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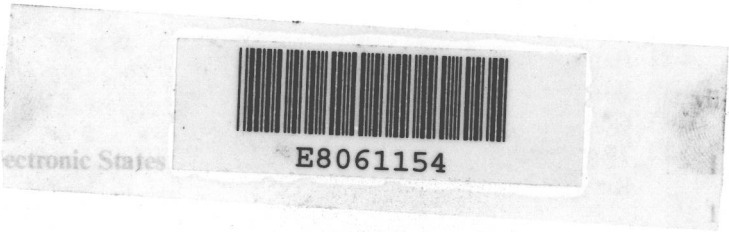

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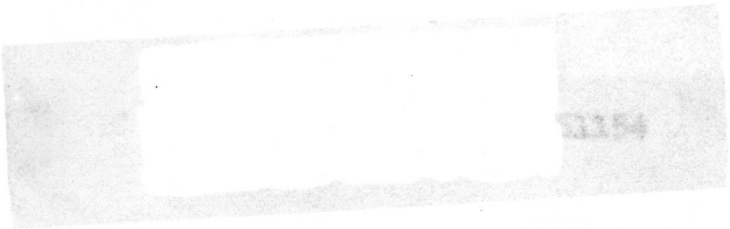

MOLECULAR ELECTRONIC STRUCTURES OF TRANSITION METAL COMPLEXES

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PREFACE

The electronic structures of inorganic complexes are to a large extent decided by the fact that these ions and molecules have a transition-metal atom situated at a center of high symmetry. The high degeneracy of the metal d- and f-valence orbitals, so characteristic of central symmetry, is therefore only removed in part. Since, furthermore, the degenerate molecular orbitals of the complex may only be partially filled with electrons, the electronic-term problem bears many similarities to that encountered in the theory of atomic spectra.

The analogies between the theory of atomic structures and the electronic structures of complexes are therefore many. Nevertheless, the all-important fact is that inorganic complexes are not just pure metal ions in disguise. As realized by Van Vleck in 1935 they are true molecular entities, and should be treated as such. The only existing theory which can give a simple consistent picture of the ground and excited molecular electronic states is the molecular orbital theory. Consequently, in this book the theory of electronic structures of complexes is developed solely from this point of view. Furthermore, the aim has been to characterize rather than to calculate.

Most chemists working with the electronic structures of inorganic transition-metal complexes have arrived at the subject via an education in inorganic chemistry. Using a variant of a simplified electronic theory, their aim is usually to extract parameters for a class of complexes and then to arrange these in some series. On the other hand, the solid-state physicists working in this field will often be content to write down an "effective hamiltonian" for one compound and add terms to this until the experimental numbers can be reproduced. Both groups therefore strive to express their experimental findings using some parameterized theory. Unfortunately the temptation is to elaborate an approximate theory and to introduce an increasing number of loosely defined "effects" in order to "explain"

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the movements of the parameters. For the uninitiated this can easily lead to great confusion, and there is little reason to expect that deeper insight can be gained in this way.

It is well known that a model may correctly describe certain features in one area of a research field but be hopelessly inadequate in others. As an obvious example the crystal field concept springs to mind. In order to avoid the many pitfalls which await a molecular spectroscopist when interpreting experimental results or when building theoretical models, it is therefore imperative to possess a sound knowledge of quantum chemistry.

I have tried to write such a text which twenty years of experience have taught me might be of help to a chemist wishing to work with the electronic structures of inorganic complexes. Rigorous mathematical derivations have not been stressed. Hopefully, enough details have been given so that the essential lines of development are transparent. I have furthermore assumed that the reader commands a working knowledge of group theory. Calculational methods, exemplified by *ab initio* and semi-empirical procedures have not been dealt with. No attempts have been made to cover the literature, either from a theoretical or experimental point of view. I have merely picked out what I considered to be the important ideas and developments, and I have illustrated them by using simple examples.

I wish to thank my colleagues Professor Dr. Jens Peder Dahl and Lektor Dr. Aage E. Hansen for many helpful discussions on the material in this book, and I am greatly indebted to Mrs. E. Ottonello for the preparation of the manuscript.

