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The Renner effect and spin-orbit coupling

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The Renner theory of vibrational–electronic interaction in linear triatomic molecules in \( \Pi \) electronic states is extended to take account of coupling between an odd electron spin and the electron orbital angular momentum. Perturbation expressions for the splittings and shifts of energy levels are obtained on the assumption that the Renner splittings and the spin–orbit coupling energy are of the same order of magnitude, but less than the energy quantum of the bending vibrations.

1. Introduction

Linear triatomic molecules in orbitally degenerate electronic states (\( \Pi, \Delta, \Phi \ldots \)) have a rather complex vibrational–electronic interaction due to the separation of the two components of the electronic state by the bending vibration. The theory of this effect was first developed by Renner [1] who gave an expansion for the splitting of the vibronic levels if this interaction was small. Recently a detailed study of the electronic spectrum of the \( \text{NH}_2 \) radical by Dressler and Ramsay [2] has suggested that this is an example of the Renner effect with large coupling and some calculations of Pople and Longuet-Higgins [3] based on a modified version of the Renner theory have given satisfactory quantitative agreement with the experimental term values.

For systems with a free electron spin as well as an electronic orbital moment, the effect of spin–orbit coupling should also be taken into account. This is small in \( \text{NH}_2 \) but it will have to be considered if it is comparable with the splittings caused by the Renner effect. In this paper an extended theory is developed to allow for a moderate coupling between the electron spin and the component of orbital electronic angular momentum along the axis of the molecule.

2. Classification of levels for a simplified model

Suppose we consider a triatomic linear molecule with an odd electron in an orbital of \( \pi \) symmetry. In the absence of any coupling between the angular motion of this electron, the bending vibration and the electron spin, the states of the system can be classified by quantum numbers \( \Lambda' \) (= \( \pm 1 \)) for the electronic orbital angular momentum along the axis, \( S'_z \) (= \( \pm \frac{1}{2} \)) for the corresponding component of spin angular momentum, \( l (= 0, 1, 2 \ldots) \) for the angular momentum of the bending vibration and \( n \) (= \( |l| + 1, |l| + 3, |l| + 5, \ldots \)) for the total number of vibrational quanta (including zero-point motion). The energy of the state \( |\Lambda', n, l, S'_z\rangle \) is then \( n \) in units of the vibrational quantum. Further quantum numbers will be associated with other degrees of freedom such as end-over-end rotation, but we shall not consider any coupling with these in the present paper.

The Renner effect follows if we introduce a coupling between the electronic orbital motion and the plane of the bent molecule. Under these circumstances,
$\Lambda'$ and $l$ are no longer quantum numbers, but the total *orbital* angular momentum component represented by

$$K = \Lambda' + l$$  \hspace{1cm} (2.1)

is still conserved, so that vibronic states may be labelled $\Sigma, \Pi, \Delta, \ldots$ according as $K = 0, 1, 2, \ldots$. This coupling leads to a splitting of the states $|1, n, K-1, S_z'\rangle$ and $|-1, n, K+1, S_z'\rangle$ which are degenerate in the unperturbed system. For $\Sigma$ states ($K=0$) the appropriate wave functions are

$$\langle |1, n, -1, S_z'\rangle + |-1, n, 1, S_z'\rangle \rangle / \sqrt{2}$$

and

$$\langle |1, n, -1, S_z'\rangle - |-1, n, 1, S_z'\rangle \rangle / \sqrt{2}$$

which have symmetries $\Sigma^+$ and $\Sigma^-$ respectively. For $K \neq 0$, the correct combinations are also approximately sums and differences in this way. The splittings due to this effect, which are dealt with in detail by Renner, are shown in the first part of the figure.

Even after the Renner splitting, each vibronic state with $|K|>0$ remains four-fold degenerate because of the two possible values of the spin quantum number.

Level splittings caused by (a) Renner effect alone, (b) Renner effect and spin–orbit coupling.

M.P.
number $S'_z = \pm \frac{1}{2}$ and the two possible signs of $K$. We now wish to investigate how these splittings are modified and extended if there is also a coupling between the electron orbital angular momentum and the electron spin. The coupling between the vibrational angular momentum and the electron spin will be much smaller and will be ignored. The simplest approximate representation of this coupling is by a Hamiltonian proportional to $\Lambda S'_z$ where $\Lambda$ and $S'_z$ are now appropriate operators. This represents a positive energy if the two components of angular momentum along the molecular axis are in the same direction. Since components of orbital angular momentum perpendicular to the molecular axis are largely quenched, a Hamiltonian of this sort takes account of the most important part of the spin–orbit coupling.

