**Lecture 16** Title: **Wigner-Eckart theorem**

Page-1

In this lecture, we will see the relation between the rotation operator and angular momentum

We will learn the calculation of matrix elements of scalar and vector quantities.

We will see that these matrix elements knowledge can be extrapolated to form the general Wigner-Eckart theorem.

We will also understand the use of Wigner-Eckart theorem to evaluate the transition selection rules.

Page-2

Angular momentum operators have a close relationship to rotations. Let us consider a coordinate system $a \equiv (X, Y, Z)$ as shown in figure-16.1. This system rotates at an infinitesimal $\delta\alpha$ around the Z axis to form the new axis system $a' \equiv (X', Y', Z')$.

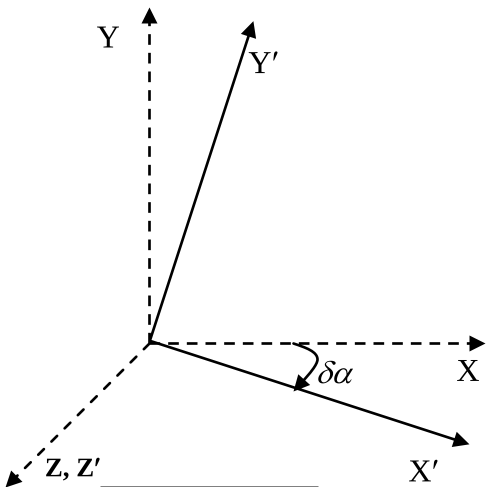


Figure-16.1

The rotation operator $R$ is related to the angular momentum as $R = 1 - i\,\delta\,\alpha\,J \cdot u$ where $u$ is the unit vector along the rotation axis Z.

Any scalar quantity is invariant under the rotation of coordinate system. Thus scalar operator commutes with the rotation oprator.

$$\langle J'm' | RA | Jm \rangle = \langle J'm' | AR | Jm \rangle$$

Thus

$$J' - J = 0 \Rightarrow \Delta J = 0$$

$$m' - m = 0 \Rightarrow \Delta m = 0$$

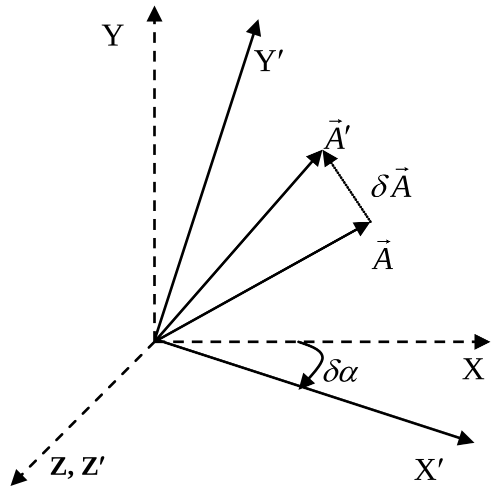


Figure-16.2

Now any vector $\vec{A}$ in the old coordinate system $a \equiv (X, Y, Z)$ as shown in figure-16.2 is related to the same vector $\vec{A}'$ in the new coordinate system $a' \equiv (X', Y', Z')$ as

$$\vec{A}' = \vec{A} + \delta\vec{A} = \vec{A} + \delta\alpha\left(\vec{u} \times \vec{A}\right)$$

In the following, we will establish a relationship between angular momentum operator and the vector.

We are removing the arrow sign for the sake of simplicity, but remember $A$ is a vector

$$\left\langle a' \middle| A \middle| a' \right\rangle = \left\langle a \middle| A \middle| a \right\rangle + \delta\alpha\, u \times \left\langle a \middle| A \middle| a \right\rangle$$

$$\left\langle a' \middle| R^{-1} A R \middle| a' \right\rangle = \left\langle a \middle| A \middle| a \right\rangle + \delta\alpha\, u \times \left\langle a \middle| A \middle| a \right\rangle$$

$$R^{-1}\vec{A}R = \vec{A} + \delta\alpha\left(\vec{u} \times \vec{A}\right)$$

Now substituting the value of the rotation operator,

$$
\begin{aligned}
&(1+i\,\delta\alpha\,J\cdot u)\,A(1-i\,\delta\alpha\,J\cdot u)=A+\delta\alpha\,(u\times A)\\
\Rightarrow\ & A-i\,\delta\alpha\,A(J\cdot u)+i\,\delta\alpha\,(J\cdot u)A=A+\delta\alpha\,(u\times A)\\
\Rightarrow\ & -i\,\delta\alpha\left[A,(J\cdot u)\right]=-i^2\delta\alpha\,(u\times A)\\
\Rightarrow\ & \left[A,(J\cdot u)\right]=i\,(u\times A)
\end{aligned}
$$

