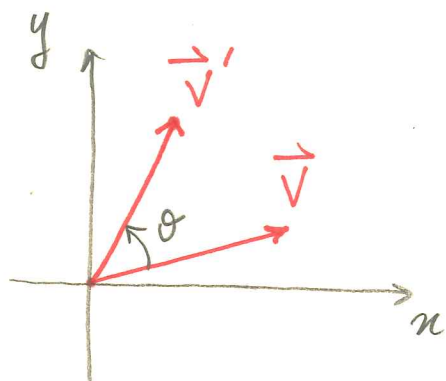


A Refreshment on Vectors, Tensors and Their Rotations



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

$$\vec{V}' = \begin{bmatrix} V'_x \\ V'_y \\ V'_z \end{bmatrix}$$

Rotated
(say by θ around z-axis)

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

$$V'_i = \sum_j R_{ij} V_j, \text{ e.g. } R_z(\theta) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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: $T_{ij} = T_{ij}^{(0)} + T_{ij}^{(1)} + T_{ij}^{(2)}$

$$T_{ij} = \underbrace{\frac{\vec{V} \cdot \vec{W}}{3} \delta_{ij}}_{\text{scalar}} + \underbrace{\frac{V_i W_j - V_j W_i}{2}}_{\text{vector}} + \underbrace{\left(\frac{V_i W_j + V_j W_i}{2} - \frac{\vec{V} \cdot \vec{W}}{3} \delta_{ij} \right)}_{\text{Symmetric, traceless rank-2 tensor}}$$

$\frac{1}{3} \text{Tr}(\vec{T})$ $\frac{1}{2} \epsilon_{ijk} (\vec{V} \times \vec{W})_k$

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:

$$\begin{aligned} \vec{V} \cdot \vec{W} &= (V_1 \hat{e}_1^* + V_0 \hat{e}_0^* + V_{-1} \hat{e}_{-1}^*) \cdot (W_1 \hat{e}_1^* + W_0 \hat{e}_0^* + W_{-1} \hat{e}_{-1}^*) \\ &\quad \left(\text{use } \hat{e}_{\pm 1}^* = -\hat{e}_{\mp 1} \quad \text{and} \quad \hat{e}_q^* \cdot \hat{e}_{q'} = \delta_{qq'} \right) \\ &= \sum_q (-1)^q V_q W_{-q} \end{aligned}$$

If we generalize this to an arbitrary rank K :

$$\vec{T}^{(K)} \cdot \vec{U}^{(K)} = \sum_q (-1)^q T_q^{(K)} U_{-q}^{(K)}$$

E.g. **Spherical Harmonics** can be treated as spherical tensors

$$T_q^{(K)} \rightarrow \underbrace{Y_{lm}(r)}_{\langle \theta, \phi | l, m \rangle} \quad \text{with rank } K = l \text{ of basis elements } q = m$$

$\langle \theta, \phi | l, m \rangle$: angular momentum eigenstates

Irreducible Spherical Tensor Operators

Next, we extend to operators. A collection of $2k+1$ operators $\hat{T}_q^{(k)}$ where $q = -k, -k+1, \dots, +k$ is defined to be an irreducible spherical tensor operator of rank $-k$ if

$$\left. \begin{aligned} * \quad [\hat{J}_z, \hat{T}_q^{(k)}] &= \hbar q \hat{T}_q^{(k)} \\ * \quad [\hat{J}_{\pm}, \hat{T}_q^{(k)}] &= \hbar \sqrt{k(k+1) - q(q \pm 1)} \hat{T}_{q \pm 1}^{(k)} \end{aligned} \right\}$$

Just like $Y_{lm}(\Omega)$ being the general spherical tensors, the operator $\hat{T}$ is the general 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

$$\sum_i [\hat{J}_i, [\hat{J}_i, \hat{T}_q^{(k)}]] = \hbar^2 k(k+1) \hat{T}_q^{(k)}$$

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:

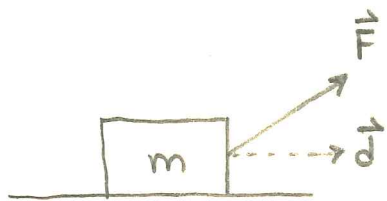
$$\langle \gamma', j', m' | \hat{T}_q^{(K)} | \gamma, j, m \rangle = \underbrace{\frac{\langle \gamma', j' || \hat{T}^{(K)} || \gamma, j \rangle}{\sqrt{2j'+1}}}_{\substack{\text{Reduced matrix el.} \\ \text{(indep. of } m, m', q)}} \underbrace{\langle j', m' | K, q; j, m \rangle}_{\substack{\text{a C-G} \\ \text{coef.}}}$$

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



$$W = \vec{F} \cdot \vec{d} = \underbrace{F d}_{\text{dynamics (reduced matrix element)}} \underbrace{\cos \theta}_{\text{geometry (C-}\theta \text{ coef.)}}$$

