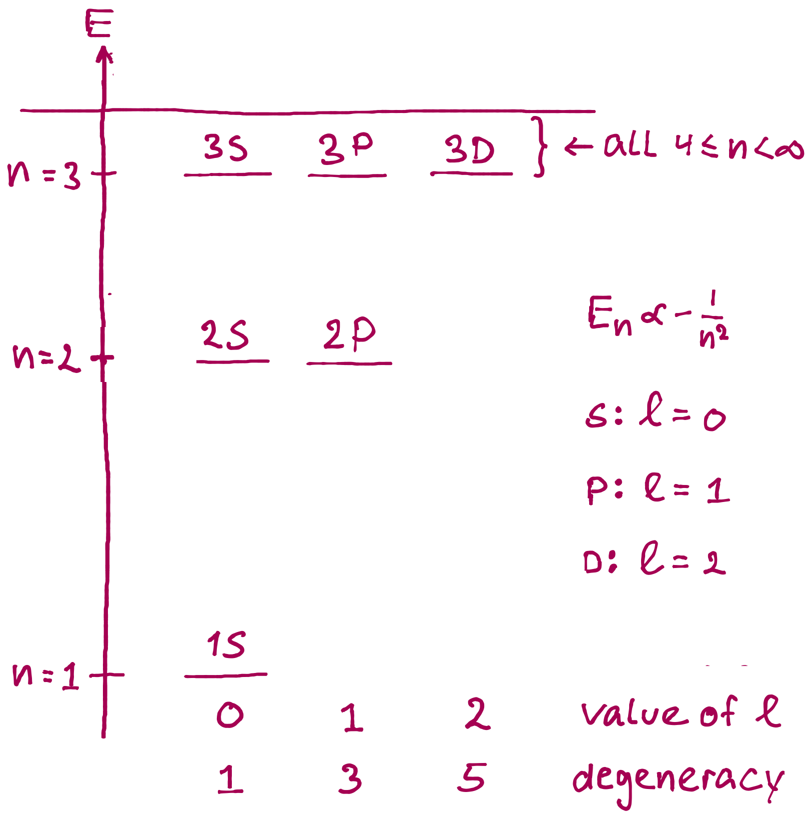
Atom-Light Interaction: Multi-Level Atoms

Starting point – the Hydrogen atom

$$\boxed{\begin{array}{l} H_a = \dfrac{p^2}{2m} - \dfrac{1}{4\pi\varepsilon_0}\dfrac{e^2}{|\vec r|} \\[2ex] V_{ext}(\vec r, \vec R, t) = -e\vec r \cdot \vec E(\vec R, t) \\[2ex] \vec r : \text{relative} \quad \vec R : \text{center-of-mass} \end{array}}$$



Note: Frequencies for transitions $n \to n'$, $n'' \to n'''$ are very 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 Selection Rules

Interaction matrix element

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

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 !

(*) This is not strictly true due to spin-orbit coupling.