C.J.B
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CHAPTER

ONE

THE ELECTRONIC STATES

1-1 THE BORN-OPPENHEIMER APPROXIMATION

The whole of chemistry is a reflection of the behavior of electrons in various potential fields. Experience has shown us that the conduct of electrons cannot be described using the classical laws of motion. Hence chemistry is one huge manifestation of quantum phenomena. Unfortunately, even for a small molecule a reasonably exact quantum-mechanical solution of the molecular Schrödinger equation is a formidable task. In order to gain some insight into electronic behavior, it is therefore necessary to introduce simplifying approximations. The nature of such approximations must of course be adjusted to the phenomena in which we are interested. We must take care not to introduce artificial features into the system, and at the same time not to throw away important traits.

The molecules and ions which we shall be interested in here contain so many nuclei that the rotational structure is washed out. On the other hand, in many interesting cases, the electronic transitions will show some vibrational structure. The wave functions for a molecule are dependent both on the nuclear and electronic coordinates. The first and fundamental approximation we shall introduce is the separation of the electronic and nuclear motions. This is performed using the so-called Born–Oppenheimer approximation.[1,2]

Let us designate the positions and masses of the nuclei μ by $(\mathbf{Q}_\mu, M_\mu)$ and the positions and masses for the electrons by $(\mathbf{r}_i, m)$, where all the vectors $\mathbf{r}$ and $\mathbf{Q}$ are referred to a laboratory-fixed coordinate system. The total nonrelativistic hamiltonian for a molecular system of N nuclei and n electrons is

$$\mathscr{H} = -\sum_\mu \frac{\hbar^2}{2M_\mu} \nabla_\mu^2 - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 + V(\mathbf{r}, \mathbf{Q}) \tag{1-1}$$

$V(\mathbf{r}, \mathbf{Q})$ is the potential energy term equal to

$$V(\mathbf{r}, \mathbf{Q}) = -\sum_{\mu,i} \frac{Z_\mu e^2}{|\mathbf{Q}_\mu - \mathbf{r}_i|} + \sum_{\mu<\nu} \frac{Z_\mu Z_\nu e^2}{|\mathbf{Q}_\mu - \mathbf{Q}_\nu|} + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1-2}$$

Let us now suppose that all the nuclear masses are infinite. Clearly, this will quench the nuclear motions, leading to an "electronic" hamiltonian of the form

$$\mathscr{H}_E = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 + V(\mathbf{r}, \mathbf{Q}) \tag{1-3}$$

The "electronic" Schrödinger equation is then defined as

$$\mathscr{H}_E \Psi_t(\mathbf{r}, \mathbf{Q}) = W_t(\mathbf{Q}) \Psi_t(\mathbf{r}, \mathbf{Q}) \tag{1-4}$$

Both $W_t(\mathbf{Q})$ and $\Psi_t(\mathbf{r}, \mathbf{Q})$ are seen to contain the nuclear positions $\mathbf{Q}$ as parameters, and are indeed continuous functions of the $3N$ nuclear coordinates. In principle, we could solve Eq. (1-4) for all values of the $3N$ nuclear coordinates, and for each nuclear arrangement we would obtain a complete set of electronic wave functions $\Psi_t(\mathbf{r}, \mathbf{Q})$ and eigenvalues $W_t(\mathbf{Q})$.

Introducing the "electronic" hamiltonian into the molecular hamiltonian of Eq. (1-1), this may be rewritten

$$\mathscr{H} = \mathscr{H}_E - \sum_\mu \frac{\hbar^2}{2M_\mu} \nabla_\mu^2 \tag{1-5}$$

We now use the variational principle to solve the molecular Schrödinger equation, and as our variational wave function we take the finite expansion

$$\Psi = \sum_{t=1}^{p} \chi_t(\mathbf{Q}) \Psi_t(\mathbf{r}, \mathbf{Q}) \tag{1-6}$$

The use of a trial wave function of this form is inspired by the fact that had the solutions to the electronic Schrödinger equation been independent of the nuclear coordinates, a single product function would be the exact solution to the hamiltonian in Eq. (1-5).