Now using this relation we can establish the commutation relations.

$$
\begin{bmatrix}
i & j & k\\
u_x & u_y & u_z\\
A_x & A_y & A_z
\end{bmatrix}
$$

$$
\begin{aligned}
\left[A_z,(J\cdot u)\right]&=i\left(u_xA_y-u_yA_x\right)\\
\left[A_x,(J\cdot u)\right]&=i\left(u_yA_z-A_yu_z\right)\\
\left[A_y,(J\cdot u)\right]&=i\left(A_xu_z-u_xA_z\right)
\end{aligned}
$$

$$
\begin{array}{lll}
\left[A_z,J_z\right]=0 & \left[A_x,J_z\right]=0 & \left[A_y,J_z\right]=-i\,A_z\\
\left[A_z,J_x\right]=i\,A_y & \left[A_x,J_x\right]=i\,A_z & \left[A_y,J_x\right]=0\\
\left[A_z,J_y\right]=-i\,A_x & \left[A_x,J_y\right]=-i\,A_y & \left[A_y,J_y\right]=i\,A_x
\end{array}
$$

$A_z$ And $J_z$ commuts.

$A_z J_z - J_z A_z = 0$

When $J = J'$

$$\langle Jm' | A_z J_z | Jm \rangle - \langle Jm' | J_z A_z | Jm \rangle = 0$$

$$\sum_{J''m''} \langle Jm' | A_z | J''m'' \rangle - \langle J''m'' | J_z | Jm \rangle - \sum_{J''m''} \langle Jm' | J_z | J''m'' \rangle - \langle J''m'' | A_z | Jm \rangle = 0$$

$$\langle Jm' | A_z | Jm \rangle (m - m') = 0$$

When $m = m'$, $\langle Jm' | A_z | Jm \rangle \neq 0$

Now the commutation with $A_+$

$$\begin{aligned}
[A_{+,} J_z] &= \frac{1}{\sqrt{2}} [A_x + iA_y, J_z] \\
&= \frac{1}{\sqrt{2}} \{ [A_x, A_z] + [A_y, J_y] \} \\
&= \frac{1}{\sqrt{2}} [-iA_y +, i(iA_x)] \\
&= -\frac{1}{\sqrt{2}} [A_x + iA_y] = -A_+
\end{aligned}$$

So,

$$A_+ J_z - J_z A_+ = -A_+$$
$$A_+ J_z - J_z A_+ + A_+ = 0$$
$$when \quad J = J''$$

$$\langle Jm' | A_+ J_z | Jm \rangle - \langle Jm' | J_z A_+ | Jm \rangle + \langle Jm' | A_+ | Jm \rangle = 0$$
$$\langle Jm' | A_+ | Jm \rangle - \langle Jm' | A_z | Jm \rangle m' + \langle Jm' | A_+ | Jm \rangle = 0$$
$$\langle Jm' | A_+ | Jm \rangle (m - m' + 1) = 0$$
$$so\, m' = m + 1$$

Now, the relation between A and J's matrix elements

$$[A_{+,} J_+] = [A_x + iA_y, J_x + iJ_y] = 0$$

$$when \;\; J = J'$$

$$\langle Jm' | A_+ J_+ | Jm \rangle - \langle Jm' | J_+ A_+ | Jm \rangle$$
$$\langle Jm+2 | A_+ | Jm+1 \rangle \langle Jm+1 | J_+ | Jm \rangle = \langle Jm+2 | J_+ | Jm+1 \rangle \langle Jm+1 | A_+ | Jm \rangle$$

$$\frac{\langle Jm+z | A_+ | Jm+1 \rangle}{\langle Jm+1 | A_+ | Jm \rangle} = \frac{\langle Jm+z | J_+ | Jm+1 \rangle}{\langle Jm+1 | J_+ | Jm \rangle} = a$$

This is true only if $\langle Jm+1 | A_+ | Jm \rangle = a \langle Jm+1 | J_+ | Jm \rangle$
Where a is a constant.

