Chapter 13. Electron Spin Double Groups

Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (1998), Chap. 18.*

13.1 Half-integer Angular Momenta and the Operation R

While determining the classification of the electronic wave function in Section 9.2 we found out that cases where there is a strong spin-orbit coupling (i.e., Hund's case a)) need special attention, as the electrons are tied to the molecule-fixed axes and their spins must be quantized along this set of axes. Because of this the spin eigenfunctions are not totally symmetric and the symmetry and classification of the electronic wave functions cannot be determined without considering them.

We considered the full rotation group K in Section 10.2 and showed that the character of its only class is given by

$$\chi^{(J)}\left[R^{\alpha}\right]=\frac{\sin\left[\left(J+1/2\right)\alpha\right]}{\sin\left(\alpha/2\right)}, \tag{13.1}$$

where R^{α} is for a rotation by an angle α, as can be calculated from the representation provided by the set of wave functions $D_{mk}^{(J)}\left(\phi,\theta,\chi\right)$ of $K\left(\mathrm{mol}\right)$ introduced in equation (4.88) of Chapter 4. We can also easily verify from equation (13.1) that

$$\begin{aligned}\chi^{(J)}\left[R^{\alpha+2\pi}\right]&=\left(-1\right)^{2J}\chi^{(J)}\left[R^{\alpha}\right]\\ \chi^{(J)}\left[R^{\alpha+4\pi}\right]&=\chi^{(J)}\left[R^{\alpha}\right].\end{aligned} \tag{13.2}$$

Something interesting happens when we consider cases where J is half-integer (remember that $\mathbf{J}=\mathbf{N}+\mathbf{S}$, with $\mathbf{S}$ the electronic spin) where we find that

$$\chi^{(J)}\left[R^{\alpha+2\pi}\right]=-\chi^{(J)}\left[R^{\alpha}\right]. \tag{13.3}$$

It would thus appear that the character of a rotation is ambiguous for half-integer angular momenta. This is because we expect that

$$\begin{aligned}\chi^{(J)}\left[R^{\alpha+2\pi}\right]&=\chi^{(J)}\left[R^{\alpha}R^{2\pi}\right]\\ &=\chi^{(J)}\left[R^{\alpha}\right],\end{aligned} \tag{13.4}$$

since a rotation by 2π should be equal to the identity operator E. It should be clear that equations (13.3) and (13.4) are at odds with each other. This apparent conflict can be resolved if we abandon the notion that $R^{2\pi}=E$… Instead we will supplement the MS group of a molecule (for cases where J is half integer) by an operator $R \equiv R^{2\pi}$ (and its product with all of the elements of the MS group) and treat it as different from E. That is to say, we now insist that

$$R^{\alpha+2\pi} \neq R^{\alpha}, \tag{13.5}$$

and as importantly that

$$R^{\alpha+4\pi} = R^{\alpha}, \tag{13.6}$$

or

$$R^{4\pi} \equiv R^{0} = E. \tag{13.7}$$

Furthermore, we require that R commutes with all elements of the MS group. This augmented group (it is twice as big as the MS group) is called the *spin double group*. It should be noted that the MS group is not a subgroup of the corresponding spin double group. The spin double group of the full rotation group is denoted by K^2.

13.1.1 **Euler Angles Transformations**

Although we need R to transform the Euler angles in the functions $D_{mk}^{(J)}(\phi,\theta,\chi)$ (where $J, k,$ and m come into play; see Section 13.1.2 below), it must obviously leave no imprint on the Euler angles when dealing with the actual rotations of the molecule-fixed axes in relation to the space-fixed axes. A simple way to allow for these is to extend the ranges of the Euler angle to $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 4\pi$, and $0 \leq \chi \leq 4\pi$, and defining

$$R^{2\pi}(\theta,\phi,\chi) = (\theta,\phi,\chi+2\pi) \text{ or } (\theta,\phi+2\pi,\chi). \tag{13.8}$$

(This is consistent with the way we calculated equation (13.1) in Chapter10, and the fact that for a given J the functions $D_{mk}^{(J)}$ transform among each other under the effect of the elements of the MS (and now the spin double) group; we therefore prefer that R not affect θ.) Therefore, if we have $R^{4\pi} = \left(R^{2\pi}\right)^2 = R^0$, then it must be that

$$R^{0}(\theta,\phi,\chi) = (\theta,\phi,\chi) \text{ or } (\theta,\phi+2\pi,\chi+2\pi). \tag{13.9}$$

