of the Taylor expansion around equilibrium coordinates $\vec{Q}_k = 0$ yielding

$$d_i \simeq d_i(0) + \sum_{k=1}^{3N-6} \left.\frac{\partial d_i}{\partial Q_{kj}}\right|_0 Q_{kj}\,, \tag{1}$$

$$\alpha_{ij} \simeq \alpha_{ij}(0) + \sum_{k=1}^{3N-6} \left.\frac{\partial \alpha_{ij}}{\partial \vec{Q}_k}\right|_0 \vec{Q}_k\,. \tag{2}$$

Each normal mode of vibration k will be oscillating at its eigenfrequency ω_k, therefore we can write $\vec{Q}_k(t) = \vec{Q}_{k0}\cos(\omega_k t)$. With this form the dipole moment of the molecule becomes

$$\begin{aligned} p_i = d_i(0) + \sum_{k=1}^{3N-6} \underbrace{\left.\frac{\partial d_i}{\partial Q_{kj}}\right|_0 Q_{k0j}\cos(\omega_k t)}_{\text{IR spectrum}} + \underbrace{\alpha_{ij}(0)E_{0j}\cos(\omega t)}_{\text{Rayleigh scat.}} \\ + \frac{1}{2}E_{0j}\sum_{k=1}^{3N-6} \left.\frac{\partial \alpha_{ij}}{\partial \vec{Q}_k}\right|_0 \vec{Q}_{k0}\left\{\underbrace{\cos[(\omega+\omega_k)t]}_{\text{anti-Stokes}} + \underbrace{\cos[(\omega-\omega_k)t]}_{\text{Stokes}}\right\}. \end{aligned} \tag{3}$$

According to this expression, there is a component at the same frequency as the incident field, called the Rayleigh scattering; additionally we have a red- and blue-shifted frequency parts which constitute the Raman scattering, where the former (latter) is called the Stokes[1] (anti-Stokes) scattered light. This derivation suggests us that Raman scattering can be seen as a frequency mixing process just like the *amplitude modulation* concept used in electronic communication: incident field, acting as the carrier signal is modulated by the nuclear vibrations, here playing the role of the information signal. Fig. 1 illustrates the basic spectrum and the transitions corresponding to Stokes and anti-Stokes lines.

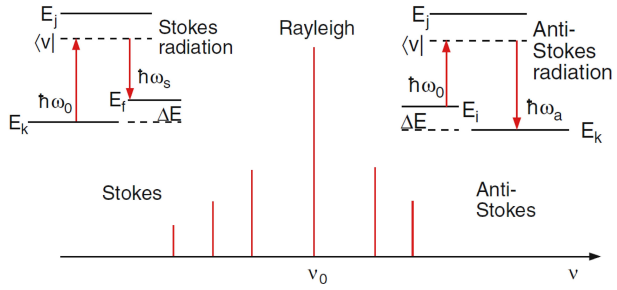


Figure 1: The spectrum showing Rayleigh and Raman signals, together with the associated transition schemes. Ref. [1].

2.2 Selection rules

As a result of the symmetries of the medium and of the vibrational modes involved in the scattering, some requirements are imposed. These are generally termed as *selection rules*, which determine whether a specific perturbation $\mathcal{V}$ yields a non-zero transition from an initial state

[1]This terminology historically originates from a somewhat similar observation by Stokes on fluorescence where the frequency of the fluorescent radiation is always less than that of the incident [3].

$|v\rangle$ to a final state $|v'\rangle$ as quantified by the matrix element $\langle v'|\mathcal{V}|v\rangle$. The study of such selection rules falls in the realm of so-called Group theory, from which we shall state a few useful remarks without any derivation [4]. For the IR and Raman spectroscopy, if we refer to Eq. (3), the operators that govern these transitions are the dipole moment d_i and polarizability α_{ij} operators, respectively. The former has components which transform as x, y and z, whereas the latter transforms as the binary products of x^2, y^2, z^2, xy, xz, yz, or equally their linear combinations such as $x^2 - y^2$. According to Group theory, if the direct product $\Gamma[v] \times \Gamma[d] \times \Gamma[v]$ contains the totally symmetric irreducible representation of the point group, the transition $v \to v'$ is IR active. Likewise, if the direct product $\Gamma[v] \times \Gamma[\alpha] \times \Gamma[v]$ contains the totally symmetric irreducible representation of the point group, the transition $v \to v'$ becomes Raman active.

