From G. Herzberg, Diatomic Molecules

CHAPTER V

FINER DETAILS ABOUT ELECTRONIC STATES AND ELECTRONIC TRANSITIONS

1. Classification of Electronic States; Multiplet Structure

In general, each molecule has a number of band systems of the type discussed in the preceding chapter and has therefore a number of electronic states. It is to be expected that the classification of these electronic states is analogous to the classification of atomic energy states, which are, of course, "pure" electronic states. This analogy is particularly apparent in the cases in which Rydberg series of bands are observed (see Chapter II). The bands of such a series must clearly have a Rydberg series of electronic states as their upper states and the reason that only one band (the 0–0 band) of each electronic transition is observed, must be due to the Franck-Condon principle, the potential curves involved all having nearly the same r* value.

Orbital angular momentum. The motion of the electrons in an atom takes place in a spherically symmetrical field of force. As a consequence (see Chapter I) the electronic orbital angular momentum L is a constant of the motion as long as the effect of electron spin is small or neglected. In a diatomic molecule the symmetry of the field in which the electrons move is reduced; there is only axial symmetry about the internuclear axis (which for the present we consider as fixed). As a consequence only the component of the orbital angular momentum of the electrons about the internuclear axis is a constant of the motion. The situation is essentially the same as that of an atom in a strong electric field, which is here the electrostatic field of the two nuclei. A precession of L takes place about the internuclear axis (internuclear axis) with constant component ML(h/2π), where ML can take only the values

\[ M_L = L, L-1, L-2, \ldots, -L. \]  

(V, 1)

For the case of the molecule this precession is illustrated in Fig. 95.

In an electric field, unlike a magnetic field, reversing the directions of motion of all electrons does not change the energy of the system but does change M_L into -M_L. Therefore, in diatomic molecules, states differing only in the sign of M_L have the same energy (are degenerate). On the other hand, states with different |M_L| have in general widely different energies since the electric field which causes this splitting is very strong. As the strength of the field increases, L precesses faster and faster about the axis of the field and consequently loses more and more its meaning as angular momentum while its component M_L remains well defined. It is therefore more appropriate to classify the electronic states of diatomic molecules according to the value of |M_L| than according to the value of L. Following the international nomenclature, we put

\[ \Lambda = |M_L| \]  

(V, 2)

The corresponding angular momentum vector \( \Lambda \) represents the component of the electronic orbital angular momentum along the internuclear axis. Its magnitude is \( \Lambda(h/2\pi) \). The quantum number \( \Lambda \) is therefore identical with that previously introduced in the treatment of the symmetrical top (see Chapter III, section 2(d)).

According to (V, 1), for a given value of L, the quantum number \( \Lambda \) can take the values

\[ \Lambda = 0, 1, 2, \ldots, L. \]  

(V, 3)

Thus in the molecule for each value of L there are \( L + 1 \) distinct states with different energy. However, often the value of L cannot be given at all, since the corresponding angular momentum L is not defined.

According as \( \Lambda = 0, 1, 2, 3, \ldots \), the corresponding molecular state is designated a \( \Sigma, \Pi, \Delta, \Phi, \ldots \), states, analogous to the mode of designation for atoms. Greek letters are used throughout in the designation of molecular quantities referring to components of electronic angular momenta, while the corresponding italic letters used for atoms refer to the electronic angular momenta themselves.

\( \Pi, \Delta, \Phi, \ldots \) states are doubly degenerate since \( M_L \) can have the two values +\( \Lambda \) and -\( \Lambda \) (see above); \( \Sigma \) states are non-degenerate.

