Lecture 21: The Wigner-Eckart theorem

The most important use of spherical tensors is to calculate matrix elements between states with well defined angular momentum. The Wigner-Eckart Theorem (W.E.T.) will allow us to express these matrix elements in terms of a factor that depends solely on geometry. This leads to "selection rules" in, for example, absorption and emission of photons by atoms. Such selection rules are statement of conservation of angular momentum.

Motivation

Consider the dipole matrix elements of the spherical tensor opertor $\hat{d}_q = -e\,\hat{x}_q$ between two Hydrogen eigenfunctions (no spin)

$$M_{(n'\ell'm')\leftarrow(n\ell m)} = \langle n'\ell'm'|\hat{d}_q|n\ell m\rangle = -e\int d^3x\; \psi^*_{n'\ell'm'}(\vec{x})\; x_q\; \psi_{n\ell m}(\vec{x})$$

$$\text{Now}\quad x_q = r\,Y^1_q(\theta,\phi)\sqrt{\frac{4\pi}{3}}$$

$$\Rightarrow M_{(n'\ell'm')\leftarrow(n\ell m)} = \underbrace{e\int r^2dr\; R_{n'\ell'}(r)\; r\; R_{n\ell}(r)}_{C(n'\ell'|n\ell)}\; \underbrace{\int d\Omega\; Y^{\ell'*}_{m'}(\theta,\phi)\; Y^1_q(\theta,\phi)\; Y^\ell_m(\theta,\phi)}_{\substack{=0 \text{ unless} \\ m'=m+q \\ |\ell-1|\le\ell'\le|\ell+1|}}$$

independent of angular geometry

Thus we see that the matrix element factorizes into a part independent of angular geometry and a factor that looks like addition of angular momenta

The Wigner-Eckert theorem : Statement

Given a tensor operator $\hat{T}^{(k)}_q$

$$\boxed{\langle \alpha'; j'm' | \hat{T}^{(k)}_q | \alpha; jm \rangle = \langle \alpha'; j' \| \hat{T}^{(k)} \| \alpha, j \rangle \langle j'm' | kq\, jm \rangle}$$

- Here α' and α are all other eigenvalues other than $j\,m$.
- $\langle j'm' | kq\, jm \rangle$ is the C.G. coeff for addition
$$\vec{J}' = \vec{J} + \vec{K}$$
- $\langle \alpha'; j \| \hat{T}^{(k)} \| \alpha, j \rangle$ is the "reduced matrix element" independent of m, m' and q

Notes: • We have chosen a particular convention for the reduced matrix element. Sakurai chooses a different normalization

• In our convention, the r.m.e. is not a true "matrix element" $\langle \alpha' j' \| \hat{T}^{(k)} \| \alpha j \rangle^* \neq \langle \alpha j \| \hat{T}^{(k)} \| \alpha' j' \rangle$

In words, the W.E.T. states that all matrix elements of $\hat{T}^{(k)}_q$ are proportional, ~~both~~ factorizing into a component independent of angular geometry, and a C.G. coeff. The C.G. coeff determines the <u>selection rules</u> according to conservation of angular momentum $\vec{J}' = \vec{J} + \vec{K}$.
The tensor operator thus acts an object that carries to angular momentum K with z-projection q

The Wigner–Eckart theorem: Proof

<u>Lemma:</u> $\langle j'm' | kq\, jm\rangle$

$$= \sum_{q' m_1' m_1} D^{(j')*}_{m_1' m'}(R)\, D^{(k)}_{q' q}(R)\, D^{(j)}_{m_1 m}(R)\, \langle j' m_1' | k q' j m_1\rangle$$

<u>Proof:</u> $\langle j'm' | kq\, jm\rangle = \langle j'm' | D^\dagger(R)\, D(R) | kq\rangle \otimes | jm\rangle$

Aside $D(R) | j' m'\rangle = \sum_{m_1'} | j' m_1'\rangle D^{(j')}_{m_1' m_1}$

$$D(R) | kq\rangle \otimes | jm\rangle = \sum_{q' m_1} | kq', j m_1\rangle D^{(k)}_{q'q}\, D^{(j)}_{m_1 m}$$

$$\Rightarrow \langle j'm' | kq\, jm\rangle = \sum_{q' m_1 m_1'} \langle j' m_1' | k q' j m_1\rangle D^{(j')*}_{m_1' m'} D^{(k)}_{q'q} D^{(j)}_{m_1 m}$$