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 $\sqrt{r}$ 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** " " "

$$\langle j', m' | K, q; j, m \rangle \Rightarrow \vec{j}' = \vec{K} + \vec{j}$$

That is, $m' = q + m$, $|j - j'| \leq K \leq j + j'$

The general procedure in employing W-E theorem is

$$\begin{array}{ccc}
 & \langle \phi | \hat{O} | \psi \rangle & \\
 \text{Expand} \swarrow & \downarrow & \searrow \\
 \sum_{\hat{j}, m'} \langle \hat{j}', m' | & \sum_q \hat{T}_q^{(K)} & \sum_{\hat{j}, m} | \hat{j}, m \rangle
 \end{array}$$

Then for $\langle \hat{j}', m' | \hat{T}_q^{(K)} | \hat{j}, m \rangle$ 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

$$\hat{T}_q^{(K)\dagger} = (-1)^q \hat{T}_{-q}^{(K)}$$

* Rank-0 Case: Spin-orbit Hamiltonian

$$\begin{aligned}
 H_{so} &= \lambda \vec{L} \cdot \vec{S}, \quad \text{using } \vec{J} = \vec{L} + \vec{S} \\
 &= \frac{\lambda}{2} [\vec{J}^2 - \vec{L}^2 - \vec{S}^2]
 \end{aligned}$$

Let's extract the rank of the spherical operator H_{so}

$$[J_z, H_{so}] = \frac{\lambda}{2} \left(\underbrace{[J_z, J^2]}_0 - \underbrace{[J_z, L^2]}_{L_z + S_z} - \underbrace{[J_z, S^2]}_0 \right)$$

$$= 0 = \hbar q \hat{T}_q^{(K)}$$

$$\text{Similarly, } [J_{\pm}, H_{so}] = 0 = \hbar \sqrt{K(K+1) - q(q \pm 1)} \hat{T}_{q \pm 1}^{(K)}$$

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:

$$\langle H_{so} \rangle_{\ell, \hat{j}, m} = \frac{\langle \ell, \hat{j} || H_{so} || \ell, \hat{j} \rangle}{\sqrt{2j+1}} \underbrace{\langle \hat{j}, m | \overset{K}{0}, \overset{q}{0}; \hat{j}, m \rangle}_1$$

So, we immediately see that $\langle H_{so} \rangle_{\ell, \hat{j}, m}$ 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!

$$\text{Let } \vec{B} = \hat{z} B, \quad \vec{\mu} = \mu_B g_J \vec{J}$$

$$\Rightarrow H_z = -g_J \mu_B J_z B$$

$$\text{Even though } [J_z, H_z] = 0, \quad [J_{\pm}, H_z] \neq 0$$

$\nwarrow$ Zeeman

Hence, H_z is not a rank-zero irreducible tensor operator. $K=1$

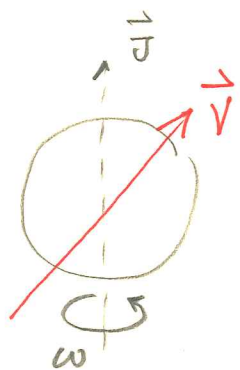
As a matter of fact, $\vec{\mu} = g_J \mu_B \vec{J}$ is a vector operator, and we can use W-E theorem to find $\langle \vec{\mu} \rangle$, and forming

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

$$\text{components, } J_q: \quad \langle J_q \rangle_{j,m} = \frac{\langle \chi, j \| J \| \chi, j \rangle}{\sqrt{2j+1}} \left\langle j, m \left| \overset{K}{\underset{j}{J}}_q \right| j, m \right\rangle$$

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,

$$\begin{aligned} \langle \mu_g \rangle_{jm} &= g_J \mu_B \langle J_g \rangle_{jm} \\ &= g_J \mu_B \frac{\langle \chi, j \| J \| \chi, j \rangle}{\sqrt{2j+1}} \langle j, m | K, 1; j, m \rangle \end{aligned}$$

* 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

$$V(\vec{r}) = V(0) + \sum_{\alpha} \chi_{\alpha} \left. \frac{\partial V}{\partial x_{\alpha}} \right|_{\vec{R}=0} + \frac{1}{2!} \sum_{\alpha, \beta} \chi_{\alpha} \chi_{\beta} \left. \frac{\partial^2 V}{\partial x_{\alpha} \partial x_{\beta}} \right|_0 + \dots$$

Inserting into energy expression gives rise to the multipole expansion

$$U = \underbrace{q V(0)}_{\text{monopole}} - \underbrace{\vec{p} \cdot \vec{E}}_{\text{dipole}} \Big|_0 - \frac{1}{6} \sum_{i,j} \underbrace{Q_{ij}}_{\text{quadrupole}} \left. \frac{\partial E_i}{\partial x_j} \right|_0 + \dots$$