2.3 An example: CO_2 molecule

In some cases, IR and Raman activity of certain vibrational modes can be extracted simply by observation, without the use of rigorous Group theory machinery. One such example is a linear symmetric molecule ABA, such as the CO_2 molecule. It has four modes of vibration: a symmetric stretching mode Q_1, an antisymmetric stretching mode Q_2, and two bending modes Q_{3a} and Q_{3b} which form a degenerate pair and have the same frequency of vibration. Three of these vibrations are shown in Fig. 2. We observe that symmetric stretching mode (on the left panel) has non-zero polarizability derivative at the equilibrium position ($\partial\alpha/\partial Q \neq 0$) therefore this vibration will give rise to an induced polarizability contribution under an incident field, hence it is Raman-active. However, as the A-B and B-A dipoles are of equal strength but pointing in opposite directions, this mode of vibration produces no net dipole moment derivative at the center ($\partial d/\partial Q \neq 0$), therefore it will be IR-silent. The situation is just the opposite for the center and right panels, as they are both IR-active but Raman-inactive.

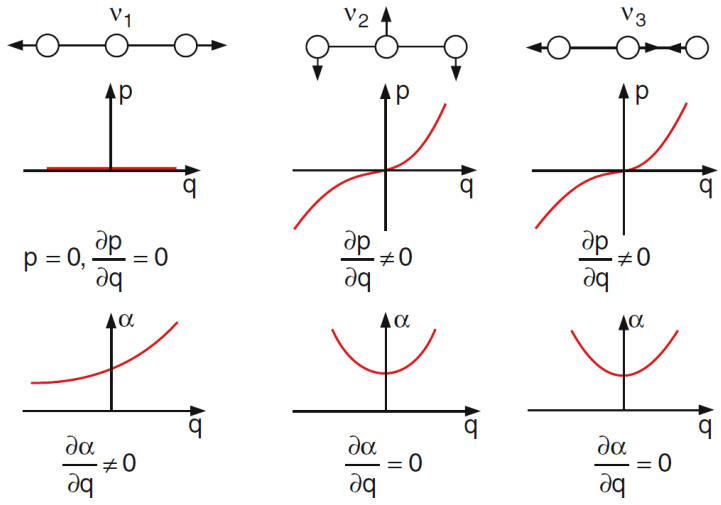


Figure 2: Polarizability and dipole moment variations in the neighbourhood of the equilibrium position for a linear ABA molecule. Ref. [1].

2.4 Extended systems

Next, we move from a *single* N-atom molecule to an *extended* system (such as a solid) having n molecules per unit volume. The relation between the molecular quantities $\vec{d}$, α_{ij}, and

those of the extended system, the permanent χ_i and induced χ_{ij} electric susceptibilities are $\chi_i = nd_i/\epsilon_0$, and $\chi_{ij} = n\alpha_{ij}\epsilon_0$, where ϵ_0 is the free-space permittivity. Similarly the polarization field of the medium is related to molecular dipole moment via $\vec{P} = n\vec{p}$. Hence, for an incoming electromagnetic wave, this time including its wave vector dependence $\vec{k}$ as well, $\vec{E}(\vec{r},t) = \vec{E}_0\cos(\vec{k}\cdot\vec{r} - \omega t)$, and expanding into Taylor series under nuclear vibrations with a form $\vec{Q}_k(\vec{r},t) = \vec{Q}_{k0}(\vec{q},\omega_k)\cos(\vec{q}\cdot\vec{r} - \omega_k t)$ yields the following terms, where we only show the Raman contributions

$$P_i = \frac{1}{2}E_{0j}\left.\frac{\partial\chi_{ij}}{\partial\vec{Q}_k}\right|_0 \vec{Q}_{k0}(\vec{q},\omega_k)\left\{\underbrace{\cos[(\vec{k}+\vec{q})\cdot\vec{r} - (\omega+\omega_k)t]}_{\text{anti-Stokes}} + \underbrace{\cos[(\vec{k}-\vec{q})\cdot\vec{r} - (\omega-\omega_k)t]}_{\text{Stokes}}\right\}. \quad (4)$$