To the approximation of this simple Hamiltonian, the quantum number $S'_z$ is conserved, since the operator $S_z$ cannot mix $\alpha$ and $\beta$ electron spin functions. We may therefore continue to classify states by the symbols $\Sigma$, $\Pi$, $\Delta$... and in addition by the total angular momentum $K + S'_z$ as a subscript. Thus $\Pi_{3/2}$ and $\Pi_{1/2}$ represent states in which an orbital and spin angular momenta are parallel and antiparallel respectively. All states with $|K| > 0$ get split in this manner as illustrated in the figure (b). It should be noted that the $\Sigma$ levels can no longer be classified as $\Sigma^+$ or $\Sigma^-$ since, for a particular value of $S'_z$, the two directions of rotation are no longer equivalent. In the next section we shall derive quantitative expressions for these splittings and shifts, assuming them to be small compared with the vibrational interval.

3. Quantitative theory

We shall only deal with the one-electron model, following the notation of Pople and Longuet-Higgins [3]. $r$ will denote the amplitude of the bending vibration, $\phi$ the angle of the plane of bending with a fixed plane through the axis of the unbent molecule and $\theta$ the angular distance of the electron from the same plane. If the bending potential is harmonic and if there is no coupling between the angles $\theta$ and $\phi$ and the electron spin, the various degrees of freedom can be separated and the wave functions written in the form

$$|\Lambda', n, l, S'_z \rangle = \exp(\text{i} \Lambda' \theta) \rho_{n\Lambda}(r) \exp(\text{i}l\phi)$$

(3.1)

where $\Lambda' = \pm 1$, $\rho_{n\Lambda}(r) \exp(\text{i}l\theta)$ is the wave function for the two-dimensional harmonic oscillator and $\alpha$ and $\beta$ are the usual spin functions for $S'_z = \pm \frac{1}{2}$. It is convenient to choose the unit of energy equal to the vibrational quantum and the unit of distance such that the unperturbed vibrational potential energy is $\frac{1}{2}r^2$.

Following Renner, we now introduce the Hamiltonian

$$H' = \epsilon r^2 \cos 2(\theta - \phi)$$

(3.2)

to couple the electronic and vibrational angular momenta. This splits the potential function into upper and lower branches

$$U^+ = \frac{1}{2}(1 + \epsilon)r^2,$$

$$U^- = \frac{1}{2}(1 - \epsilon)r^2.$$  

(3.3)

We also introduce a second perturbing Hamiltonian

$$H' = \xi \Lambda S_z$$

(3.4)

to allow for spin–orbit coupling.
Since the quantum number $K$ is conserved, we need to diagonalize the total energy matrix for the complete set of functions (3.1) with $\Lambda' + l = K$. For convenience we shall suppose $K > 0$. These functions are conveniently collected in pairs $|1, n, K-1, S_z'\rangle$ and $|-1, n, K+1, S_z'\rangle$ which are degenerate in the absence of the perturbation. For $|K| > 0$, however, the state corresponding to lowest unperturbed energy $|1, K, K-1, S_z'\rangle$ will be non-degenerate. The matrices of $\epsilon^{-1}H'$ will be the same for both values of $S_z'$ and have been evaluated by Renner using a rather different notation. A typical block of this matrix is shown on p. 20. All elements in blocks further removed from the diagonal are zero. If $K > 0$, the first row and column corresponding to $|1, K, K-1\rangle$ are not paired and the top left-hand corner of the matrix has the form

$$
\begin{pmatrix}
0 & 0 & 1/2\sqrt{[K(K+1)]} \\
0 & 0 & 1/2\sqrt{[K(K+1)]} \\
1/2\sqrt{[K(K+1)]} & 1/2\sqrt{[K(K+1)]} & 0
\end{pmatrix}
$$

If $K=0$, however, this row and column do not occur.