That is, there are two possible transformations for the Euler angles under the identity element. Similarly, referring to Table 9-3 on page 154 we find that

$$\begin{aligned} R_z^{\beta}(\theta,\phi,\chi) &= (\theta,\phi,\chi+\beta) \text{ or } (\theta,\phi+2\pi,\chi+2\pi+\beta) \\ R_\alpha^{\pi}(\theta,\phi,\chi) &= (\pi-\theta,\phi+\pi,2\pi-2\alpha-\chi) \text{ or } (\pi-\theta,\phi+3\pi,4\pi-2\alpha-\chi), \end{aligned} \tag{13.10}$$

and

$$\begin{aligned} R^{2\pi} R_z^{\beta}(\theta,\phi,\chi) &= (\theta,\phi,\chi+2\pi+\beta) \text{ or } (\theta,\phi+2\pi,\chi+\beta) \\ R^{2\pi} R_{\alpha}^{\pi}(\theta,\phi,\chi) &= (\pi-\theta,\phi+\pi,4\pi-2\alpha-\chi) \text{ or } (\pi-\theta,\phi+3\pi,2\pi-2\alpha-\chi). \end{aligned} \tag{13.11}$$

The existence of two representations is not a problem in practice, as they both lead to the same solution.

It is possible to determine classes, irreducible representations, and character tables for any spin double group, just as it is the case for any MS group. Two examples of character tables for spin double groups are given below.

Table 13-1 – The character table of the $C_{2\mathrm{v}}(\mathrm{M})^2$ spin double group.

$C_{2\mathrm{v}}(\mathrm{M})^2$:	E	(12)	E^*	$(12)^*$	R
	1	2	2	2	1
R_{rot} :	R^0	R_b^{π}	R_c^{π}	R_a^{π}	$R^{2\pi}$
A_1 :	1	1	1	1	1
A_2 :	1	1	−1	−1	1
B_1 :	1	−1	−1	1	1
B_2 :	1	−1	1	−1	1
$E_{1/2}$:	2	0	0	0	−2

In general, character tables, such as Table 13-1 for the $C_{2\mathrm{v}}(\mathrm{M})^2$ spin double group, can have ordinary permutation (or permutation-inversion) R-type operators within one class. In $C_{2\mathrm{v}}(\mathrm{M})^2$, $\{(12),R(12)\}$, $\{E^*,RE^*\}$, and $\{(12)^*,R(12)^*\}$ are different classes, for example. Also, the MS group corresponding to a spin double group is restricted to the sub-table confined on the "top-left" corner of the latter (the $C_{2\mathrm{v}}(\mathrm{M})$ character table is delimited by the dotted lines in Table 13-1).

Table 13-2 – The (simplified) character table for the $C_{3\mathrm{v}}(\mathrm{M})^2$ spin double group.

$C_{3\mathrm{v}}(\mathrm{M})^2$:	E	(123)	$(23)^*$	R	$R(123)$	
	1	2	6	1	2	
R_{rot} :	R^0	$R_z^{2\pi/3}$	$R_{\pi/2}^{\pi}$	$R^{2\pi}$	$R_z^{8\pi/3}$	
A_1 :	1	1	1	1	1	
A_2 :	1	1	−1	1	1	
E :	2	−1	0	2	−1	
$E_{1/2}$:	2	1	0	−2	−1	
$E_{3/2}$:	2	−2	0	−2	2	: sep

For more complicated tables some classes can be grouped together to simplify the table. For example, in the case of $C_{3\mathrm{v}}(\mathrm{M})^2$ in Table 13-2 the column for the $(23)^*$ class actually stands for two classes that have complex conjugate characters for the $E_{3/2}$ irreducible representation; "sep" in the last column stands for "separable". The complete, unabridged, character table can then be easily guessed. The full character table for $C_{3\mathrm{v}}(\mathrm{M})^2$ is given in Table 13-3; it is seen that $E_{3/2}$ is actually made up of two one-dimensional irreducible representations (take note that $E_{1/2}$ is not separable and is a true two-dimensional irreducible representation).