For an isolated molecule the Raman scattering occurs in all directions with no angular preference. However, in an extended system we see that the Stokes shifted wave has $\vec{k}_S = \vec{k} - \vec{q}$ while the anti-Stokes is $\vec{k}_{AS} = \vec{k} + \vec{q}$. This means that in this case, the observation direction for the scattered wave inherently selects the participating phonon mode through the above momentum conservation relations. Furthermore, note that for the visible light which is commonly used in Raman spectroscopy, its spectroscopic wavenumber is of the order of 10^5 cm^{-1} which makes up only a tiny proportion with respect to the extend of a typical Brillouin zone $\sim 10^7$ cm^{-1}. Therefore, in the case of crystals, because of the above momentum conservation requirement only the zone center phonons $q \to 0$ participate in a Raman process.

As the nuclear vibrations attain larger amplitudes one may have to retain higher order terms in the Taylor series expansion. These bring cross terms which will give rise to Raman shifts as $\pm\omega_n \pm \omega_m$ for the second-order. When these modes are identical, the resultant two-phonon peak is called an *overtone*.

2.5 Raman tensor

The intensity for the Raman scattered wave polarized along the unit vector direction $\hat{e}_s$ in response to an incident polarization along $\hat{e}_i$ is proportional to

$$I_S \propto \left|\hat{e}_s \cdot \left.\frac{\partial\chi_{ij}}{\partial\vec{Q}_k}\right|_0 \vec{Q}_{k0}(q=0,\omega_k)\cdot\hat{e}_i\right|^2. \quad (5)$$

Therefore the scattering is governed by a third-rank tensor $\partial\chi_{ij}/\partial\vec{Q}_k$, where i,j run over Cartesian directions and k labels any of the optical phonon modes at the zone center. By introducing a unit vector along every available normal mode phonon displacements $\hat{Q} = \vec{Q}/|\vec{Q}|$, we can essentially introduce a second-rank (with the same components as χ_{ij}) for each specific phonon polarization, called the *Raman tensor* as[2] $\overleftrightarrow{\mathcal{R}} = (\partial\chi/\partial\vec{Q})_0\hat{Q}(\omega_k)$, so that I_S becomes

$$I_S(\omega_S) \propto \frac{\omega_S^4}{c^4}\left|\hat{e}_s\cdot\overleftrightarrow{\mathcal{R}}\cdot\hat{e}_i\right|^2.$$

Note that, we explicitly show the $k^4 = \omega^4/c^4$ wavelength dependence which is ubiquitous in any form of sub-wavelength scattering like the Rayleigh scattering as popularized by the explanation of the blueness of the sky. If we neglect the small frequency difference between the incident and scattered waves, the Raman tensor can be accepted as symmetric with respect to its Cartesian indices, just like the electric susceptibility χ_{ij}.

[2]Here, we supress the phonon polarization subscript on the Raman tensor.

3 Quantum mechanical features of the Raman process

Next, we discuss features which necessitate a quantum mechanical treatment [2]. First, we notice from Eq. (5) that the scattered intensity is proportional to the vibration amplitude $\vec{Q}$ squared. Hence, according to the classical treatment there would be no Stokes scattering if no atomic vibration is present. However, once we quantize the vibrational modes into *phonons*, in Stokes scattering where a phonon is excited in the medium by the incident radiation, the intensity becomes proportional to N_q+1, while the anti-Stokes will be proportional to N_q. Here, N_q is the phonon occupancy, which is given in the case of equilibrium by the Bose-Einstein distribution. For low temperatures $N_q \ll 1$, therefore the '+1' contribution in Stokes scattering intensity dominates. As one can recall, it arises from zero-point oscillations, a hallmark of quantum mechanics, and gives rise to spontaneous phonon emission even at zero temperature having $N_q \to 0$.

Based on these facts, we can write the intensity ratio, anti-Stokes over the Stokes as

$$\left(\frac{\omega+\omega_k}{\omega-\omega_k}\right)^4 \frac{N_q}{N_q+1},$$

where the first term is again from the k^4 dependence for each frequency, while the second term contains the temperature dependence which simplifies to $e^{-\hbar\omega_q/k_BT}$. A fringe benefit of this is that *the intensity ratio of the two lines can be used to extract the lattice temperature.* In the light of this discussion, Stokes lines will be more intense as they originate from the $v=0$ zero-phonon level, whereas anti-Stokes lines originate from the $v=1$ one-phonon level with much less population.