The next step is to add the matrices of $H'$ and $H''$ and then treat them as a perturbation on the unperturbed energy matrix (which has diagonal elements equal to $n$). The matrix of $H''$ is diagonal and has the form

$$
\begin{pmatrix}
\xi S_z' & 0 & 0 \\
0 & \xi S_z' & 0 \\
0 & 0 & -\xi S_z'
\end{pmatrix}
$$

(the first row and column again being absent if $K = 0$).

To apply perturbation theory, we first have to apply an orthogonal transformation to the total energy matrix which will remove off-diagonal elements between states which are degenerate in the unperturbed situation. In the absence of spin–orbit coupling, this is accomplished by replacing the pair of functions $|1, n, K-1\rangle$ and $|-1, n, K+1\rangle$ by their sum and difference (normalized) if $n > K$ and leaving $|1, K, K-1\rangle$ unaltered ($K \neq 0$). Our problem is slightly more complicated for the corresponding $2 \times 2$ block of the perturbation matrix is now

$$
\begin{pmatrix}
\xi S_z' & \frac{1}{2}\epsilon\sqrt{[n^2-K^2]} \\
\frac{1}{2}\epsilon\sqrt{[n^2-K^2]} & -\xi S_z'
\end{pmatrix}
$$
| $|1, n-2, K-1\rangle$ | $|--1, n-2, K+1\rangle$ | $|1, n, K-1\rangle$ | $|--1, n, K+1\rangle$ | $|1, n+2, K-1\rangle$ | $|--1, n+2, K+1\rangle$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\langle 1, n-2, K-1 | 0 | 1/2 \sqrt{[(n+K-2)(n+K)]}$ | 0 | 0 | 0 | 0 |
| $\langle -1, n-2, K+1 | 0 | 1/2 \sqrt{[(n-K)(n-K-2)]}$ | 0 | 0 | 0 | 0 |
| $\langle 1, n, K-1 | 0 | 1/2 \sqrt{[(n-K)(n-K-2)]}$ | 0 | 0 | 0 | 0 |
| $\langle -1, n, K+1 | 0 | 1/2 \sqrt{[(n-K)(n-K-2)]}$ | 0 | 0 | 0 | 0 |
| $\langle 1, n+2, K-1 | 0 | 1/2 \sqrt{[(n+K-2)(n+K)]}$ | 0 | 0 | 0 | 0 |
| $\langle -1, n+2, K+1 | 0 | 1/2 \sqrt{[(n+K-2)(n+K)]}$ | 0 | 0 | 0 | 0 |
The Renner effect and spin–orbit coupling

If we define an angle \( \gamma(n, K, S_{z'} \) between 0 and \( \pi \) by

\[
\cos 2\gamma(n, K, S_{z'}) := \sin 2\gamma(n, K, S_{z'}) = 1 = \xi S_{z'} = \frac{1}{2} \varepsilon \sqrt{[n^2 - K^2]} = \frac{1}{2} \varepsilon \sqrt{[\xi^2 + \varepsilon^2(n^2 - K^2)]}
\]

(3.5)

then the appropriate transformation matrix is

\[
S = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \gamma(n, K, S_{z'}) & -\sin \gamma(n, K, S_{z'}) \\
0 & \sin \gamma(n, K, S_{z'}) & \cos \gamma(n, K, S_{z'})
\end{pmatrix}
\]

(3.6)

where elements outside each 2 x 2 diagonal block are zero. If \( K = 0 \), the first row and column are omitted. If \( H \) is the energy matrix for the original functions, \( S^{-1}HS \) now has the required property and the perturbation can be carried out to second order.

If \( K > 0 \) (\( \Pi \), \( \Lambda \), \( \Phi \) states) and \( n > K \), the four states corresponding to a given value of \( n \) are separated, the energies to second order being

\[
E_{n, K, \pm 1/2}^{(+)} = n + \frac{1}{2} \varepsilon \sqrt{[\xi^2 + \varepsilon^2(n^2 - K^2)]} - \frac{1}{2} \varepsilon^2 n \pm \frac{1}{6} \varepsilon \xi K \sqrt{[\xi^2 + \varepsilon^2(n^2 - K^2)]},
\]

\[
E_{n, K, \pm 1/2}^{(-)} = n - \frac{1}{2} \varepsilon \sqrt{[\xi^2 + \varepsilon^2(n^2 - K^2)]} - \frac{1}{2} \varepsilon^2 n \mp \frac{1}{6} \varepsilon \xi K \sqrt{[\xi^2 + \varepsilon^2(n^2 - K^2)]}.
\]

(3.7)

The notation is that the indicial \( (+) \) or \( (-) \) indicates the upper or lower state for the Renner splitting, and the third suffix gives the value of the spin angular momentum \( S_{z'} \). For example \( E_{3, 1/2}^{(+)} \) is the upper \( \Pi_{3/2} \) state originating in the unperturbed level \( n = 3 \). This is the highest level shown in the figure (b) and is designated \( \Pi_{3/2}^{(+)} \).