Table 13-3 - The full character table for the $C_{3\mathrm{v}}(\mathrm{M})^2$ spin double group.

$C_{3\mathrm{v}}(\mathrm{M})^2$:	E	(123)	$(23)^*$	R	$R(123)$	$R(23)^*$
	1	2	3	1	2	3
R_{rot} :	R^0	$R_z^{2\pi/3}$	$R_{\pi/2}^{\pi}$	$R^{2\pi}$	$R_z^{8\pi/3}$	$R_{\pi/2}^{3\pi}$
A_1 :	1	1	1	1	1	1
A_2 :	1	1	-1	1	1	-1
E :	2	-1	0	2	-1	0
$E_{1/2}$:	2	1	0	-2	-1	0
$E_{3/2}$:	1	-1	i	-1	1	$-i$
	1	-1	$-i$	-1	1	i

It is usual to make the following simplifications in the notation of equivalent rotations in character tables

$$\begin{aligned} R^{2\pi}R_z^{\beta} &\to R_z^{\beta+2\pi} \\ R^{2\pi}R_\alpha^{\pi} &\to R_\alpha^{3\pi}. \end{aligned} \tag{13.12}$$

13.1.2 **Rotational Wave Function Transformations**

We now seek to evaluate how the rotational wave functions $|J,k,m\rangle$ transform under the elements of the $K(\mathrm{mol})^2$ group. In a way similar to what we did in Section 9.4.1, we build up these vectors from the fundamental $|J,1/2,1/2\rangle$ vector with

$$|J,\pm k,\pm m\rangle = N_\pm \left(\hat{J}_{\mathrm{m}}^{\mp}\right)^{k\mp 1/2}\left(\hat{J}_{\mathrm{s}}^{\pm}\right)^{m\mp 1/2}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle, \tag{13.13}$$

where $N_\pm$ is some positive normalization constant. We know from equations (4.86) to (4.88) that

$$\left\langle J,\frac{1}{2},\frac{1}{2}\middle|\theta,\phi,\chi\right\rangle = Ne^{i(\phi+\chi)/2}\sum_{\sigma=0}^{J-1/2}(-1)^{\sigma}\frac{\left[\cos(\theta/2)\right]^{2J-2\sigma}\left[\sin(\theta/2)\right]^{2\sigma}}{(\sigma!)^{2}\left(J-\frac{1}{2}-\sigma\right)!\left(J+\frac{1}{2}-\sigma\right)!}, \quad (13.14)$$

where

$$N=\sqrt{\frac{2J+1}{8\pi^{2}}}\left(J+\frac{1}{2}\right)!\left(J-\frac{1}{2}\right)!. \quad (13.15)$$

Using the fact that $\cos(\theta/2)=\sin\left[(\pi-\theta)/2\right]$ and $\sin(\theta/2)=\cos\left[(\pi-\theta)/2\right]$, we can transform equation (13.14) to

$$\begin{aligned}&\left\langle J,\frac{1}{2},\frac{1}{2}\middle|\pi-\theta,\phi+\pi,2\pi-2\alpha-\chi\right\rangle =\\ &\qquad e^{-i\alpha}Ne^{i(\phi-\chi)/2}\sum_{\sigma=0}^{J-1/2}(-1)^{\sigma}\frac{\left[\sin(\theta/2)\right]^{2J-2\sigma}\left[\cos(\theta/2)\right]^{2\sigma}}{(\sigma!)^{2}\left(J-\frac{1}{2}-\sigma\right)!\left(J+\frac{1}{2}-\sigma\right)!}.\end{aligned} \quad (13.16)$$

Effecting the change of variable $\tau=J-1/2-\sigma$ in this equation yields

$$\begin{aligned}&\left\langle J,\frac{1}{2},\frac{1}{2}\middle|\pi-\theta,\phi+\pi,2\pi-2\alpha-\chi\right\rangle =\\ &\qquad (-1)^{J-1/2}e^{i\pi/2}e^{-i\alpha}Ne^{i(\phi-\chi)/2}\sum_{\tau=0}^{J-1/2}(-1)^{\tau}\frac{\left[\sin(\theta/2)\right]^{2\tau+1}\left[\cos(\theta/2)\right]^{2J-1-2\tau}}{\tau!(\tau+1)!\left[\left(J-\frac{1}{2}-\tau\right)!\right]^{2}},\end{aligned} \quad (13.17)$$

which upon comparison with equation (4.86) gives

$$\left\langle J,\frac{1}{2},\frac{1}{2}\middle|\pi-\theta,\phi+\pi,2\pi-2\alpha-\chi\right\rangle = e^{i\pi J}e^{-i\alpha}\left\langle J,-\frac{1}{2},\frac{1}{2}\middle|\theta,\phi,\chi\right\rangle. \quad (13.18)$$