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 electro quadrupole interaction is governed by the product of these rank-2 tensors

$$H_Q = \underbrace{\overrightarrow{Q}^{(2)}}_{\substack{\text{nuclear} \\ \text{quadrupole} \\ \text{moment tensor (depends on nuclear charge distr.)}}} \underbrace{\overrightarrow{U}^{(2)}}_{\substack{\text{electric field gradient tensor (depends on electronic} \\ \text{charge distr.)}}}$$

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, $\vec{J}$. Likewise, for the case of nuclear properties (here, quadrupole moment), we can construct a rank-2 spherical tensor operator, $\hat{T}^{(2)}$ using the product of nuclear angular momentum operator $\vec{I}$ with itself, as follows:

$$T_{\pm 2}^{(2)} = I_{\pm 1}^2$$

$$T_{\pm 1}^{(2)} = \frac{1}{\sqrt{2}} [I_{\pm 1} I_0 + I_0 I_{\pm 1}]$$

$$T_0^{(2)} = \frac{1}{\sqrt{6}} [3I_0^2 - I^2]$$

This operator will act on the nuclear spin states $|I, m_I\rangle$

where $m_I = \underbrace{-I, \dots, +I}_{2I+1}$

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

$$\frac{\langle r_j m | T_q^{(K)} | r'_j m' \rangle}{\langle r_j m | U_q^{(K)} | r'_j m' \rangle} = \frac{\langle r_j || \hat{T}^{(K)} || r'_j \rangle}{\langle r_j || \hat{U}^{(K)} || r'_j \rangle} \equiv A$$

a const.

Thus, applying to our case $\begin{cases} K=2, j \rightarrow I, m \rightarrow I, q=0 \\ U^{(2)} \rightarrow Q^{(2)} \end{cases}$

$$\frac{1}{2} e Q \langle I, m_I = I | Q_0^{(2)} | I, m_I = I \rangle = A \langle I, I | T_0^{(2)} | I, I \rangle$$

this particular matrix element is chosen on purpose, as it has a physical significance in terms of so-called **spectroscopic quadrupole moment**, Q

$$\therefore A = \sqrt{\frac{3}{2}} \frac{eQ}{I(2I-1)}$$

!! 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

$$Q_{\pm 2}^{(2)} = \sqrt{\frac{3}{2}} \frac{eQ}{I(2I-1)} I_{\pm 1}^2$$

$$Q_{\pm 1}^{(2)} = \frac{\sqrt{3}}{2} \frac{eQ}{I(2I-1)} [I_{\pm 1} I_0 + I_0 I_{\pm 1}]$$

$$Q_2^{(2)} = \frac{1}{2} \frac{eQ}{I(2I-1)} [3I_0^2 - I^2]$$

Similarly, for the EFG tensor (first in terms of Cartesian components):

$$\begin{aligned} \frac{\partial^2}{\partial x_i \partial x_j} \left(\frac{-e}{4\pi\epsilon_0 r} \right) &= \frac{-e}{4\pi\epsilon_0} \left[\frac{3x_i x_j - r^2 \delta_{ij}}{r^5} \right], \quad i, j = x, y, z \\ &= V_{ij} = V_{ji} \end{aligned}$$

it is possible to establish a connection bet. the spherical harmonics

$l=2$ $Y_{2,m}$ and $\vec{U}^{(2)}$ as

$$\vec{U}^{(2)} = \frac{-e}{4\pi\epsilon_0} \frac{\vec{Y}^{(2)}}{r^3} \sqrt{\frac{4\pi}{5}}$$

So, if we express quadrupole Hamiltonian in terms of spherical tensor components:

$$H_Q = \vec{Q}^{(2)} \cdot \vec{U}^{(2)}$$

$$= Q_{+2}^{(2)} U_{-2}^{(2)} - Q_{+1}^{(2)} U_{-1}^{(2)} + Q_0^{(2)} U_0^{(2)} - Q_{-1}^{(2)} U_{+1}^{(2)} + Q_{-2}^{(2)} U_{+2}^{(2)}$$

If we switch to a coordinate system (EFG principal axes) where the off-diagonal Cartesian comp's $V_{ij} = 0$ for $i \neq j$, H_Q takes the form

$$H_Q = \frac{eQ}{4I(2I-1)} \left[V_{zz} (3I_z^2 - I^2) + (V_{xx} - V_{yy}) (I_{+1}^2 + I_{-1}^2) \right]$$

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

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \quad 0 \leq \eta \leq 1$$

$$\text{Defining: } \langle V_{zz} \rangle \equiv eq, \quad \langle V_{xx} - V_{yy} \rangle = \eta \langle V_{zz} \rangle = e\eta q$$

Hence, after integrating over electronic coordinates we get

$$H_Q = \frac{e^2 q Q}{4I(2I-1)} \left[3I_z^2 - I^2 + \eta (I_{+1}^2 + I_{-1}^2) \right]$$