If the spin–orbit coupling parameter \( \xi \) is small compared with \( \varepsilon \), these formulae simplify to

\[
E_{n, K, \pm 1/2}^{(+)} = n + \frac{1}{2} \varepsilon \sqrt{[\xi^2 + \varepsilon^2(n^2 - K^2)]} - \frac{1}{6} \varepsilon^2 n \pm \frac{1}{6} \varepsilon \xi K\sqrt{[(n^2 - K^2)]},
\]

(3.8)

\[
E_{n, K, \pm 1/2}^{(-)} = n - \frac{1}{2} \varepsilon \sqrt{[\xi^2 + \varepsilon^2(n^2 - K^2)]} - \frac{1}{6} \varepsilon^2 n \mp \frac{1}{6} \varepsilon \xi K\sqrt{[(n^2 - K^2)]}.
\]

If \( n = K > 0 \), the two states are split, the corresponding energies being

\[
E_{K, K, \pm 1/2} = K + \frac{1}{6} \varepsilon \xi \sqrt{[\xi^2 + \varepsilon^2(K^2)]}.
\]

(3.9)

For \( K = 1 \), the two levels are \( \Pi_{3/2} \) and \( \Pi_{1/2} \) as shown at the bottom of the figure (b). The splitting of these levels to the order of this calculation is \( \xi \) as it would be if there were no Renner effect.

For \( K = 0 \) (\( \Sigma \) states), the two directions of the spin give the same energy and the four states split into two pairs

\[
E_{n, 0, \pm 1/2}^{(+)} = n + \frac{1}{2} \varepsilon \sqrt{[\xi^2 + \varepsilon^2n^2]} - \frac{1}{6} \varepsilon^2 n,
\]

(3.10)

\[
E_{n, 0, \pm 1/2}^{(-)} = n - \frac{1}{2} \varepsilon \sqrt{[\xi^2 + \varepsilon^2n^2]} - \frac{1}{6} \varepsilon^2 n.
\]
The separation of the two $\Sigma$ levels is $\sqrt{[\xi^{2} + \epsilon^{2}n^{2}]}$. For $n=2$, these are the two lowest $\Sigma$ levels shown in the figure (b) (designated $\Sigma^{(+)}$ and $\Sigma^{(-)}$ rather than $\Sigma^{+}$ and $\Sigma^{-}$ since the appropriate symmetry is reduced).

4. Discussion

The principal modifications of the Renner theory caused by spin–orbit coupling may be summarized as follows.

(1) The Renner effect causes pairs of $\Sigma$ levels to split into levels of symmetries $\Sigma^{+}$ and $\Sigma^{-}$. Spin–orbit coupling increases the separation of these pairs (equation (3.10)) and the classification as $\Sigma^{+}$ and $\Sigma^{-}$ ceases to be precise.

(2) The lowest vibronic levels of $\Pi, \Delta, \Phi \ldots$ symmetries are little changed by the Renner effect, but they are split into pairs (e.g. $\Pi_{3/2}$ and $\Pi_{1/2}$) by the spin–orbit coupling. These splittings are all equal to the spin–orbit coupling energy $\xi$ (equation (3.9)).

(3) All other $\Pi, \Delta, \Phi \ldots$ vibronic states are split into pairs (designated $\Pi^{(+)}$, $\Pi^{(-)}$, etc.) by the Renner effect. Spin–orbit coupling causes further splitting to groups of four ($\Pi_{3/2}^{(+)}$, $\Pi_{1/2}^{(+)}$, $\Pi_{1/2}^{(-)}$, $\Pi_{3/2}^{(-)}$, etc.). However, the second splittings are small (being of order $\epsilon\xi$).

References