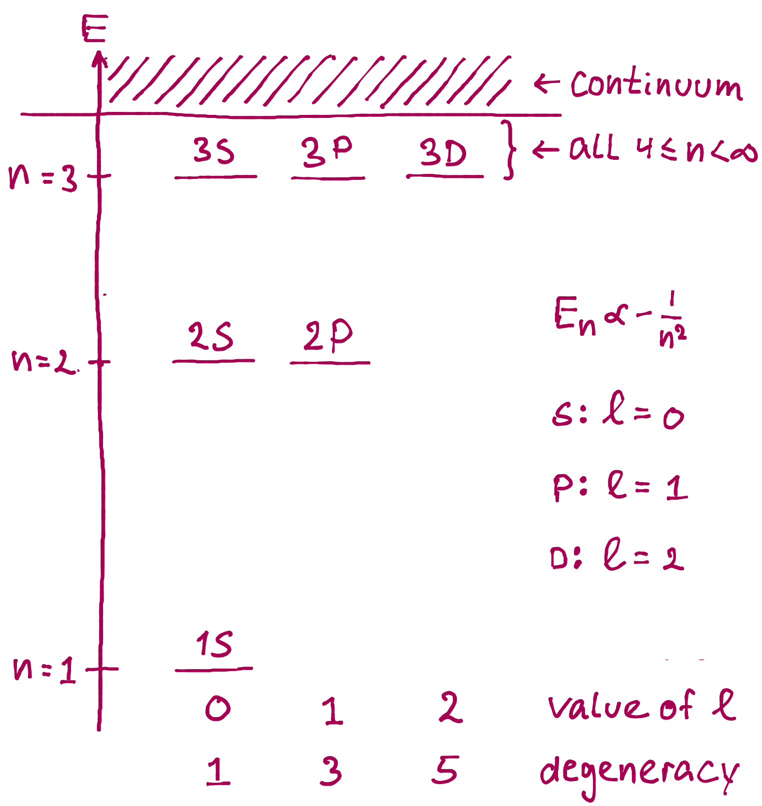
Atom-Light Interaction: Multi-Level Atoms

Starting point – the Hydrogen atom

$$\boxed{H_a = \frac{p^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}|}}$$

$$V_{ext}(\vec{r},\vec{R},t) = -e\vec{r}\cdot\vec{E}(\vec{R},t)$$

$\vec{r}$: relative $\quad \vec{R}$: center-of-mass



Note: Frequencies for transitions $n \to n'$, $n'' \to n'''$ are <u>very</u> different ⇨ near-resonant approx. with a single transition frequency $\omega \sim \omega_0$

Levels $|n\ell\rangle$ are generally degenerate with respect to the quantum number m, so we cannot isolate a 2-level system only through its transition frequency.

We must therefore consider <u>Selection Rules</u>

Interaction matrix element

$$\boxed{\langle n'\ell' m' | V_{ext} | n\ell m\rangle \propto \int_{-\infty}^{\infty} dr^3\, \varphi^*_{n'\ell' m'}(\vec{r})\,\vec{r}\,\varphi_{n\ell m}(\vec{r})}$$

Wavefunction parity is even/odd depending on ℓ

$$\boxed{\varphi_{n\ell m}(\vec{r}) = (-1)^{\ell}\varphi_{n\ell m}(-\vec{r})}$$

⇨ $\langle |V| \rangle$ can be non-zero only if $(\ell - \ell')$ is odd.

This is the Parity Selection Rule !

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Next: We will find selection rules that derive from the angular symmetry of the matrix element

We need to develop the proper math language
➡ spherical basis vectors and harmonics

Consider an arbitrary set of orthonormal basis vectors $\vec{\varepsilon}_i, \vec{\varepsilon}_j, \vec{\varepsilon}_k$. We can always write

$$\vec{r} = (\vec{r}\cdot\vec{\varepsilon}_i)\,\vec{\varepsilon}_i + (\vec{r}\cdot\vec{\varepsilon}_j)\,\vec{\varepsilon}_j + (\vec{r}\cdot\vec{\varepsilon}_k)\,\vec{\varepsilon}_k$$

Cartesian basis: $\vec{\varepsilon}_i = \vec{\varepsilon}_x \quad \vec{\varepsilon}_j = \vec{\varepsilon}_y \quad \vec{\varepsilon}_k = \vec{\varepsilon}_z$
(real-valued)