Mathematically the angular momentum \( \Lambda \) may be introduced in the following way: We consider the nuclei as fixed in the z axis and introduce cylindrical coordinates \( \rho, \phi, \psi \) for each electron, where \( \rho \) is the distance from the axis and \( \phi, \psi \) the azimuth. Furthermore it is convenient to introduce relative azimuths \( \phi', \psi', \phi'' \) for all but the first electron. If the wave equation is expressed in terms of \( \rho, \phi, \psi \), changing \( \psi' \) simply means a rotation about the axis which must leave the wave equation unchanged. For this reason the electronic eigenfunction \( \psi \) must have the form (see Wigner and Wittmer (712) and Hund (384))

\[ \psi = \chi e^{\pm i\phi}; \quad \psi' = \bar{\chi} e^{\mp i\phi}, \quad \psi'' = \chi' e^{\pm i\phi} \]  

(V, 4)

where \( \chi \) and \( \bar{\chi} \) are functions of all electronic coordinates \( \rho, \phi, \psi \), except \( \psi \), and where the function \( \chi \) differs from \( \chi \) only in that the \( \phi \) are replaced by their negatives. The constant \( \Lambda \) is a positive integer. If \( \Lambda \) were not integral \( \phi \) would not be single-valued. It is easily verified that the form (V, 4) is the only one that leaves \( \psi \) invariant against any change of \( \phi \).

The possible values of the angular momentum about the z axis are the eigenvalues of the operator \((h/2\pi)\partial/\partial\phi_1 \) (see p. 18). Operating with this operator on the two functions (V, 4) yields \((h/2\pi)\partial\psi_\Lambda/\partial\phi_1 = -\partial\psi_\Lambda/\partial\phi_1 \) and \((h/2\pi)\partial\psi_\Lambda/\partial\phi_1 = \partial\psi_\Lambda/\partial\phi_1 \) respectively, that is, the corresponding values of the angular momentum are \( \Delta\Lambda/2\pi \) and \(-\Delta\Lambda/2\pi \), respectively. Thus the two functions (V, 4) correspond to the rotation of the electrons in one sense or the opposite sense, respectively, about the line joining the nuclei and for a given \( \Lambda \) and \( \chi \) belong to the same eigenvalue (twofold
Spin. A closer investigation of the fine structure of electronic bands shows in many cases a multiplet structure either of the whole bands or of individual lines or both (see Chapter II). As in the case of atoms this multiplet structure is due to the electron spin.

Just as for atoms, the spins of the individual electrons form a resultant $S$, the corresponding quantum number $S$ being integral or half integral according as the total number of electrons in the molecule is even or odd. In $S$ states (similar to $S$ states of atoms) the resultant spin $S$, since it is unaffected by an electric field, is fixed in space as long as the molecule does not rotate and if there is no external magnetic field. On the other hand, if $\Lambda \neq 0$, ($\Pi$, $\Delta$, \ldots states), there is an internal magnetic field in the direction of the internuclear axis resulting from the orbital motion of the electrons. This magnetic field causes a precession of $S$ about the field direction (that is, in this case the internuclear axis) with a constant component $M_S(h/2\pi)$. For molecules, $M_S$ is denoted by $\Sigma$, in order to bring out the analogy better (this quantum number $\Sigma$ must not be confused with the symbol $\Sigma$ for terms with $\Lambda = 0$). The values of $\Sigma$ allowed by the quantum theory are (see Chapter I for $M_S$)

$$\Sigma = S, S-1, S-2, \ldots, -S.$$  

That is to say, $2S + 1$ different values are possible. In contrast to $\Lambda$, the quantum number $\Sigma$ can be positive and negative. It is not defined for states with $\Lambda = 0$—that is, $S$ states.

Total angular momentum of the electrons; multiplets. The total electronic angular momentum about the internuclear axis, denoted by $\Omega$, is obtained by adding $\Lambda$ and $\Sigma$, just as the total electronic angular momentum $J$ for atoms is obtained by adding $L$ and $S$. Whereas, however, a vector addition has to be carried out for atoms, for molecules an algebraic addition is sufficient, since the vectors $L$ and $\Sigma$ both lie along the line joining the nuclei. Thus for the quantum number of the resultant electronic angular momentum about the internuclear axis we have

$$\Omega = |\Lambda + \Sigma|. \quad (V,7)$$

If $\Lambda$ is not equal to zero, according to (V, 6) there are $2S + 1$ different values of $\Lambda + \Sigma$ for a given value of $\Lambda$ (that is, of $\Omega$ as well, if $\Lambda \geq S$). As a result of the interaction of $S$ with the magnetic field produced by $\Lambda$, these different values of $\Lambda + \Sigma$ give rise to $2S + 1$ different states, the states with the same value of $\Lambda + \Sigma$ being called an $S$ state. $\Sigma$ states are not physical in the case of $\Lambda = 0$ but only when $\Lambda$ is different from zero, and such states are therefore called $\Sigma$ states.