Now,

$$[A_{z,}J_{+}]=[A_{z,}J_x+iJ_y]$$
$$=iA_y+i\left(-iA_x\right)$$
$$=iA_x+iA_y=A_{+}$$

$$A_zJ_{+}-J_{+}A_z+iA_{+}=0$$
$$\left\langle Jm'|A_{+}J_{+}|Jm\right\rangle-\left\langle Jm'|J_{+}A_z|Jm\right\rangle-\left\langle Jm'|A_{+}|Jm\right\rangle=0$$
$$\left\langle Jm+1|A_z|Jm+1\right\rangle-\left\langle Jm+1|J_{+}|Jm\right\rangle-\left\langle Jm+1|J_{+}|Jm\right\rangle\left\langle Jm|A_z|Jm\right\rangle-a\left\langle Jm+1|J_{+}|Jm\right\rangle=0$$

$$[\left\langle Jm+1|A_z|Jm+1\right\rangle-\left\langle Jm|A_z|Jm\right\rangle-a]\left\langle Jm+1|J_{+}|Jm+1\right\rangle=0$$
$$\left\langle Jm+1|A_z|Jm+1\right\rangle-\left\langle Jm|A_z|Jm\right\rangle=a$$

This relation is true if we take

$$\left\langle J\,m|A_z|J\,m\right\rangle=a\,m+b$$
$$\left\langle J\,m+1|A_z|J\,m+1\right\rangle=a\left(m+1\right)+b$$

$$\left\langle J\,m+1|A_z|J\,m+1\right\rangle-\left\langle J\,m|A_z|J\,m\right\rangle=\cancel{am}+a+\cancel{b}-\cancel{am}-\cancel{b}=a$$

<u>What is the value of b?</u>

$$A_z=\sum_{m=-J}^{+J}\left\langle J\,m|A_z|J\,m\right\rangle=\sum_{m=-J}^{+J}a\,m+b=\left(2J+1\right)b$$
$$A_z=\frac{1}{i}\left[A_x,J_y\right]=\frac{1}{i}\left(A_xJ_y-J_yA_x\right)$$
$$Trace\,A_z=Tr\,\frac{1}{i}\left(A_xJ_y-J_yA_x\right)\qquad\left[Tr\;AB=Tr\;BA\right]$$
$$=0$$
$$So,\ \left(2J+1\right)b=0\qquad or,\ b=0$$

$$\left\langle J\,m|A_z|J\,m\right\rangle=a\,m=a\left\langle J\,m|J_z|J\,m\right\rangle$$
$$\left\langle J\,m+1|A_{+}|J\,m\right\rangle=a\left\langle J\,m+1|J_{+}|J\,m\right\rangle$$
$$\left\langle J\,m+1|A_{-}|J\,m\right\rangle=a\left\langle J\,m+1|J_{-}|J\,m\right\rangle$$

In general form:

$$\left\langle J\, m' \,|\, A_q^1 \,|\, J\, m \right\rangle = a \left\langle J\, m' \,|\, J_q \,|\, J\, m \right\rangle$$

$$\left.\begin{array}{ll} m' = m & when\ q = 0 \\ m' = m+1 & when\ q = +1 \\ m' = m-1 & when\ q = -1 \end{array}\right\}$$

$$\left\langle J' m' \,|\, A'_q \,|\, J\, m \right\rangle = a \left\langle J' m' \,|\, U'_q \,|\, J\, m \right\rangle$$

$$\Rightarrow \frac{\left\langle J' m' \,|\, A'_q \,|\, J\, m \right\rangle}{\left\langle J' m' \,|\, U'_q \,|\, J\, m \right\rangle} = a$$

From the above matrix elements relations we write the general form of Wigner Eckart theorem.