It is now straightforward to show from the first transformation on the right hand side of equations (13.10), and equations (13.14) and (13.18) that

$$\begin{aligned}R_{z}^{\beta}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle &= e^{i\beta/2}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle\\ R_{\alpha}^{\pi}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle &= e^{i\pi J}e^{-i\alpha}\left|J,-\frac{1}{2},\frac{1}{2}\right\rangle.\end{aligned} \quad (13.19)$$

Since we already from equations (9.62), (9.63), and (9.64) that

$$\begin{aligned}
R_z^{\beta}\hat{J}_{\mathrm{m}}^{\pm} &= e^{\mp i\beta}\hat{J}_{\mathrm{m}}^{\pm}R_z^{\beta}\\
R_{\alpha}^{\pi}\hat{J}_{\mathrm{m}}^{\pm} &= e^{\pm i2\alpha}\hat{J}_{\mathrm{m}}^{\mp}R_{\alpha}^{\pi}\\
R_z^{\beta}\hat{J}_{\mathrm{s}}^{\pm} &= \hat{J}_{\mathrm{s}}^{\pm}R_z^{\beta}\\
R_{\alpha}^{\pi}\hat{J}_{\mathrm{s}}^{\pm} &= \hat{J}_{\mathrm{s}}^{\pm}R_{\alpha}^{\pi},
\end{aligned} \tag{13.20}$$

then from equation (13.13) we find that

$$\begin{aligned}
R_z^{\beta}\left|J,k,m\right\rangle &= e^{ik\beta}\left|J,k,m\right\rangle\\
R_{\alpha}^{\pi}\left|J,k,m\right\rangle &= e^{i\pi J}e^{-2ik\alpha}\left|J,-k,m\right\rangle.
\end{aligned} \tag{13.21}$$

We see that equations (13.21) are a generalization that simplifies to equations (9.66) when J is an integer.

13.2 Correlation Tables (cf., Section 11.2 in Chapter 11)

We already know that there can be many symmetry groups for a given molecule. Of course, the MS group is one but there are others such the CNPI, the full rotation group ($K(\mathrm{mol})$), and the spin double groups. Since each of these groups each have their character table, the question arises as to how do these diverse tables and irreducible representations relate to each other? More precisely, given a group G, how will its irreducible representations correlate to one of his subgroup H?

Let us assume that G is of order g with elements $\{G_1, G_2, \ldots, G_g\}$, and that H is of order $h < g$ with elements $\{H_1, H_2, \ldots, H_h\}$. We also simplify things by assuming that $G_j = H_j$, for $j = 1, 2, \ldots, h$. This last assumption implies that we know how (the elements of) G transforms under (the elements of) H. This is a situation we have encountered many time previously, as a representation Γ_α of G will be in general reducible when restricted to H in such a manner. We, therefore, only need to apply equations (6.60) to find the number of times $a_i^{(\alpha)}$ that an irreducible representation Γ_i of H will appear in the reducible representation Γ_α

$$a_i^{(\alpha)} = \frac{1}{h}\sum_{j=1}^{h}\chi^{\Gamma_\alpha}\left[H_j\right]\chi^{\Gamma_i}\left[H_j\right]^*, \tag{13.22}$$

where $\chi^{\Gamma_\alpha}\left[H_j\right]$ and $\chi^{\Gamma_i}\left[H_j\right]$ are the characters for Γ_α and Γ_i for the operator $H_j = G_j$. We then find that

$$\Gamma_\alpha = \sum_i a_i^{(\alpha)}\Gamma_i. \tag{13.23}$$

Table 13-4 – The character table for $C_s(\mathrm{M})$.