Now consider: $\langle \alpha'; j'm' | \hat{T}^{(k)}_q | \alpha, jm\rangle$

$$\qquad\qquad D^\dagger D \quad D^\dagger D$$

$$= \sum_{q' m_1' m_1} \langle \alpha'; j' m_1' | \hat{T}^{(k)}_{q'} | \alpha j\, m_1\rangle D^{(j')*}_{m_1' m'} D^{(k)}_{q'q} D^{(j)}_{m_1 m}$$

Since these are linearly independent equation

$$\Rightarrow \langle \alpha' j' m_1' | \hat{T}^{(k)}_{q'} | \alpha\, jm\rangle = C(\alpha' j', k, \alpha j)\, \langle j'm' | kq\, jm\rangle$$

C is the reduced matrix element

Q.e.d.

Application of W.E.T. : Dipole selection rules

Recall from classical electromagnetic theory that ~~as~~ a localized charge/current distribution can be decomposed into multipole moments. We ~~take~~ an E/M wave, interacts with the distribution, if wavelength $\lambda >> $ (size of distribution), the lowest nonvanishing moment dominates the interaction.

For an atom, size $\sim 1\,\mathring{A}$, interacting with light $\lambda \sim 1\,\mu m$ $\Rightarrow$ Multipole expansion is <u>excellent</u>

$\Rightarrow$ Typically <u>electric dipole</u> transitions dominate (E1)

Interaction Hamiltonian $\hat{H}_{int} = -\hat{\vec{d}} \cdot \vec{E}(\vec{x}_0, t)$ ← atom position

Here we treat $\vec{E}$ as a classical field. For a monochromatic wave $\vec{E}(\vec{x}_0, t) = \mathrm{Re}\left(\vec{e}\, E(\vec{x}_0)\, e^{-i\omega t}\right)$

$\vec{e}$: polarization; $E(\vec{x}_0)$: amplitude

$$\Rightarrow \hat{H}_{int} = -\frac{1}{2}\left[\hat{\vec{d}} \cdot \vec{e}\, E(\vec{x}_0)\, e^{-i\omega t} + \hat{\vec{d}} \cdot \vec{e}^{\,*}\, E^*(\vec{x}_0)\, e^{i\omega t}\right]$$

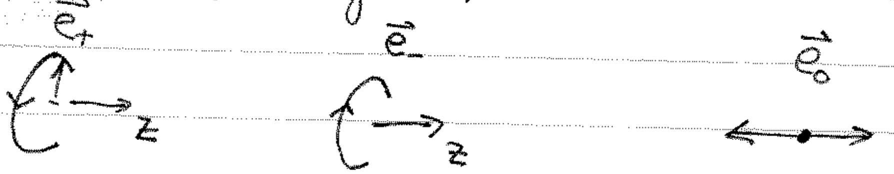
This is a time dependent Hamiltonian, and thus its effect on the atom requires time dependent perturbation theory. We will study this later in the semester. We will find that the first term ($\sim e^{-i\omega t}$) leads to <u>absorption</u> of photons and the second ($\sim e^{i\omega t}$) leads to <u>emission</u> of photons.

The transition probability for absorption occurs at a rate proportional to

$$W_{f\leftarrow i} = |\langle \Psi_f | \hat{\vec{d}}\cdot\vec{\epsilon}_L\, E(\vec{x}_0) | \Psi_i \rangle|^2$$
$$= \underbrace{|\langle \Psi_f | \hat{\vec{d}}\cdot\vec{\epsilon}_L | \Psi_i \rangle|^2}_{(\text{dipole matrix element})^2} \quad \underbrace{|E(\vec{x}_0)|^2}_{\sim \text{Intensity}}$$

Thus, the important quantity is $\langle \Psi_f | \hat{\vec{d}}\cdot\vec{\epsilon}_L | \Psi_i \rangle$

Expand $\vec{\epsilon}_L$ in the spherical basis w.r.t. space fixed quantization axis (z-axis). For monochromatic light at frequency ω, the field vector oscillates:



Define: σ_+ light $\qquad$ σ_- light $\qquad$ π light

Note: If $\vec{E}$ is a plane wave, the z axis need not be the same direction as the wave vector $\vec{k}$ (thought it can be). We choose z by convenience. If z axis $= \vec{k}$ direction then $\vec{\epsilon}_L = \sigma_\pm$ polarization only.

The atom sees only the local field, not the wave over all space. Thus, it only "cares" about how its charges are perturbed in time. The three vector oscillations about ($\sigma_\pm$ and π) represent the three motions with definite angular momentum about the z-axis.