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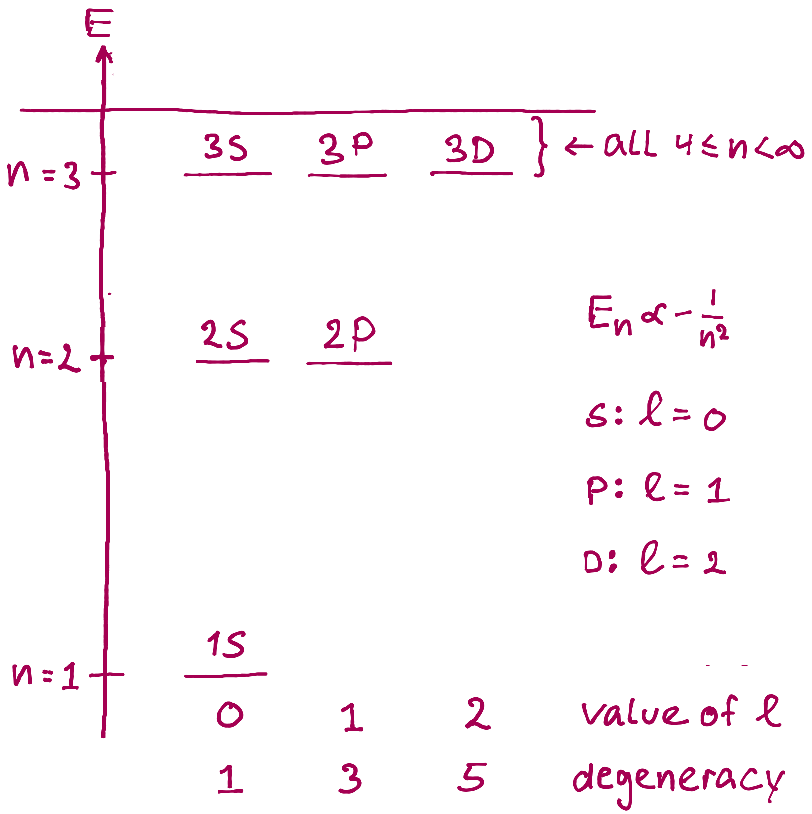

$E_n \propto -\frac{1}{n^2}$

S: $\ell = 0$

P: $\ell = 1$

D: $\ell = 2$

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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)

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

Reminder: Scalar products of complex vectors

Dirac notation	Regular notation
$\{|a\rangle + i|b\rangle, |c\rangle\}$	$(\vec{a} + i\vec{b})\cdot\vec{c}$
$= (\langle a| - i\langle b|)|c\rangle$	$= \vec{a}\cdot\vec{c} - i\vec{b}\cdot\vec{c}$
$= \langle a|c\rangle - i\langle b|c\rangle$	(anti-linear in 1st factor)

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Math Preamble: The Spherical Basis

(1) Prove the relations (Homework)

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

(2) Show that

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

where $Y_1^{\pm1}(\theta,\phi) = \pm\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$

$$Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

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Atom-Light Interaction: Multi-Level Atoms

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Example:

$$\vec{\varepsilon}_1 = \frac{1}{\sqrt{2}}(\vec{\varepsilon}_x + i\vec{\varepsilon}_y) \Rightarrow \vec{r}\cdot\vec{\varepsilon}_1 = -\frac{1}{\sqrt{2}}(\vec{r}\cdot\vec{\varepsilon}_x + i\vec{r}\cdot\vec{\varepsilon}_y)$$

Substitute: **(Spherical Coordinates)**

$$\vec{r}\cdot\vec{\varepsilon}_x = r\sin\theta\cos\phi \qquad \vec{r}\cdot\vec{\varepsilon}_y = r\sin\theta\sin\phi$$

$$\vec{r}\cdot\vec{\varepsilon}_1 = r\frac{1}{\sqrt{2}}(\sin\theta\cos\phi + i\sin\theta\sin\phi)$$

$$= r\frac{1}{\sqrt{2}}\sin\theta \, e^{i\phi} = r\sqrt{\frac{4\pi}{3}}\, Y_1^1(\theta,\phi)$$

Relations for $q = 0, -1$ follow similarly.

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End Math Preamble

Atom-Light Interaction: Multi-Level Atoms

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End Math Preamble

Back to the Dipole Matrix Elements. First:

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

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

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

↑ electric field polarization

$$V_{ext} = -\sqrt{\pi/3}\, e E_0 r \overbrace{\Big(\sum_{q'} Y_1^{q'} \underbrace{\vec{\varepsilon}_{q'}\Big)\cdot\Big(\vec{\varepsilon}_q}_{\delta_{q'q}} e^{-i\omega t} + (-1)^q \vec{\varepsilon}_{-q}}^{\delta_{q'(-q)}} e^{i\omega t}\Big)$$

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

Atom-Light Interaction: Multi-Level Atoms

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electric field polarization

$$V_{ext} =$$

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The matrix element = overlap integral