$C_s(\mathrm{M})$:	E	E^*
	1	1
R_{rot} :	R^0	R_c^π
A' :	1	1
A'' :	1	−1

As an example, let us reduce or correlate $C_{2v}(\mathrm{M})$ (see the top-left corner of Table 13-1 for $C_{2v}(\mathrm{M})$ and Table 13-4 for $C_s(\mathrm{M})$). Applying equation (13.22) we find

$$\begin{aligned} a_{A'}^{(A_1)} &= a_{A'}^{(B_2)} = \frac{1}{2}(1+1) = 1 \\ a_{A''}^{(A_1)} &= a_{A''}^{(B_2)} = \frac{1}{2}(1-1) = 0 \\ a_{A'}^{(A_2)} &= a_{A'}^{(B_1)} = \frac{1}{2}(1-1) = 0 \\ a_{A''}^{(A_2)} &= a_{A''}^{(B_1)} = \frac{1}{2}(1+1) = 1, \end{aligned} \tag{13.24}$$

and from equation (13.23)

$$\begin{aligned} A_1\left[C_{2v}(\mathrm{M})\right] &= B_2\left[C_{2v}(\mathrm{M})\right] = A'\left[C_s(\mathrm{M})\right] \\ A_2\left[C_{2v}(\mathrm{M})\right] &= B_1\left[C_{2v}(\mathrm{M})\right] = A''\left[C_s(\mathrm{M})\right]. \end{aligned} \tag{13.25}$$

In this simplest of example, every representation from $C_{2v}(\mathrm{M})$ correlates to only one irreducible representation of $C_s(\mathrm{M})$. But this is not the rule; it is more common to have "one-to-many" correlations.

It is also often the case that we don't know ahead of time how a group transforms under the group it is to be correlated to. This information must then be obtained on a case-by-case basis. For example, let us consider the correlation of $D^{(1/2)}$ belonging to $K(\mathrm{mol})^2$ and $C_{3v}(\mathrm{M})^2$.

We must find the character of $D^{(1/2)}$ under the elements of $C_{3v}(\mathrm{M})^2$. To do so, we use equation (13.1), which we rewrite here for convenience

$$\chi^{(J)}\left[R^\alpha\right] = \frac{\sin\left[(J+1/2)\alpha\right]}{\sin(\alpha/2)}, \tag{13.26}$$

and the first of equations (13.2) when $R^{2\pi}$ is involved

$$\chi^{(J)}\left[R^{2\pi}R^{\alpha}\right]=(-1)^{2J}\chi^{(J)}\left[R^{\alpha}\right]. \tag{13.27}$$

We will also need the following for cases where $\sin\left[(J+1/2)\alpha\right]=\sin(\alpha/2)=0$

$$\chi^{(J)}\left[R^{\alpha}\right]=\frac{2(J+1/2)\cos\left[(J+1/2)\alpha\right]}{\cos(\alpha/2)}. \tag{13.28}$$

The procedure consists into applying the equivalent rotation, i.e., R_{rot}, for each elements of $C_{3\text{v}}(\text{M})^2$ in Table 13-2 in $D^{(1/2)}$, and calculate the corresponding characters using equations (13.26) to (13.28). We can therefore calculate the following

$$\begin{aligned} E &\to R^{0}, & \chi^{(1/2)}\left[R^{0}\right]&=2\\ (123) &\to R_{z}^{2\pi/3}, & \chi^{(1/2)}\left[R_{z}^{2\pi/3}\right]&=1\\ (23)^{*} &\to R_{\pi/2}^{\pi}, & \chi^{(1/2)}\left[R_{\pi/2}^{\pi}\right]&=0\\ R &\to R^{2\pi}, & \chi^{(1/2)}\left[R^{2\pi}\right]&=-2\\ R(123) &\to R^{2\pi}R_{z}^{2\pi/3}, & \chi^{(1/2)}\left[R^{2\pi}R_{z}^{2\pi/3}\right]&=-1 \end{aligned} \tag{13.29}$$

We could use equations (13.22) and (13.23), but it is clear from Table 13-1 that

$$\Gamma_{\text{es}}\left[D^{(1/2)}\right]=E_{1/2}. \tag{13.30}$$

We can perform the same procedure for $D^{(1)}$ to find

$$\begin{aligned} E &\to R^{0}, & \chi^{(1)}\left[R^{0}\right]&=3\\ (123) &\to R_{z}^{2\pi/3}, & \chi^{(1)}\left[R_{z}^{2\pi/3}\right]&=0\\ (23)^{*} &\to R_{\pi/2}^{\pi}, & \chi^{(1)}\left[R_{\pi/2}^{\pi}\right]&=-1 \end{aligned} \tag{13.31}$$