\text{As long as the coupling of spin and orbital motion is small the electronic eigenfunction $\psi_{\alpha}$ may be written as a product of a coordinate function $\psi_{\alpha}$, as in (V, 4) or (V, 5), and a spin function $\beta$, that is}

$$\psi_{\alpha} = \psi_{\alpha}\beta \quad (V, 9)$$

The form of the spin function is the same as for atoms with the same number of electrons. For the case of two electrons see A.A., p. 124 and Kronig (21a), for the general case see Wigner and Witmer (712).

Symmetry properties of the electronic eigenfunctions. For the classification of molecular electronic states, in addition to the quantum numbers introduced above, the symmetry properties of the electronic eigenfunctions are of great importance. These symmetry properties depend on the symmetry properties of the field in which the electrons move (compare the general discussion in Chapter I, p. 24).

In a diatomic molecule (and similarly in a linear polyatomic molecule) any plane through the internuclear axis is a plane of symmetry. Therefore the electronic eigenfunction of a non-degenerate state ($\Sigma$ state) either remains unchanged or changes sign when reflected at any plane passing through both nuclei. In the first case, the state is called a $\Sigma^+$ state, and in the second case it is called a $\Sigma^-$ state.

The eigenfunctions of $\Sigma$ states according to (V, 4) do not depend on $\Psi_1$ but only on the relative azimuths of the electrons. In the case of two electrons, an eigenfunction that changes sign for a reflection at any plane through the internuclear axis ($\Sigma^-$) is, for example, $\sin \varphi_1$, if $\varphi_1$ is the azimuthal angle between electrons 1 and 2, whereas $\cos \varphi_1$ is an example of an eigenfunction that does not change sign for such a reflection ($\Sigma^+$)

For degenerate states ($\Pi$, $\Delta$, \ldots states) the electronic eigenfunction need not remain unchanged or only change sign when a symmetry operation is carried out, but may also go over into another of the functions belonging to the same eigenvalue (other than $-\Psi$). For example, by reflection at a plane through the internuclear axis (exchange of all the azimuthal angles with their negative values), the first of the functions (V, 4) goes over into the second, and vice versa. However, linear combinations (V, 5) can easily be found such as remain unchanged or go over into their negatives by the reflection—namely, the functions

$$\psi_{\alpha}^+ = c\psi_{\alpha} + d\psi_{\alpha}$$  

It can be seen immediately that when all the $\varphi_i$ are replaced by $-\varphi_i$, the function $\psi_{\alpha}^+$ remains unaltered, whereas $\psi_{\alpha}^+$ goes over into $-\psi_{\alpha}^-$. The functions $\psi_{\alpha}^+$ and $\psi_{\alpha}^-$ are linearly independent of each other and can therefore also be chosen as the two eigenfunctions of the degenerate state in place of (V, 4). That is to say, all the eigenfunctions of this state can be represented by

$$\psi_{\alpha} = c\psi_{\alpha}^+ + d\psi_{\alpha}^- \quad (V, 11)$$

where $c$ and $d$ are two constants.

According as the eigenfunction is $\psi_{\alpha}^+$ or $\psi_{\alpha}^-$, we may therefore also distinguish $\Pi^+$, $\Pi^-$, $\Delta^+$, $\Delta^-$, \ldots states, similar to the $\Sigma^+$ and $\Sigma^-$ states but with the difference that $\Pi^+$ and $\Pi^-$ (and correspondingly the other pairs) have exactly equal energies, so that it is usually superfluous to make this distinction. However, if we take account of the influence of the rotation of the molecule (see below), a splitting takes place into two components of slightly different energy with just the eigenfunctions $\psi_{\alpha}^+$ and $\psi_{\alpha}^-$, and not into two components with eigenfunctions
In section 1 we have considered the electronic motions in the field of two fixed nuclei (two-center system) and have disregarded the fact that in the actual molecule rotation and vibration take place simultaneously with the electronic motions. It is now necessary to consider in which way these different motions influence one another.

