Begin 01-30-2024

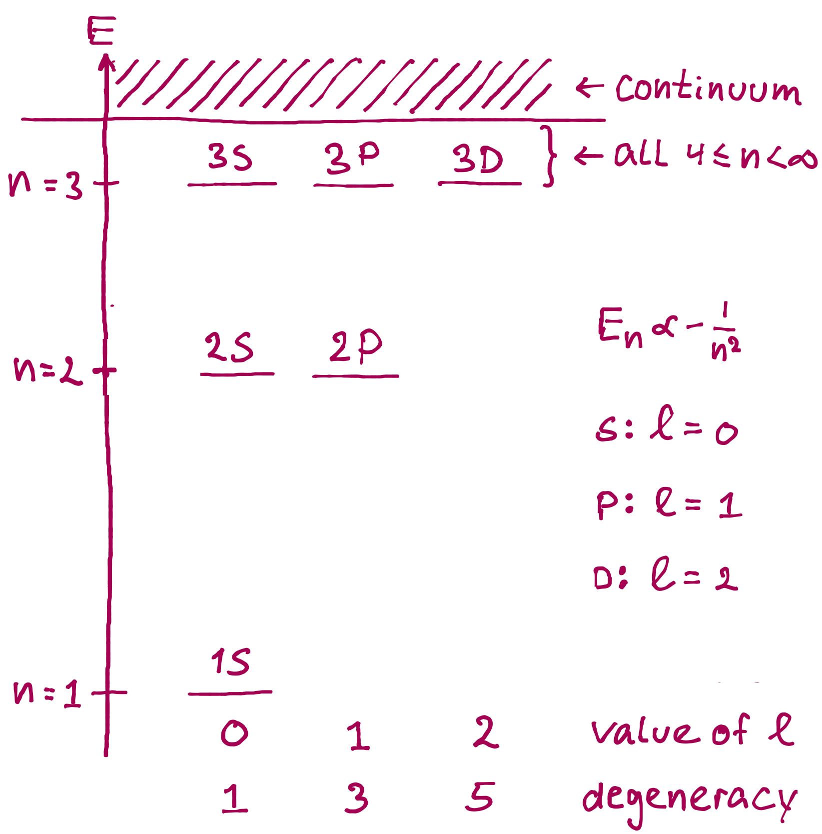
Atom-Light Interaction: Multi-Level Atoms

Starting point – the Hydrogen atom

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

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

$\vec{r}$: 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 <u>Parity</u> Selection Rule !

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

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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: $\vec{\varepsilon}_i = \vec{\varepsilon}_x,\ \vec{\varepsilon}_j = \vec{\varepsilon}_y,\ \vec{\varepsilon}_k = \vec{\varepsilon}_z$
(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)

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Math Preamble: **The Spherical Basis**

(1) Prove the relations (Homework)

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

(2) Show that

$$\vec{r} = \sum_{q=0,\pm 1} (\vec{r}\cdot\vec{\varepsilon}_q)\vec{\varepsilon}_q = r\sqrt{\frac{4\pi}{3}} \sum_{q=0,\pm 1} Y_1^q \vec{\varepsilon}_q$$

where $$Y_1^{\pm 1}(\theta,\phi) = \pm\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{\pm i\phi}$$

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

(Spherical Harmonics)

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

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End Math Preamble

Back to the Dipole Matrix Elements. First:

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

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

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

electric field polarization

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

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

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

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

The matrix element = overlap integral

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

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

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

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

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

Thus, to within a constant factor

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

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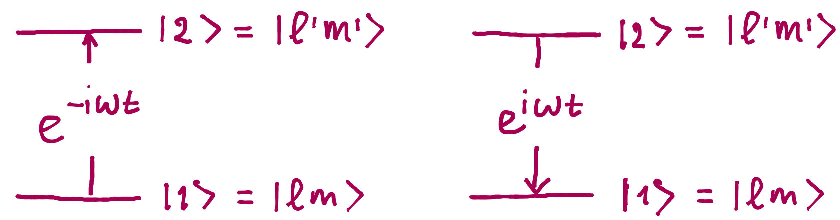
Resonant terms:



Recall from 2-level system:

$$\boxed{\begin{aligned} i\dot{a}_1 &= -\tfrac{1}{2}\left(\chi_{12} e^{-i\omega t} + \chi_{21}^* e^{i\omega t}\right) a_2 \\ i\dot{a}_2 &= \omega_{21} a_2 - \tfrac{1}{2}\left(\chi_{21} e^{-i\omega t} + \chi_{12}^* e^{i\omega t}\right) a_1 \end{aligned}}$$

$$\boxed{\begin{aligned} i\dot{c}_1(t) &= -\tfrac{1}{2}\left(\chi_{12} e^{-i2\omega t} + \chi_{21}^*\right) c_2(t) \\ i\dot{c}_2(t) &= (\omega_{21}-\omega) c_2(t) - \tfrac{1}{2}\left(\chi_{21} + \chi_{12}^* e^{i2\omega t}\right) c_1(t) \end{aligned}}$$

(RWA)

$$\boxed{\begin{aligned} i\dot{c}_1(t) &= -\tfrac{1}{2}\chi_{21}^* c_2(t) \\ i\dot{c}_2(t) &= \Delta c_2(t) - \tfrac{1}{2}\chi_{21} c_1(t) \end{aligned}}$$

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The matrix element = overlap integral

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

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

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In the RWA we have $(Y_\ell^m)^* = (-1)^m Y_\ell^{-m}$, giving us

$$V_{21} \propto \langle \ell' m' | Y_1^q e^{-i\omega t} | \ell m\rangle$$

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

dropping factor $(-1)^q$

$$V_{21} \propto \int d\Omega\, (Y_{\ell'}^{m'})^* Y_1^q Y_\ell^m \propto \langle 1, q; \ell m | \ell' m'\rangle$$

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

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

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

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