Another important feature is that the Raman lines have non-zero *widths* which further increase with temperature. Primarily it is due to the fact that the optical phonons taking part in the Raman process themselves are not of infinite lifetime because of the inherent anharmonicity of lattice vibrations causing phonon-phonon interactions. Therefore, they decay into two longitudinal acoustic phonons with large and opposite momenta. This finite phonon lifetime broadens the Raman resonances into a Lorentzian or a Gaussian line shape. The thermal variation of the width of the Raman line is given by [5]

$$\Gamma(\omega_k,T) = \Gamma(\omega_k,0)\left(1+\frac{2}{e^{\hbar\omega_k/2k_BT}-1}\right). \tag{6}$$

A further important deficiency of the classical picture is that it does not reflect the microscopic mechanism of how Raman scattering actually takes place. As a matter of fact, the direct excitation of phonons via photons is extremely weak. Therefore, this scattering proceeds quite differently in at least three steps.

1. An incident photon with an energy $\hbar\omega_i$ interacts with the charges within the sample through $\mathcal{H}_{rad-X}$, exciting the medium into an intermediate state $|n\rangle$ by creating a so-called *exciton* which is the bound state of an electron and hole pair.

2. This exciton being composed of an electron and a hole interacts strongly with the environment (lattice) via the electron-phonon (or hole-phonon) interaction ($\mathcal{H}_{e-ion}$) and gets scattered into another state by emitting a phonon (considering the Stokes case) of energy $\hbar\omega_k$. This intermediate excitonic state will be denoted as $|n'\rangle$.

3. The exciton in state $|n'\rangle$ spontaneously recombines radiatively via $\mathcal{H}_{rad-X}$ with the emission of a so-called scattered photon of energy $\hbar\omega_S$.

So, this reveals that the electrons mediate the Raman scattering of phonons although they remain unchanged after the process. Since the transitions involving the electrons are virtual they do not have to conserve energy, although they still have to conserve (crystal) momentum. The corresponding Feynman diagram describing this process is shown in Fig. 3. Note that there are higher-order virtual processes other than the one above which also contribute Raman scattering. However, if we limit ourselves to only this lowest-order mechanism, then the Raman scattering rate can be calculated using Fermi's Golden Rule as

$$W_R(\omega_S) = \frac{2\pi}{\hbar}\left|\sum_{n,n'}\frac{\langle i|\mathcal{H}_{rad-X}(\omega_S)|n'\rangle\langle n'|\mathcal{H}_{e-ion}(\omega_k)|n\rangle\langle n|\mathcal{H}_{rad-X}(\omega_i)|i\rangle}{[\hbar\omega_i-(E_n-E_i)]\,[\hbar\omega_i-\hbar\omega_k-(E_{n'}-E_i)]}\right|^2 \times\delta(\hbar\omega_i-\hbar\omega_k-\hbar\omega_S)\,. \quad (7)$$

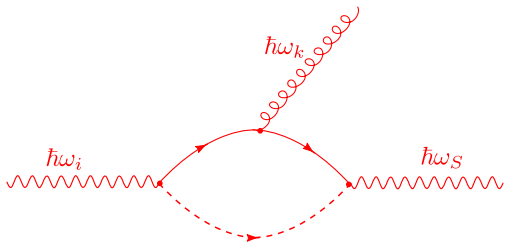


Figure 3: The Feynman diagram corresponding to the basic Raman process. The left and right wiggly lines represent incident and scattered photon propagators, solid and dashed lines correspond to electron and hole propagators, and the spiral line is that of the phonon.

4 Variants of the Raman process

The basic Raman process discussed above in practice comes with quite a few variations, with each one having a different utility and/or novelty. Some of these are very briefly mentioned below [3, 1, 2].

- **Brillouin Scattering** – Inelastic scattering of light by acoustic waves was first proposed by Brillouin. As a result, this kind of light scattering spectroscopy is known as Brillouin scattering. There is very little difference between Raman scattering and Brillouin scattering. In solids the main difference between them arises from the difference in dispersion between optical and acoustic phonons.

