IX. The Wigner-Eckart theorem

We will now touch on a result that relates very deeply to the rotational symmetry of space. However, its practical consequences are somewhat limited, and so we will only go over it in faint detail. The basic thing that we observe is that simply looking at how quantum states behave under rotation gave us a terrific amount of insight into the quantum theory of angular momentum. One can ask the corresponding question about operators: how do quantum operators behave when we rotate the system and what do we learn about operators in general (and most importantly, their matrix representations!) by studying their rotational character? We will find many connections to our results for the addition of angular momenta.

a. Spherical Tensors

Key to the statement of the Wigner-Eckart theorem is the definition of **spherical tensor operators.** This is rendered quite difficult by the fact that most chemists and physicists do not know what a spherical tensor is (never mind the operator part). This is just a geometrical concept, and once again we will find that the transition to quantum mechanics is trivial; all the "weirdness" is classical.

Under rotation, a classical observable T changes as
$$T(\mathbf{r}, \mathbf{p}) \xrightarrow{\quad R \quad} T(\mathbf{R}_n(\theta) \cdot \mathbf{r}, \mathbf{R}_n(\theta) \cdot \mathbf{p})$$
where "$\xrightarrow{\quad R \quad}$" indicates the act of rotation and $\mathbf{R}_n(\theta)$ is a matrix rotates vectors by an angle θ about a unit vector $\mathbf{n}$, as in the section on angular momentum. Now, the interesting fact is that there are certain **groups** of observables that are related to one another by rotation. Further, one finds that these groups always have an **odd** number of members! Any such group of observables with $2k+1$ elements is said to compose a spherical tensor of rank k (also called *irreducible* tensors). By convention, these operators are indexed with the $2k+1$ numbers $q = -k, -k+1, \ldots k-1, k$. Mathematically, we require that any rotated element of the tensor be expressible as a linear combination of the un-rotated elements:

$$T_k^q \xrightarrow{\ R\ } \sum_{q'=-k}^{k} T_k^{q'} D_{q'}^q$$

where the coefficients $D_{q'}^q$ will depend on the axis and angle of rotation. A few examples are helpful:

1) **Rank 0:** These are typically called scalars. Examples include all pure numbers and the dot product of any two vectors, for example:

$$\mathbf{r}^T \cdot \mathbf{r} \xrightarrow{\ R\ } \mathbf{r}^T \cdot \mathbf{R}_n^T(\theta) \cdot \mathbf{R}_n(\theta) \cdot \mathbf{r} = \mathbf{r}^T \cdot \mathbf{r}$$

R is unitary

2) **Rank 1:** These are typically called vectors. Examples include angular momentum ($\mathbf{L}$) as well as $\mathbf{r}$ and $\mathbf{p}$:

$$r_i \xrightarrow{\ R\ } (\mathbf{R}_n(\theta) \cdot \mathbf{r})_i = \sum_{j=1}^{3} (\mathbf{R}_n(\theta))_{ij} r_j$$

If we want to associate the components of the vector with the $q = -1, 0, 1$ ordering, it is convenient to define

$$r_{+1} = x + iy \qquad r_0 = z \qquad r_{-1} = x - iy .$$

Note the similarity with angular momentum and the $\hat{J}_+, \hat{J}_z, \hat{J}_-$ operators.

3) **Rank 2:** No special name here, but one can typically extract a spherical tensor of rank 2 from a matrix $\mathbf{M} = \mathbf{u} \otimes \mathbf{v}$ (where $\mathbf{u}$ and $\mathbf{v}$ are vectors) by subtracting its trace (a scalar) and a term that looks like the cross product of $\mathbf{u}$ and $\mathbf{v}$ (a vector). To be precise:

$$\tilde{M}_{ij} = M_{ij} - \frac{\mathbf{u}^T \cdot \mathbf{v}}{3} \delta_{ij} - \frac{u_i v_j - u_j v_i}{2}$$

The original matrix had 3x3=9 components so removing 1 with the scalar and 3 with the vector leaves 9-1-3=5 left-over components that conveniently make up a second rank tensor $\tilde{\mathbf{M}}$.