Without loss of generality we can take $\Psi_t(\mathbf{r}, \mathbf{Q})$ to be real and normalized

$$\int |\Psi_t(\mathbf{r}, \mathbf{Q})|^2 \, d\mathbf{r} = 1 \tag{1-7}$$

Notice in particular that $\Psi_t(\mathbf{r}, \mathbf{Q})$ is assumed normalized for all values of $\mathbf{Q}$.

Using Eq. (1-5) together with Eq. (1-6) now leads to

$$-\sum_\mu \frac{\hbar^2}{2M_\mu} \left\{ \sum_t \Psi_t(\mathbf{r}, \mathbf{Q}) \nabla_\mu^2 \chi_t(\mathbf{Q}) + 2 \sum_t \nabla_\mu \Psi_t(\mathbf{r}, \mathbf{Q}) \nabla_\mu \chi_t(\mathbf{Q}) + \sum_t \chi_t(\mathbf{Q}) \nabla_\mu^2 \Psi_t(\mathbf{r}, \mathbf{Q}) \right\}$$
$$+ \mathscr{H}_E \sum_t \chi_t(\mathbf{Q}) \Psi_t(\mathbf{r}, \mathbf{Q}) = W \sum_t \chi_t(\mathbf{Q}) \Psi_t(\mathbf{r}, \mathbf{Q}) \tag{1-8}$$

Multiplying Eq. (1-8) by $\Psi_u(\mathbf{r}, \mathbf{Q})$, and integrating over the electronic coordinates making use of the orthonormal properties of the set $\Psi_t(\mathbf{r}, \mathbf{Q})$, leads to

$$-\sum_{\mu}\frac{\hbar^2}{2M_\mu}\nabla_\mu^2\chi_u(\mathbf{Q})+W_u(\mathbf{Q})\chi_u(\mathbf{Q})-W\chi_u(\mathbf{Q})$$

$$-\sum_{\mu}\frac{\hbar^2}{2M_\mu}\sum_{t}2\langle\Psi_u(\mathbf{r},\mathbf{Q})\,|\,\nabla_\mu\,|\,\Psi_t(\mathbf{r},\mathbf{Q})\rangle\nabla_\mu\chi_t(\mathbf{Q})$$

$$-\sum_{\mu}\frac{\hbar^2}{2M_\mu}\sum_{t}\langle\Psi_u(\mathbf{r},\mathbf{Q})\,|\,\nabla_\mu^2\,|\,\Psi_t(\mathbf{r},\mathbf{Q})\rangle\chi_t(\mathbf{Q})=0 \tag{1-9}$$

If we define an operator $\hat{C}_{u,t}$ equal to

$$\hat{C}_{u,t}=\sum_{\mu}\frac{\hbar^2}{2M_\mu}2\langle\Psi_u(\mathbf{r},\mathbf{Q})\,|\,\nabla_\mu\,|\,\Psi_t(\mathbf{r},\mathbf{Q})\rangle\nabla_\mu+\sum_{\mu}\frac{\hbar^2}{2M_\mu}\langle\Psi_u(\mathbf{r},\mathbf{Q})\,|\,\nabla_\mu^2\,|\,\Psi_t(\mathbf{r},\mathbf{Q})\rangle \tag{1-10}$$

we can write Eq. (1-9) as

$$\left\{-\sum_{\mu}\frac{\hbar^2}{2M_\mu}\nabla_\mu^2+W_\mu(\mathbf{Q})-W-\hat{C}_{u,u}\right\}\chi_u(\mathbf{Q})-\sum_{u\neq t}\hat{C}_{u,t}\chi_t(\mathbf{Q})=0 \tag{1-11}$$

The set (1-11) of coupled differential equations can be used to determine the expansion coefficients $\chi_t(\mathbf{Q})$. In principle we can get the total wave function for the molecule by solving the electronic Schrödinger Eq. (1-4) for all values of $\mathbf{Q}$, thereby getting all of the electronic wave functions, $\Psi(\mathbf{r},\mathbf{Q})$. These should then be multiplied by the nuclear wave functions, $\chi(\mathbf{Q})$, to obtain Eq. (1-6). The Eqs. (1-11) can then be used to determine the complete wave functions to any degree of accuracy.

This method to derive the total wave function for a molecular system is called the Born–Oppenheimer separation; it is seen to lead to two different sets of equations, one governing the electronic motions, Eq. (1-4), and one governing the nuclear motions, Eq. (1-11), that is the molecular vibrations and rotations.