Wigner Eckart theorem:

$$\left\langle J' m' \,|\, T_q^k \,|\, J\, m \right\rangle = \underbrace{\left\langle J' k\, m' q \,|\, j' k\ j\, m \right\rangle}_{\text{Coupling coefficient / Symmetry part}} \underbrace{\left\langle J' \,|\, T^k \,|\, J \right\rangle}_{\text{Reduced matrix element / Physical interaction}}$$

$$then \quad \left\langle J' m' \,|\, U_q^k \,|\, J\, m \right\rangle = \left\langle J' k\, m' q \,|\, J' k\ j\, m \right\rangle \left\langle J' \,|\, U^k \,|\, J \right\rangle$$

Application:

$$\left\langle J' m' \,|\, A_q^1 \,|\, J\, m \right\rangle = \left\langle J' \,|\, A \,|\, J \right\rangle \left\langle J' 1 m' q \,|\, J' 1 J\, m \right\rangle$$

$$\left\langle J' m' \,|\, J_q \,|\, J\, m \right\rangle = \left\langle J' \,|\, J \,|\, J \right\rangle \left\langle J' 1 m' q \,|\, J' 1 J\, m \right\rangle$$

$$\left\langle J' m' \,|\, A_q^1 \,|\, J\, m \right\rangle = \left\{ \frac{\left\langle J' \,|\, A \,|\, J \right\rangle}{\left\langle J' \,|\, J \,|\, J \right\rangle} \right\} \left\langle J' m' \,|\, J_q \,|\, J\, m \right\rangle$$

$$= a \left\langle J' m' \,|\, J_q \,|\, J\, m \right\rangle$$

Page-9

General Statement:

$$\left\langle J'm'|T_q^k|J\,m\right\rangle = \frac{1}{\sqrt{2J+1}}\left\langle J'k\,m'q\,|\,J'k\,J\,m\right\rangle\left\langle J\,|T^k|\,J\right\rangle$$

$$= (-1)^{J-m}\frac{1}{\sqrt{2j+1}}\begin{pmatrix} J' & k & J \\ -m' & q & m \end{pmatrix}\left\langle J\,\|T^k\|\,J\right\rangle$$

Here $T_q^k$ is a tensor and $T^k$ is the reduced tensor.

If we know the three j properties, we can evaluate selection rule for which matrix element will be zero.

Properties of 3j:

$m' = m + q$

$$\Delta(j_1\,j_2\,j):\begin{cases} j_1 + j_2 + j = n \\ j_1 + j_2 - j \ge 0 \\ j_1 - j_2 + j \ge 0 \\ -j_1 + j_2 + j \ge 0 \end{cases}$$

For scalar

$$\left\langle J'm'|T_0^0|J\,m\right\rangle = 0 \quad \textit{unless} \quad J'+0+J = n$$

$$\begin{matrix} J' = J \\ m' = m \\ J'+J \ge 0 \end{matrix} \qquad \left.\begin{matrix} J'+0+J \ge 0 \\ J'+0+J \ge 0 \\ J'+0+J \ge 0 \end{matrix}\right\} \left\{\begin{matrix} J'-J = 0 \Rightarrow \Delta J = 0 \\ m'-m = 0 \Rightarrow \Delta m = 0 \end{matrix}\right\}$$

For vector

$$\left\langle J'm'|T_q^1|J\,m\right\rangle = 0 \quad \textit{unless} \quad \Delta J = 0, \pm 1$$

$$J'+J \ge 1$$

$$m' = m - q \quad (q = 1, 0, -1)$$

$$\Delta m = 0, \pm 1$$

Now we will evaluate the selection rules for the transitions

We know that in the electric dipole approximation the dipole matrix elements $\langle \psi' | e\vec{r} | \psi \rangle$ should be evaluated. If the dipole matrix element is nonzero the transition is allowed, otherwise, it is forbidden.

Let us take the case of central field orbitals. The wavefunctions are characterized by the quantum numbers $n, l, m_l, s, m_s$
so

$$\langle s'm_s' | \langle l'm_l' | e\vec{r} | lm_l \rangle | sm_s \rangle = \langle s'm_s' | sm_s \rangle \langle l'm_l' | e\vec{r} | lm_l \rangle$$

The dipole being the space operator, does not operator on spin functions. So $\Delta s = 0$.
Now $e\vec{r}$ is a vector. So, we evaluate the vector matrix elements

$$\left\langle l'm' | T_q^1 | l\, m \right\rangle = 0 \qquad unless \;\; \begin{aligned} &\Delta l = 0, \pm 1 \\ &l' + l \geq 1 \\ &\Delta m = 0, \pm 1 \end{aligned}$$