Spherical basis:
(complex-valued)

$$\begin{cases} \vec{\varepsilon}_i = \vec{\varepsilon}_1 = -\frac{1}{\sqrt{2}}(\vec{\varepsilon}_x + i\vec{\varepsilon}_y) \\ \vec{\varepsilon}_j = \vec{\varepsilon}_{-1} = \frac{1}{\sqrt{2}}(\vec{\varepsilon}_x - i\vec{\varepsilon}_y) \\ \vec{\varepsilon}_k = \vec{\varepsilon}_0 = \vec{\varepsilon}_z \end{cases}$$

Reminder: Scalar products of complex vectors

Dirac notation

$$\{|a\rangle + i|b\rangle, |c\rangle\} = (\langle a| - i\langle b|)\,|c\rangle = \langle a|c\rangle - i\langle b|c\rangle$$

Regular notation

$$(\vec{a} + i\vec{b})\cdot\vec{c} = \vec{a}\cdot\vec{c} - i\,\vec{b}\cdot\vec{c}$$

(anti-linear in 1st factor)

Scalar Products in the spherical basis

Homework: prove the relations

$$\boxed{\vec{\varepsilon}_q^{\,*} = (-1)^q\,\vec{\varepsilon}_{-q}, \quad \vec{\varepsilon}_{q'}\cdot\vec{\varepsilon}_q = \delta_{-qq'}, \quad \vec{\varepsilon}_{q'}\cdot\vec{\varepsilon}_q^{\,*} = (-1)^q\,\delta_{q'q}}$$

Next: Rewrite $\vec{r}\cdot\vec{\varepsilon}_q$ in polar coordinates

$$\vec{r}\cdot\vec{\varepsilon}_x = x = r\sin\theta\cos\varphi$$
$$\vec{r}\cdot\vec{\varepsilon}_y = y = r\sin\theta\sin\varphi$$
$$\vec{r}\cdot\vec{\varepsilon}_z = z = r\cos\theta$$

Compare to the Spherical Harmonics

$$Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta, \quad Y_1^{\pm1}(\theta,\varphi) = \pm\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$$

$$\left.\begin{aligned} x &= -r\sqrt{\frac{2\pi}{3}}\left(Y_1^1 - Y_1^{-1}\right) \\ y &= ir\sqrt{\frac{2\pi}{3}}\left(Y_1^1 + Y_1^{-1}\right) \\ z &= r\sqrt{\frac{4\pi}{3}}\,Y_1^0 \end{aligned}\right\} \Rightarrow \boxed{\vec{r}\cdot\vec{\varepsilon}_q = r\sqrt{\frac{4\pi}{3}}\,Y_1^q}$$

to verify, plug in $\vec{\varepsilon}_q$ in terms of $\vec{\varepsilon}_x, \vec{\varepsilon}_y, \vec{\varepsilon}_z$

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This finally gives us $\vec{\varepsilon}_q$ in the spherical basis:

$$\boxed{\vec{r} = \sum_{q=0,\pm1} (\vec{r}\cdot\vec{\varepsilon}_q)\vec{\varepsilon}_q = r\sqrt{\frac{4\pi}{3}} \sum_{q=0,\pm1} Y_1^q \vec{\varepsilon}_q}$$

End math preamble

Back to the Matrix Elements

First:

$$V_{ext} = -e\vec{r}\cdot\vec{E}(t)$$

electric dipole interaction

$$\vec{E}(t) = \frac{1}{2}E_0\left(\vec{\varepsilon}_q e^{-i\omega t} + \vec{\varepsilon}_q^{\,*} e^{i\omega t}\right)$$

$$= \frac{1}{2}E_0\left(\vec{\varepsilon}_q e^{-i\omega t} + (-1)^q \vec{\varepsilon}_q e^{i\omega t}\right)$$

electric field polarization $\vec{\varepsilon}_q$

$$V_{ext} = -\sqrt{\pi/3}\, eE_0 r \left(\sum_{q'} Y_1^{q'} \underbrace{\vec{\varepsilon}_{q'}\Big)\cdot\Big(\vec{\varepsilon}_q}_{\delta_{q'q}} \overbrace{e^{-i\omega t} + (-1)^q \vec{\varepsilon}_{-q}}^{\delta_{q'(-q)}} e^{i\omega t}\right)$$

$$\boxed{V_{ext} \propto r\left(Y_1^q e^{-i\omega t} + (-1)^q Y_1^{-q} e^{i\omega t}\right)}$$