For orders of magnitude of the electronic, vibrational, and rotational energies we have

$$w_{\text{el}}=\frac{\hbar^2}{ma_0^2}$$

and

$$w_{\text{rot}}=\frac{\hbar^2}{Ma_0^2}$$

where a_0 is a characteristic length of the molecule. With $w_{\text{vib}}=h\nu=\hbar\sqrt{k/M}$ we can also write $w_{\text{el}}=\hbar\sqrt{k/m}$ since at equilibrium the same forces act on the electrons and nuclei. Hence

$$w_{\text{vib}}=\sqrt{\frac{m}{M}}\,w_{\text{el}}\quad\text{and}\quad w_{\text{rot}}=\frac{m}{M}\,w_{\text{el}}$$

The original Born–Oppenheimer separation used an expansion[3] in the parameter $\eta=(m/M)^{1/4}$. For a harmonic oscillator in its ground state we have for the average value of the displacement, $\langle\xi^2\rangle$, of the system from its equilibrium position

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$\langle \xi^2 \rangle = \hbar/2\pi\nu M$, where ν is the classical vibrational frequency. Defining the dimensionless quantity

$$\eta = \frac{\sqrt{\langle \xi^2 \rangle}}{a_0} \equiv \left(\frac{m}{M}\right)^{1/4} \tag{1-12}$$

we can see the physical background for the expansion parameter.

The equations show that for molecules of a certain size the rotational energies are very small indeed. We shall therefore, in what follows, completely neglect the rotational energies and only consider the electronic and vibrational motions.

1-2 THE ADIABATIC APPROXIMATION

The operators $\hat{C}_{u,t}$ contain integrals which depend on the first and second derivatives of the electronic wave functions with respect to the nuclear coordinates. For the diagonal terms $\hat{C}_{u,u}$ we have, recalling the normalization condition of Eq. (1-7)

$$\nabla_\mu \int |\Psi_u(\mathbf{r}, \mathbf{Q})|^2 \, d\mathbf{r} = 0$$

or

$$\langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu | \Psi_u(\mathbf{r}, \mathbf{Q}) \rangle = 0 \tag{1-13}$$

To estimate $\hbar^2/2M_\mu \langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu^2 | \Psi_u(\mathbf{r}, \mathbf{Q}) \rangle$ we observe that nuclei and electrons experience roughly the same Coulombic forces, since the interaction between them is determined by the value of $|\mathbf{Q}_\mu - \mathbf{r}_i|$. Hence $\nabla_\mu^2 \Psi_u(\mathbf{r}, \mathbf{Q}) \approx \nabla_i^2 \Psi_u(\mathbf{r}, \mathbf{Q})$. We have then

$$\frac{\hbar^2}{2M_\mu} \langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_i^2 | \Psi_u(\mathbf{r}, \mathbf{Q}) \rangle \approx \frac{\hbar^2}{2M_\mu a_0^2} \approx W_{\text{rot}}$$

where a_0 is the Bohr radius and W_{rot} is the energy of a rotational quantum of the molecule.

The electronic integrals contained in the off-diagonal operators $\hat{C}_{u,t}$ can be evaluated by differentiating Eq. (1-4) with respect to $\mathbf{Q}_\mu$. This yields

$$\Psi_t(\mathbf{r}, \mathbf{Q}) \nabla_\mu \mathscr{H}_E + \mathscr{H}_E \nabla_\mu \Psi_t(\mathbf{r}, \mathbf{Q}) = \Psi_t(\mathbf{r}, \mathbf{Q}) \nabla_\mu W_t(\mathbf{Q}) + W_t(\mathbf{Q}) \nabla_\mu \Psi_t(\mathbf{r}, \mathbf{Q}) \tag{1-14}$$