(c) Symmetry Properties of the Rotational Levels

The symmetry properties of the rotational levels introduced in Chapter III, section 2(f)—positive-negative, and, for identical nuclei, symmetric-antisymmetric—are, as we have already mentioned, influenced by the symmetry of the electronic eigenfunctions. Now that we have become acquainted with the different kinds of electronic eigenfunctions, we can discuss this in greater detail.

\[ \Sigma \] states. A more detailed discussion (see below) shows that for \( \Sigma^+ \) states the even-numbered rotational levels are positive and the odd are negative, whereas for \( \Sigma^- \) states the even are negative and the odd are positive. For multiplet \( \Sigma \) states the character positive-negative depends on whether \( K \) (not \( J \)) is even or odd [see Wigner and Witmer (712)]. The symmetry properties of the rotational levels of \( 1\Sigma^+, 2\Sigma^+, 3\Sigma^+ \), and \( 1\Sigma^-, 2\Sigma^-, 3\Sigma^- \) states are represented schematically in Fig. 114(a). The positive and negative rotational levels are indicated by \( \Theta \) or \( \Theta \), respectively, on the horizontal lines. The spacing of the circles does not correspond to the separation of the rotational levels.

A molecular state is called positive or negative [see Chapter III, section 2(f)] according as the total eigenfunction remains unaltered or changes its sign by reflection of all the particles (including the nuclei) at the origin (inversion). The vibrational and rotational eigenfunctions, \( \psi_e \) and \( \psi_r \), depend on the coordinates of the nuclei only. According to our previous discussion, \( \psi_r \) remains unchanged or changes its sign for an inversion depending on whether \( K \) is even or odd [see Wigner and Witmer (712)]. The vibrational eigenfunction of \( \psi_e \) remains unaltered, since it depends only on the magnitude of the internuclear distance. In order to see how the electronic eigenfunction \( \psi_e \) behaves for an inversion we must take account of the fact that an inversion is equivalent to a rotation of the molecule through 180° about
an axis perpendicular to the internuclear axis, followed by a reflection at a plane perpendicular
to this rotational axis and passing through the internuclear axis. The first operation does
not influence \( \psi \), since \( \psi \) depends only on the co-ordinates of the electrons relative to the nuclei
(as well as on the internuclear distance), whereas the second operation (which affects the
electrons only) leaves \( \psi \) unaltered for \( \Sigma^+ \) states and changes its sign for \( \Sigma^- \) states (see the
definition of \( \Sigma^+ \) and \( \Sigma^- \) states, p. 217); that is, \( \psi \) remains unaltered or changes its sign for
an inversion depending on whether the electronic state is \( \Sigma^+ \) or \( \Sigma^- \). From these considera-
tions it follows that the total eigenfunction \( \psi = \psi_e \cdot (1/r) \psi_r \cdot \psi \) for a \( \Sigma^+ \) state remains
unaltered or changes its sign for an inversion—that is, a rotational level of a \( \Sigma^+ \) state is positive
or negative—according as the rotational quantum number is even or odd, whereas for \( \Sigma^- \)
states just the converse holds.

Thus far \( \psi_e \) was considered to be the electronic coordinate function. It has to be multi-
plied by a function representing the orientation of the electron spins. In case (b) (which
always holds for \( \Sigma \) states) this spin function is independent of an inversion [see Kronig (21a)]
and therefore levels with different \( J \) but equal \( K \) have the same (+, −) symmetry [see Fig.
114(a)].

If the two nuclei of the molecule are identical we have to consider in addition
the symmetry with respect to an exchange of the nuclei. It is easily seen (see below)
that the positive rotational levels are symmetric and the negative are anti-
symmetric for even electronic states (for example, \( \Sigma_e \)), and the negative are sym-
metric and the positive are antisymmetric for odd states (for example, \( \Sigma_o \)).
These properties are represented in Fig. 114(b) for \( \Sigma_e^+ \), \( \Sigma_e^- \), \( \Sigma_o^+ \), and \( \Sigma_o^- \).
Multiplet \( \Sigma \) states show a corresponding behavior.

An exchange of the nuclei can be brought about by first reflecting all particles at the
origin and then reflecting only the electrons at the origin. In the first reflection the eigen-