Overall, we stress the resemblance of a spherical tensor of rank k to a system with k units of angular momentum.

b. <u>Spherical tensor operators</u>

To put it succinctly, a spherical tensor operator in quantum mechanics is simply an operator that behaves like a spherical tensor under rotations. Thus, for a tensor operator of rank k:

$$\hat{T}_k^q \Rightarrow \sum_{q'=-k}^{k} \hat{T}_k^{q'} D_{q'}^q$$

The quantum definition is more general than the classical one, in that it encompasses (in principle) a greater variety of possible rotations, including ones in "spin" space. However, in practice we will be most interested in physical rotations.

c. <u>The Wigner –Eckart Theorem</u>

The Wigner-Eckart theorem tells us what information we can discern about the matrix elements of a spherical tensor operator $\hat{\mathbf{T}}_k$ between angular momentum eigenstates. The reason we are interested in this is that we know that tensor operators have a special relationship to rotations, and these rotations are generated by angular momentum. Note that this is only interesting if the eigenstates and the tensor are defined with respect to the same type of rotation. For example, if the operators form a spherical tensor with respect to spin rotations, there need be no special relationship of these operators between orbital angular momentum eigenstates.

We thus wish to compute a matrix element like:

$$\langle \alpha', j', m' | T_k^q | \alpha, j, m \rangle$$

where α and α' symbolize the values of all other quantum numbers in the system (e.g. principal quantum number, spins, vibrational quantum numbers, etc.). The Wigner-Eckart theorem tells us

$$\langle \alpha', j', m' | T_k^q | \alpha, j, m \rangle = \langle j, m; k, q | j', m'; j, k \rangle \langle \alpha', j' \| T_k \| \alpha, j \rangle$$

the first term is just the CG coefficient for two angular momenta (of magnitudes j and k) coupling together to make a total angular momentum of magnitude j'. The second term is called the *reduced* matrix element. The theorem does not give us any way to construct this, but the important point is it depends only on α, j', j and k. We

will not prove this result, but a proof can be found in several different text books (e.g. Sakurai p.239 and Merzbacher, p. 396, but not CTDL).

What insight does this give us? Well, first it is important to note that this result jives with our observation that $\hat{\mathbf{T}}_k$ behave as if they had angular momentum of magnitude k - the CG coefficients involve coupling j units of angular momentum (from the ket) with k additional units to make a total angular momentum j' (in the bra).

Where else could the angular momentum be coming from, if not $\hat{\mathbf{T}}_k$? Second, this allows us to apply our selection rules for the CG coefficients to drastically reduce the number of coefficients we calculate. Specifically, the matrix element is zero unless:
$$q = m' - m \quad \text{and} \quad |j - j'| \le k \le j + j'.$$
The first relation is just conservation of total m applied to the CG coefficient and the second is the triangle rule at work. Finally, it is important to note that the reduced matrix element does not depend on which element of $\hat{\mathbf{T}}_k$ we choose (i.e. does not depend on q) and it does not depend on m or m'. This drastically reduces the work we have to do in practice. For example, if we want to compute the matrix elements of z between the Hydrogenic eigenfunctions, we note that z is a component of the rank 1 tensor $\mathbf{r}$ and so:
$$\langle n', l', m' | z | n, l, m \rangle = \langle l, m; 1, 0 | l', m'; l, 1 \rangle \langle n', l' \| z \| n, l \rangle$$
which implies that this matrix element is zero unless
$$m' - m = 0 \quad \text{and} \quad |j - j'| \le k \le j + j'$$
which is more familiar as
$$\Delta m = 0 \quad \text{and} \quad \Delta j = 0, \pm 1$$
with $j = j' = 0$ excluded. This is an example of a *selection rule*. You will see a great many more relations like this next semester.