It is to be noted that there is no need to calculate characters for operators involving R, since this operator does not affect the character when J is integer (see equation (13.27)). We therefore find that

$$\Gamma_{\text{es}}\left[D^{(1)}\right]=A_2\oplus E. \tag{13.32}$$

13.3 An Example: The CH_3O Symmetric Top Radical

We now make use of everything covered so far in this chapter to evaluate the symmetry of the states for the CH_3O symmetric top, which is a radical (called the methoxy radical) of $C_{3\text{v}}(\text{M})^2$ symmetry. This molecule has an ${}^2E$ electronic ground state (i.e., $S = 1/2$) with a totally symmetric (i.e., A_1) vibrational ground state.

13.3.1 **Hund's Case b)**

In this case of weak spin orbit coupling, the symmetry of the electronic spin wave function is $\Gamma_{\text{es}} = A_1$ and, therefore $\Gamma_{\text{eso}} = E$ ('eso' stands for 'electronic spin and orbit'). Although $J = N \pm 1/2$, the term "weak coupling" of the electron spin to the molecule-fixed axis implies that the symmetry of a rotational wave function is solely determined with the N quantum number (an integer), not J (half-integer in this case). We must therefore determine the classification of the rotational wave function $\left|N, \pm K, m\right\rangle$ through its transformation under the different R_{rot} of $C_{3\text{v}}(\text{M})$. Using equations (13.21), we find

$$\begin{aligned}
E\left|N,\pm K,m\right\rangle &= R^0\left|N,\pm K,m\right\rangle = \left|N,\pm K,m\right\rangle \\
(123)\left|N,\pm K,m\right\rangle &= R_z^{2\pi/3}\left|N,\pm K,m\right\rangle = e^{\pm i2K\pi/3}\left|N,\pm K,m\right\rangle \\
(23)^*\left|N,\pm K,m\right\rangle &= R_{\pi/2}^{\pi}\left|N,\pm K,m\right\rangle = (-1)^J e^{\mp iK\pi}\left|N,\mp K,m\right\rangle \\
&= (-1)^{N+K}\left|N,\mp K,m\right\rangle.
\end{aligned} \tag{13.33}$$

This leads to the following characters

$C_{3\text{v}}(\text{M})$:	E	(123)	$(23)^*$
$K = 0$:	1	1	$(-1)^N$
$K > 0$:	2	$2\cos(2K\pi/3)$	0

and irreducible representations

K		Γ_{rot}
0	N even	A_1
	N odd	A_2
$3n \pm 1$		E
$3n \pm 2$		E
$3n \pm 3$		$A_1 \oplus A_2$

for n an integer. It is to be noted that the species realized for a given N can be directly obtained by correlating $D^{(N)}$ and $C_{3\text{v}}(\text{M})$. We would then find that