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

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

where $\varphi_{nlm}(\vec{r}) = R_{nl}(r)\, Y_l^m(\theta,\varphi)$

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

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

radial integral

angular integral

Thus, to within a constant factor

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

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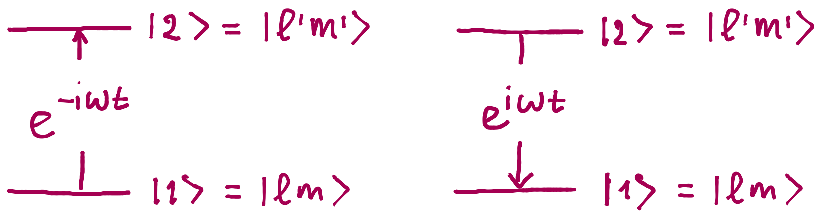
Resonant terms:



Recall from 2-level system:

$$\boxed{\begin{aligned} i\dot a_1 &= -\tfrac12\left(\chi_{12} e^{-i\omega t} + \chi_{21}^* e^{i\omega t}\right) a_2 \\ i\dot a_2 &= \omega_{21} a_2 - \tfrac12\left(\chi_{21} e^{-i\omega t} + \chi_{12}^* e^{i\omega t}\right) a_1 \end{aligned}}$$

$$\boxed{\begin{aligned} i\dot c_1(t) &= -\tfrac12\left(\chi_{12} e^{-i2\omega t} + \chi_{21}^*\right) c_2(t) \\ i\dot c_2(t) &= (\omega_{21}-\omega) c_2(t) - \tfrac12\left(\chi_{21} + \chi_{12}^* e^{i2\omega t}\right) c_1(t) \end{aligned}}$$

(RWA)

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Atom-Light Interaction: Multi-Level Atoms

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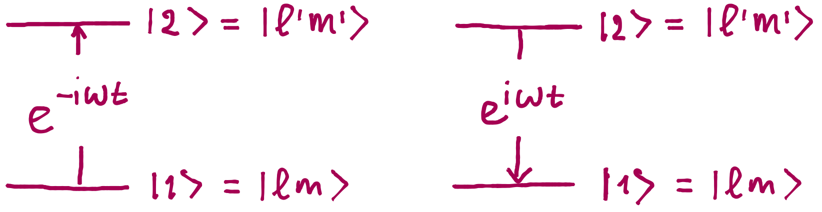

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And thus in the RWA we get ($(Y_\ell^m)^* = (-1)^m Y_\ell^{-m}$)

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

dropping 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

Atom-Light Interaction: Multi-Level Atoms

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Selection Rules for Electric Dipole Transitions

Revisit: Addition of Angular Momenta

Let $\vec{J} = \vec{J}_1 + \vec{J}_2$ ⇨ eigenstates $\left\{ \begin{array}{l} |j_1 m_1\rangle \\ |j_2 m_2\rangle \\ |jm\rangle \end{array} \right.$

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

$$|jm\rangle = \overbrace{\sum_{m_1, m_2} |j_1 m_1; j_2 m_2\rangle\langle j_1 m_1; j_2 m_2|}^{\text{identity}}|jm\rangle$$
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Clebsch-Gordan coefficients

CG's are non-zero when
(Conservation of Angular Momentum)

$$\boxed{\begin{array}{c} |j_1 - j_2| \leq j \leq j_1 + j_2 \\ m_1 + m_2 = m \end{array}}$$

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

$\underset{\uparrow}{|1q\rangle}$ combined w/ $\underset{\uparrow}{|\ell m\rangle}$ is consistent w/ $\underset{\uparrow}{|\ell' m'\rangle}$

"photon" AM ground state AM excited state AM

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The corresponding Selection Rules are

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

Combining this with the Parity Rule we get

Electric Dipole Selection Rules

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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
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General ED Selection Rules

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

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

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

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

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

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