- **Hyper-Raman** – The intensity of Raman scattering is directly proportional to the irradiance of the incident radiation and so such scattering can be described as a linear process. When the intensity of the incident light wave becomes sufficiently large, the induced oscillation of the electron cloud surpasses the linear regime. This implies that the induced dipole moment p of the molecules are no longer proportional to the electric field E, but the E^2 and E^3 terms in the Taylor expansion of $p(E)$ need to be retained giving rise to hyper-polarizability and second-hyper-polarizabilities, respectively. Such nonlinear optical effects are named as hyper-Raman processes having quite different selection rules compared to linear one. The *overtones* of the main Raman signal as mentioned previously, are nothing but the manifestations of the hyper-Raman processes.

- **Electronic Raman** – If the frequency difference $\omega_i - \omega_k$ corresponds to an electronic transition of the system, we speak of electronic Raman scattering, which gives complementary information to electronic-absorption spectroscopy. This is because the initial and final states must have the same parity, and therefore a direct dipole-allowed electronic transition $|i\rangle \rightarrow |f\rangle$ is not possible.

- **Resonant Raman** – The enhancement of the Raman cross section near an electronic resonance is also known as resonant Raman scattering. Obviously, resonant Brillouin scattering is defined similarly. The enhancement in the Raman cross section at resonance is only two orders of magnitude relative to the nonresonant background. On the other hand, both free excitons and bound excitons have been shown to enhance the Raman cross section by several orders of magnitude because of their small damping constants (with a typical width of 3 meV) at low temperatures. Such strong resonance effects have made possible the observation of new phenomena, such as wavevector-dependent electron-LO phonon interaction, electric-dipole forbidden transitions, higher-order Raman scattering involving more than three phonons, and the determination of exciton dispersions.

- **Fourier-transform Raman** – The combination of Raman spectroscopy with Fourier-transform spectroscopy allows the simultaneous detection of larger spectral ranges in the Raman spectra.

- **Surface-Enhanced Raman Scattering** – Raman scattering cross-section is typically 14-15 orders of magnitude smaller over that of the fluorescence of efficient dye molecules. The intensity of Raman scattered light may be enhanced by several orders of magnitude if the molecules are adsorbed on a surface. A number of mechanisms contribute to this enhancement. Since the amplitude of the scattered radiation is proportional to the induced dipole moment, $p_i = \alpha_{ij} E_j$, the increase of the polarizability α by the interaction of the molecule with the surface is one of the causes for the enhancement. In the case of metal surfaces due to the presence of *plasmonic* effects, the electric field E at the surface may also be much larger than that of the incident radiation, which also leads to an increase of the induced dipole moment. Both effects depend on the orientation of the molecule relative to the surface normal, on its distance from the surface, and on the morphology, in particular the roughness of the surface. Small metal clusters on the surface increase the intensity of the molecular Raman lines. The frequency of the exciting light also has a large influence on the enhancement factor. In the case of metal surfaces it becomes maximum if it is close to the plasma frequency of the metal. Giant enhancement factors as high as 10^{14} have been reported on *single-molecule* studies [6]. Because of these dependencies, surface-enhanced Raman spectroscopy has been successfully applied for surface analysis and also for tracing small concentrations of adsorbed molecules.

- **Coherent anti-Stokes Raman Scattering** – Ordinary Raman scattering is an incoherent spontaneous process and as a result the intensity of scattering from a material system of N non-interacting molecules is simply N times that from one molecule. There are also non-spontaneous Raman processes, the three important ones are the stimulated Stokes Raman scattering, stimulated anti-Stokes Raman scattering and coherent anti-Stokes Raman scattering (CARS). The most popular is the last one where two incident laser beams are used with an energy difference deliberately chosen to match a Raman-active vibrational mode of the sample. This produces highly directional beams of scattered radiation with small divergences. In particular, the intensity of the anti-Stokes signal is by far larger than in spontaneous Raman spectroscopy. The scattered intensity is proportional (a) to the square of the number of scattering molecules and (b) to the square of the irradiance

of the incident radiations. With pulsed lasers time-dependent processes in molecules and their influence on the change of level populations can be studied by CARS; two examples being photosynthesis and the visual processes in our eyes.

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