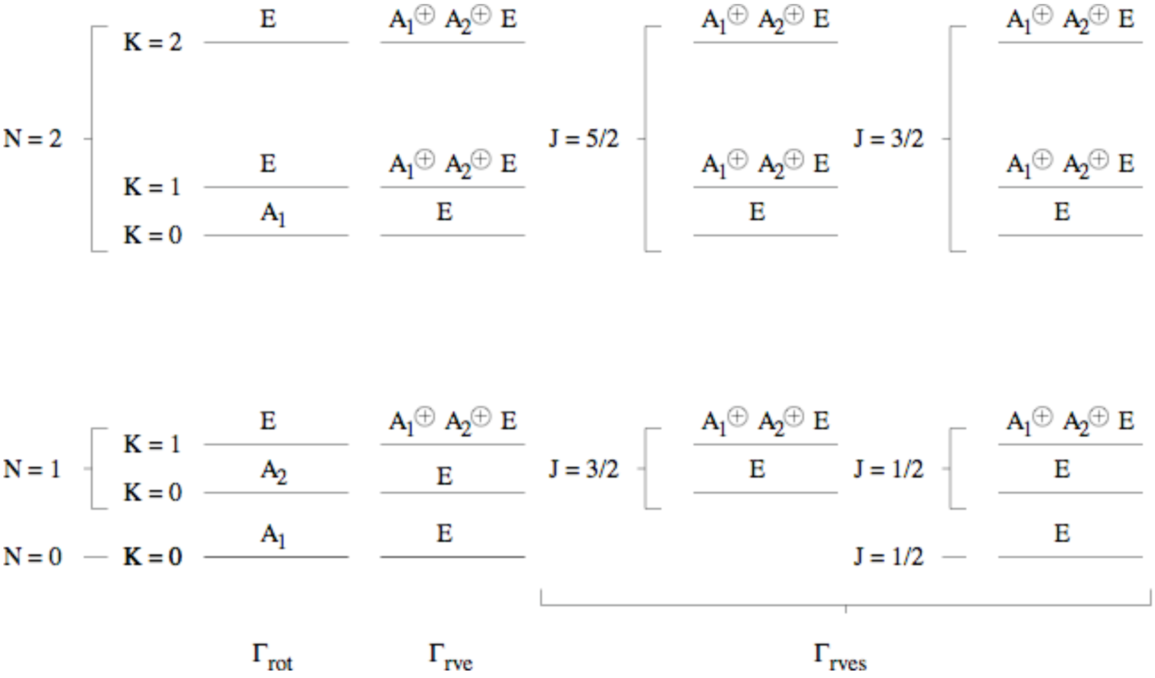

Figure 13-1 – The symmetry labels of the energy levels of the $\mathrm{CH_3O}$ radical in the ${}^2E$ vibronic ground state using Hund's case b) ('rves' stands for 'rovibronic and electronic spin').

$$\begin{aligned}\Gamma_{\mathrm{rot}}\left[D^{(0)}\right] &= A_1\\ \Gamma_{\mathrm{rot}}\left[D^{(1)}\right] &= A_2 \oplus E\\ \Gamma_{\mathrm{rot}}\left[D^{(2)}\right] &= A_1 \oplus 2E,\ \ldots,\end{aligned} \tag{13.34}$$

which is in agreement with the previous result. The rovibronic-electron spin species Γ_{rves} are given in Figure 13-1.

13.3.2 **Hund's Case a)**

We now have strong spin orbit coupling, and we must now use the spin double group $C_{3\mathrm{v}}(\mathrm{M})^2$. Since $S = 1/2$, then we must correlate $D^{(1/2)}$ of $K(\mathrm{mol})^2$ with $C_{3\mathrm{v}}(\mathrm{M})^2$ to find the electronic spin symmetry. This was done previously, resulting in equation (13.30) rewritten here for convenience

$$\Gamma_{\mathrm{es}}\left[D^{(1/2)}\right] = E_{1/2}. \tag{13.35}$$

We can then write from Table 13-2

$$\Gamma_{\mathrm{eso}} = E_{1/2} \otimes E = E_{1/2} \oplus E_{3/2}. \tag{13.36}$$

We must now realize that the term “strong coupling” of the electronic spin to the molecule-fixed axis implies that the symmetry of a rotational wave function must be determined with the J quantum number, not N. We must now consider the fact that J is half-integer for determining the classification of the rotational wave functions. Using once again equation (13.21) we have

$$\begin{aligned} E\left|J,\pm K,m\right\rangle &= R^0\left|J,\pm K,m\right\rangle = \left|J,\pm K,m\right\rangle \\ (123)\left|J,\pm K,m\right\rangle &= R_z^{2\pi/3}\left|J,\pm K,m\right\rangle = e^{\pm i2K\pi/3}\left|J,\pm K,m\right\rangle \\ (23)^*\left|J,\pm K,m\right\rangle &= R_{\pi/2}^{\pi}\left|J,\pm K,m\right\rangle = e^{i\pi J}e^{\mp iK\pi}\left|J,\mp K,m\right\rangle \\ &= e^{i(J\mp K)\pi}\left|J,\mp K,m\right\rangle \\ R\left|J,\pm K,m\right\rangle &= R^{2\pi}\left|J,\pm K,m\right\rangle = e^{\pm i2K\pi}\left|J,\pm K,m\right\rangle \\ R(123)\left|J,\pm K,m\right\rangle &= R^{2\pi}R_z^{2\pi/3}\left|J,\pm K,m\right\rangle = e^{\pm i8K\pi/3}\left|J,\pm K,m\right\rangle. \end{aligned} \tag{13.37}$$

