Symmetry and spectroscopy

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Transition between initial and final state

$$\left\langle f \left| \mathbf{A}_0 \cdot \mathbf{p} e^{i\mathbf{k}\cdot\mathbf{r}} \right| i \right\rangle \tag{1}$$

Performing a Taylor expansion of the exponential factor gives

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} + \ldots$$

The first order approximation, $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$.

This corresponds to the electronic dipole transition. With radiation incident in the x-direction, we get

$$\langle f \left| p_x \right| i \rangle = \frac{im}{\hbar} \left\langle f \left| x(E_f - E_i) \right| i \right\rangle \tag{2}$$

Higher order transitions, include $i\mathbf{k}\cdot\mathbf{r}$.
Again with radiation incident in the x-direction

$$\langle f\,|\mathbf{A}_0\cdot\mathbf{p}(1+i\mathbf{k}\cdot\mathbf{r})|\,i\rangle = \left\langle f\,\left|A_0 p_y\,(1+ikx)\right|\,i\right\rangle \tag{3}$$

Using $\hbar l_z = xp_y - p_x y$

$$xp_y = \frac{\hbar}{2}l_z + \frac{1}{2}(xp_y + p_x y) \tag{4}$$

$$\left\langle f\,\left|p_y x\right|\,i\right\rangle = \frac{1}{2}\left(\langle f\,|\hbar l_z|\rangle + \left\langle f\,\left|(xp_y + p_x y)\right|\,i\right\rangle\right) \tag{5}$$

The first term here corresponds to the magnetic dipole contribution.
The second term can be rewritten as to the form

$$\langle f\,|xy|\,i\rangle \tag{6}$$

This is the electric quadrupole transition.

We have seen that the electric dipole moment operator transforms like coordinates (x,y,z). (polar vector). For example, consider a rotation of angle φ around the z-axis

$$\Gamma^V(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{7}$$

This gives the character of the transformation

$$\chi^V(\varphi) = 1 + 2\cos\varphi \tag{8}$$

If this is combined with an inversion, there is a sign change

$$\Gamma^V(\varphi) = \begin{pmatrix} -\cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & -\cos\varphi & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{9}$$

This causes the character to change sign as well

$$\chi^V(\varphi, i) = -(1 + 2\cos\varphi) \tag{10}$$

For the magnetic dipole moment, it will instead transform like rotations (an axial vector). For the rotation, this is the same, but it is invariant under rotations. Hence the character of the magnetic dipole moment operator will always be

$$\chi^A(\varphi) = 1 + 2\cos\varphi \tag{11}$$

To to illustrate how the coordinates transform, let us use C_{3v} as an example. The character table of C_{3v} looks like

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y), (R_x, R_y)$

let us first check how each operator changes the vector r

$$P_E\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\y\\z\end{pmatrix} \qquad P_{C_3}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-\frac{x}{2}+\frac{\sqrt{3}y}{2}\\-\frac{\sqrt{3}x}{2}-\frac{y}{2}\\z\end{pmatrix}$$

$$P_{\sigma_v}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\-y\\z\end{pmatrix} \tag{12}$$

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	$(x,y),(R_x,R_y)$

Electric dipole - coordinates

Magnetic dipole - Rotations

Looking at

$$\left\langle f \left| \mathbf{A}_0 \cdot \mathbf{p} e^{i\mathbf{k}\cdot\mathbf{r}} \right| i \right\rangle$$

the initial and final states must transform like irreducible representations of the group. since the operator also transform like IR we can make a selection rule.

$$\left\langle \Gamma_i \left| \Gamma_T \right| \Gamma_f \right\rangle = \left\langle \Gamma_i | \Gamma_T \otimes \Gamma_f \right\rangle \neq 0 \tag{13}$$

The direct product can be decomposed into a sum of irreducible representations using the following relation

$$(\gamma\beta|\alpha) = \frac{1}{g} \sum_{classes} r_a \chi^{\beta}(K_a) \chi^{\gamma}(K_a) \chi^{\alpha}(K_a)^* \tag{14}$$

For example in C_{3v} the direct product table will look like this

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	$A_1 + A_2 + E$

electric dipole transitions.

z component - A_1

x,y - E

magnetic dipole transitions

z component - A_2

x,y - E

LCAO-MO model for NH_3

reducible representation for H_3

C_{3v}	E	$2C_3$	$3\sigma_v$
χ	3	0	1

$$\Gamma_{reducible} = A_1 + E$$

can construct molecular orbitals of A_1 and E symmetry