The matrix element = overlap integral of the form

$$V_{21} = \langle n'\ell' m' | V_{ext} | n\ell m\rangle$$

$$\propto \int_{\mathbb{R}^3} d^3r\, \varphi^*_{n'\ell' m'}(\vec{r})\, \overbrace{r\left(Y_1^q e^{-i\omega t} + (-1)^q Y_1^{-q} e^{i\omega t}\right)}^{V_{ext}} \varphi_{n\ell m}(\vec{r})$$

where the wavefunctions $\varphi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\, Y_\ell^m(\theta,\varphi)$

$$V_{21} = \langle n'\ell' m' | V_{ext} | n\ell m\rangle$$

$$= \mathcal{R} \times \underbrace{\int_{4\pi} d\Omega\, (Y_{\ell'}^{m'})^* \left(Y_1^q e^{-i\omega t} + (-1)^q Y_1^{-q} e^{i\omega t}\right) Y_\ell^m}_{\text{angular integral}}$$

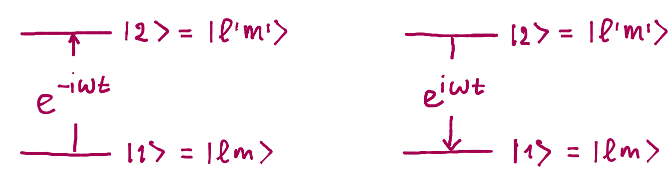
radial integral

angular integral

Thus, to within a constant factor

$$V_{21} = \langle \ell' m' | Y_1^q e^{-i\omega t} + (-1)^q Y_1^{-q} e^{i\omega t} | \ell m\rangle = V_{12}^*$$

From the RWA, we know the resonant terms are



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And thus in the RWA we get (use $(Y_\ell^m)^* = (-1)^m Y_\ell^{-m}$)

$$\boxed{\begin{aligned} V_{21} &\propto \langle \ell' m' | Y_1^q e^{-i\omega t} | \ell m \rangle \\ V_{12} &\propto \langle \ell m | (-1)^q Y_1^{-q} e^{i\omega t} | \ell' m' \rangle \end{aligned}}$$

dropping the factor $(-1)^q$

$$\boxed{\begin{aligned} V_{21} &\propto \int d\Omega \, (Y_{\ell'}^{m'})^* Y_1^q Y_\ell^m \propto \langle 1, q; \ell m | \ell' m' \rangle \\ V_{12} &\propto \int d\Omega \, (Y_\ell^m)^* Y_1^{-q} Y_{\ell'}^{m'} \propto \langle 1, -q; \ell' m' | \ell m \rangle \end{aligned}}$$

Clebsch-Gordan coefficients

Next: We can understand this as conservation of angular momentum when a photon is absorbed or emitted

Selection Rules for Electric Dipole Transitions

Reminder: **Addition of Angular Momenta**

Let $\vec{J} = \vec{J}_1 + \vec{J}_2$ ⇨ eigenstates $\begin{cases} |j_1 m_1\rangle \\ |j_2 m_2\rangle \\ |j m\rangle \end{cases}$

We can write $|jm\rangle$ in the basis $|j_1 m_1\rangle |j_2 m_2\rangle$

$$|jm\rangle = \underbrace{\sum_{m_1, m_2} |j_1 m_1; j_2 m_2\rangle\langle j_1 m_1; j_2 m_2|}_{\text{identity}} |jm\rangle$$

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

Clebsch-Gordan coefficients

CG's are non-zero when

$$\boxed{\begin{aligned} |j_1 - j_2| \le j &\le j_1 + j_2 \\ m_1 + m_2 &= m \end{aligned}}$$

Conservation of Angular Momentum

Going back to the matrix element, $V_{21} \neq 0$

when $|1q\rangle$ combined w/ $|\ell m\rangle$ is consistent w/ $|\ell' m'\rangle$

"photon" AM — ground state AM — excited state AM

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The corresponding Selection Rules are

$$\ell' - \ell = 0, \pm 1, \quad m' - m = q, \quad q = 0, \pm 1$$

Combining with the Parity Rule, this gives us the

Electric Dipole Selection Rules

$$\boxed{\ell' - \ell = \pm 1, \quad m' - m = q, \quad q = 0, \pm 1}$$

Remarkably

* These selection rules generalize to complex many – electron atoms, and after we include both electron and nuclear spins in the theory.
* From a physics perspective, this reflects the conservation of angular momentum in rotationally invariant systems, and therefore transitions that do not conserve angular momentum are forbidden
* To find the Clebsch-Gordan coefficients for different transitions we would need to use the Wigner-Eckart theorem, the proof of which is beyond this course.

General ED Selection Rules

$\Delta L = \pm 1$ $\quad \vec{L}$: total e orbital A. M.