Although it shows $\Delta l = 0, \pm 1$, but $\langle l' | \vec{r} | l \rangle = 0$ if $\Delta l = 0$ due to parity. The $e\vec{r}$ connects only opposite parity states. Thus the selection rules are

$$\Delta l = \pm 1$$
$$l' + l \geq 1$$
$$\Delta m = 0, \pm 1$$

Now for the transitions between the terms. The wavefunctions are characterized by $L, M_L, S, M_S$

$$\langle S'M_s' | \langle L'M_L' | e\vec{r} | LM_L \rangle | SM_S \rangle = \langle S'M_s' | sm_s \rangle \langle L'M_L' | e\vec{r} | LM_L \rangle$$

Using the same argument

$$\left\langle L'M' | T_q^1 | LM_L \right\rangle = 0 \;\; unless \;\; \begin{aligned} &\Delta L = 0, \pm 1, \quad \Delta S = 0 \\ &L' + L \geq 1 \\ &\Delta M_L = 0, \pm 1 \end{aligned}$$

How to evaluate a:

$$J\cdot A = J_x A_x + J_y A_y + J_z A_z$$
$$= \frac{1}{2}\left[J_+ A_- + J_- A_+\right] + J_z A_z$$

$$\left\langle J\,m \,|\, J\cdot A \,|\, J\,m\right\rangle = \sum_{m''}\frac{1}{2}\left\langle J\,m \,|\, J_+ \,|\, J\,m''\right\rangle\left\langle J\,m'' \,|\, A_- \,|\, J\,m\right\rangle + \frac{1}{2}\sum_{m''}\left\langle J\,m \,|\, J_- \,|\, J\,m''\right\rangle\left\langle J\,m'' \,|\, A_+ \,|\, J\,m\right\rangle$$
$$+\sum_{m''}\left\langle J\,m \,|\, J_z \,|\, J\,m''\right\rangle\left\langle J\,m'' \,|\, A_z \,|\, J\,m\right\rangle$$
$$= \frac{1}{2}a\sum_{m''}\left\langle J\,m \,|\, J_+ \,|\, J\,m''\right\rangle\left\langle J\,m'' \,|\, J_- \,|\, J\,m\right\rangle + \frac{1}{2}a\sum_{m''}\left\langle J\,m \,|\, J_- \,|\, J\,m''\right\rangle\left\langle J\,m'' \,|\, J_+ \,|\, J\,m\right\rangle$$
$$+\sum_{m''}\left\langle J\,m \,|\, J_z \,|\, J\,m''\right\rangle\left\langle J\,m'' \,|\, A_z \,|\, J\,m\right\rangle$$
$$= a\left\langle J\,m \,\middle|\, \frac{1}{2}\left(J_+ J_- + J_- J_+\right) J_z J_z \,\middle|\, J\,m\right\rangle$$
$$= a\left\langle J\,m \,|\, J_x^2 + J_y^2 + J_z^2 \,|\, J\,m\right\rangle$$
$$= a\left\langle J\,m \,|\, J^2 \,|\, J\,m\right\rangle = a\,J\left(J+1\right)$$

$$\left\langle J\,m \,|\, A\cdot J \,|\, J\,m\right\rangle = \sum_{m'}\left\langle J\,m \,|\, A \,|\, J\,m'\right\rangle\left\langle J\,m' \,|\, J \,|\, J\,m\right\rangle$$

$$= a\,J\left(J+1\right)$$
$$\Rightarrow a = \frac{\left\langle J\,m \,|\, A\cdot J \,|\, J\,m\right\rangle}{J\left(J+1\right)}$$
$$S\,o, \left\langle J\,m' \,|\, A \,|\, J\,m\right\rangle = \frac{\left\langle J\,m \,|\, A\cdot J \,|\, J\,m\right\rangle}{J\left(J+1\right)}\left\langle J\,m' \,|\, J \,|\, J\,m\right\rangle$$

This is a special form of W-E theorem known as Lande’ formula. We will use this relation later.

In this lecture, we understood the calculation of matrix elements of scalar and vector quantities.

We use these matrix elements to extrapolate the general form of Wigner-Eckart theorem.

This is used to evaluate the transition selection rules.

We will also use the special form of W-E theorem known as Lande' formula later.