Consider states with good quantum numbers $\underbrace{nLS}_{\alpha} J M_J$

<u>Dipole selection rules</u> : $\vec{\epsilon}_L = \vec{e}_q \quad \hat{\vec{d}} = \sum \vec{e}_q^{\,*} d_q$

$$\boxed{\langle \alpha'; J'M_J' | \hat{d}_q | \alpha; JM_J \rangle = \langle \alpha' J' \| d \| \alpha J \rangle \langle J'M_J' | 1 q J M_J \rangle}$$

$\Rightarrow$ <u>E1 selection rules</u>

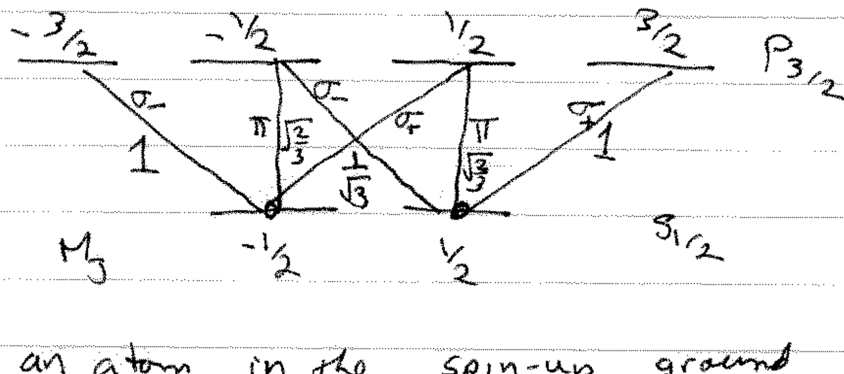
- $M_J' - M_J = 0, -1, 1$ $0 \Rightarrow \pi$ light, $\pm 1 \Rightarrow \sigma_\pm$ light
- $J' < J+1 \Rightarrow |\Delta J| = 0$ or 1
  but no $J=0 \rightarrow J'=0$ transitions
- Parity odd $\Rightarrow \Delta L$ odd $\Rightarrow \Delta L = \pm 1$

  Also $\Delta S = 0$

If ~~these~~ any of these rules are violated the transition is said to be (electric dipole) <u>forbidden</u>.

$J=0 \rightarrow J=0$ <u>Strictly forbidden</u> for any multipole.

Typically we draw allowed transitions with the CG coeff denoting the probability amplitude e.g. the D1 line $nS_{1/2} \rightarrow n'P_{3/2}$



Thus, an atom in the spin-up ground state is three times more likely to absorb σ_+ than σ_- light.

Physical Picture

The electromagnetic field carries angular momentum

Intrinsic angular momentum : spin 1 : $+\hbar$

Two helicity states $\curvearrowright\!\!\rightarrow_{\vec{k}}$ $+\hbar$ along $\vec{k}$

$\curvearrowleft\!\!\rightarrow \vec{k}$ $-\hbar$ along $\vec{k}$

No angular momentum projection $\perp$ to $\vec{k}$

(Massless photon)

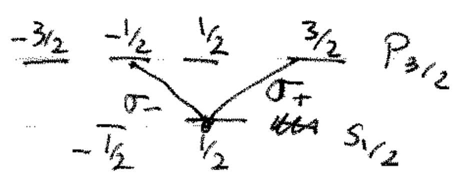
$\Rightarrow$ Choosing quantization axis along $\vec{k} \rightarrow$ only σ_+ and σ_- transitions

$\sigma_+ \Rightarrow \Delta M = +1$ one unit of angular momentum along quant-axis

$\sigma_- \Rightarrow \Delta M = -1$ $-$one unit

Suppose $\vec{\epsilon}_L = \vec{e}_x = \dfrac{-\vec{e}_+ + \vec{e}_-}{\sqrt{2}} \Rightarrow$ superposition of σ_+ and σ_-

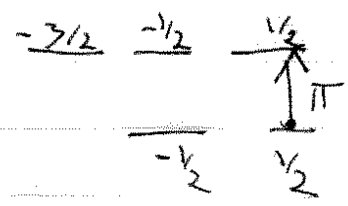
e.g.



Atom driven into coherent superposition of $M_J = -\frac{1}{2}$ and $\frac{3}{2}$

If take quantization axis $\perp$ to $\vec{k} \Rightarrow \pi$ light along quantization axis (say the old x-direction).

<u>Note:</u> With this choice of q-axis only one transition with old $\vec{e}_x$



$\boxed{\text{This is just a change of basis}}$