$\Delta F = 0, \pm 1$ $\quad \vec{F}$: total orbital + spin A. M.

$\Delta m_F = q = 0, \pm 1$ $\quad q$: polarization of EM field

Clebsch-Gordan coefficients $\quad (E_{F',m_F'} > E_{F,m_F})$

$$\langle F', m_F' | V | F, m_F \rangle \propto \langle 1, q; F, m_F | F', m_F' \rangle$$

$$\langle F, m_F | V | F', m_F' \rangle \propto \langle 1, -q; F' m_F' | F, m_F \rangle$$

Hydrogen atom

$1S - 2S$: forbidden $\qquad 1S - 2P$: allowed

Total spin: $\vec{F} = \vec{J} + \underset{\text{nuclear}}{\vec{I}}, \quad \vec{J} = \underset{\text{orbital}}{\vec{L}} + \underset{\text{electron spin}}{\vec{S}}$

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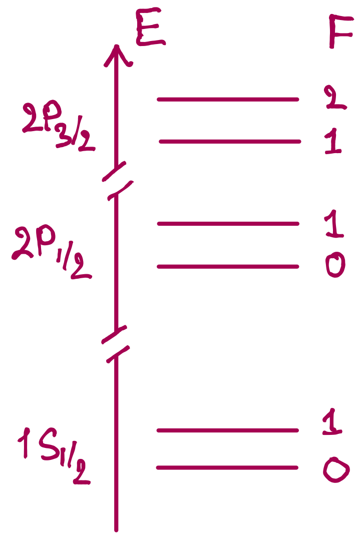
1S State:

$J = 1/2, \quad F = 0, 1$

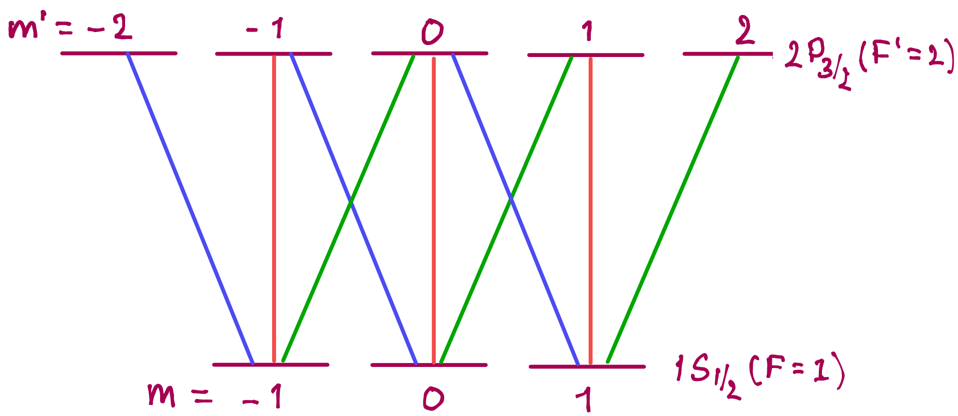
2P State:

$J = 1/2, \quad F = 0, 1$

$J = 3/2, \quad F = 1, 2$



Level diagram for transitions $1S_{1/2}(F=1) \rightarrow 2P_{3/2}(F=2)$



Polarization: $q=0$ $\quad q=1$ $\quad q=-1$

Note: When the field polarization is pure linear or circular the levels are coupled in pairs, and the oscillator strengths depend on the Clebsch-Gordan coefficients

Demo: Clebsch-Gordan Coefficients and Oscillator Strengths from Mathematica

- Dense or hot gases: Collisions redistribute Atoms between *m*-levels on very short time scales and the gas looks like a gas of 2-level atoms w/an effective coupling strength. If the dipole is oriented at random with the field, Then $\langle \vec{r} \cdot \vec{\mathcal{E}}_q \rangle_{angles} \sim \frac{1}{3} |\langle \vec{r} \rangle|$.
  The same is true for unpolarized light

- Short interaction time: If the atoms are "unpolarized"(random *m*-level populations) and the interaction too brief to change this, the atoms behave as an ensemble with different oscillator strengths

- Optical pumping: In dilute gases without collisions, atoms can be "pumped" into a single, pure state, e. g., $1S_{1/2}(F=1, m_F=1)$.
  If driven with $\vec{\mathcal{E}}_{q=1}$ polarization this will realize a true 2-level system, as $2P_{3/2}(F'=2, m_F'=2)$ can only decay back to $1S_{1/2}(F=1, m_F=1)$

- If more than one frequency or polarization is Present, one can often drive Raman transitions