This leads to the following characters

$C_{3\mathrm{v}}(\mathrm{M})^2$:	E	(123)	$(23)^*$	R	$R(123)$
	2	$2\cos(2K\pi/3)$	0	$2\cos(2K\pi)$	$2\cos(8K\pi/3)$

and irreducible representations

K	Γ_{rot}	K	Γ_{rot}	K	Γ_{rot}
$3n\pm 1/2$	$E_{1/2}$	$3n\pm 3/2$	$E_{3/2}$	$3n\pm 5/2$	$E_{1/2}$

for n an integer. Correlation of $D^{(J)}$ of $K(\mathrm{mol})^2$ with $C_{3\mathrm{v}}(\mathrm{M})^2$ will yield

$$\begin{aligned} \Gamma_{\mathrm{rot}}\left[D^{(1/2)}\right] &= E_{1/2} \\ \Gamma_{\mathrm{rot}}\left[D^{(3/2)}\right] &= E_{1/2}\oplus E_{3/2} \\ \Gamma_{\mathrm{rot}}\left[D^{(5/2)}\right] &= 2E_{1/2}\oplus E_{3/2},\ \ldots, \end{aligned} \tag{13.38}$$

which is in agreement with the previous result. The rovibronic-electron spin species Γ_{rves} are given in Figure 13-2.

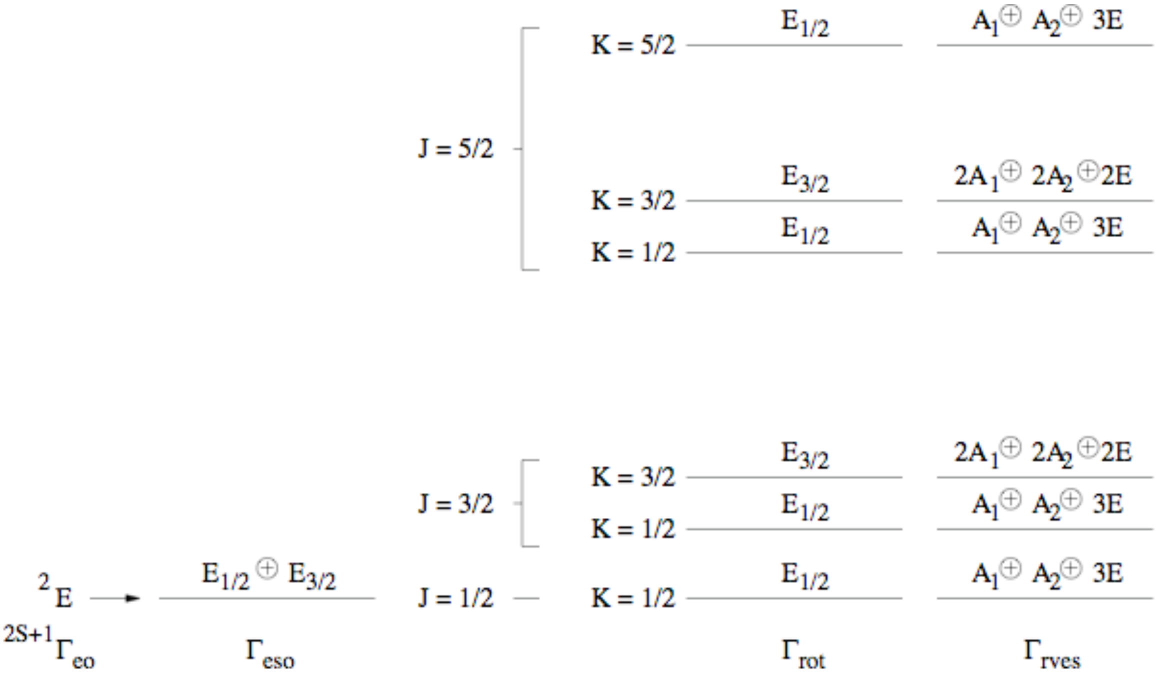

Figure 13-2 - The symmetry labels of the energy levels of the CH_3O radical in the ^2E vibronic ground state using Hund's case a) ('eo' stands for 'electronic orbit').