Multiplying from the left by $\Psi_u(\mathbf{r}, \mathbf{Q})$ and integrating over the electronic coordinates gives

$$W_t(\mathbf{Q}) \langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu | \Psi_t(\mathbf{r}, \mathbf{Q}) \rangle = W_u(\mathbf{Q}) \langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu | \Psi_t(\mathbf{r}, \mathbf{Q}) \rangle + \langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu V(\mathbf{r}, \mathbf{Q}) | \Psi_t(\mathbf{r}, \mathbf{Q}) \rangle$$

or for the case where Ψ_t and Ψ_u are nondegenerate

$$\langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu | \Psi_t(\mathbf{r}, \mathbf{Q}) \rangle = \frac{\langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu V(\mathbf{r}, \mathbf{Q}) | \Psi_t(\mathbf{r}, \mathbf{Q}) \rangle}{W_t(\mathbf{Q}) - W_u(\mathbf{Q})} \tag{1-15}$$

Differentiating Eq. (1-13) we obtain

$$\langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu^2 | \Psi_u(\mathbf{r}, \mathbf{Q}) \rangle + \langle \nabla_\mu \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu | \Psi_u(\mathbf{r}, \mathbf{Q}) \rangle = 0 \qquad (1\text{-}16)$$

We have found that the first term of this equation is of the order of magnitude a_0^{-2}. We observe that the second term in Eq. (1-16) is just $\langle \nabla_\mu \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu \Psi_u(\mathbf{r}, \mathbf{Q}) \rangle$. The norm of $\nabla_\mu \Psi_u(\mathbf{r}, \mathbf{Q})$ is consequently a_0^{-1}. Therefore using the Schwarz inequality

$$|\langle \phi | \psi \rangle| < \sqrt{\langle \phi | \phi \rangle \langle \psi | \psi \rangle}$$

we get

$$\frac{\hbar^2}{2M_\mu} \langle \Psi_u(\mathbf{r}, \mathbf{Q}) | \nabla_\mu^2 | \Psi_t(\mathbf{r}, \mathbf{Q}) \rangle < \frac{\hbar^2}{2M_\mu a_0^2} \approx W_{\text{rot}}$$

Since we are here only interested in large molecules and ions we may neglect the very small rotational energies. We note that under these conditions the operator $\hat{C}_{u,u}$ disappears and that $\hat{C}_{u,t}$ reduces to the first term in Eq. (1-10). Furthermore, provided that there are no close-lying electronic states we notice from Eq. (1-15) that the first term in Eq. (1-10) is also small. For nondegenerate electronic wave functions it may safely be neglected.

When all the off-diagonal operators $\hat{C}_{u,t}$ in Eq. (1-11) are thrown away, the molecular wave function (1-6) is seen to reduce to a single term

$$\Psi = \chi_t(\mathbf{Q}) \Psi_t(\mathbf{r}, \mathbf{Q}) \qquad (1\text{-}17)$$

This form of Ψ is called the *adiabatic approximation* to the molecular wave function. In this scheme each "electronic" wave function $\Psi_t(\mathbf{r}, \mathbf{Q})$ is determined by the "electronic" Schrödinger Eq. (1-4) and the associated nuclear wave function is determined by the simplified form of Eq. (1-11):

$$\left\{ -\sum_\mu \frac{\hbar^2}{2M_\mu} \nabla_\mu^2 + W_t(\mathbf{Q}) \right\} \chi_{t,v}(\mathbf{Q}) = W_{t,v} \chi_{t,v}(\mathbf{Q}) \qquad (1\text{-}18)$$

The nuclear functions $\chi_{t,v}(\mathbf{Q})$ are seen in the adiabatic approximation to be given as the solutions to a wave equation in which the "electronic" energy $W_t(\mathbf{Q})$ acts as the potential energy.

It is quite obvious from the form of Eq. (1-15) that had our electronic wave function belonged to a degenerate set, an adiabatic wave function would have been a very bad approximation to a molecular wave function. In this case, the coupling operator $\hat{C}_{u,t}$ assumes great importance, and the total wave function will be of the type shown in Eq. (1-6). This situation and its consequences are dealt with under the heading of the Jahn–Teller effect (section 1-6).

1-3 THE NUCLEAR MOTIONS

In the adiabatic approximation, as leading to Eqs. (1-17) and (1-18), $W_t(\mathbf{Q})$ and $\chi_{t,v}(\mathbf{Q})$ are functions of the $3N$ cartesian coordinates of the N nuclei:

$$\mathbf{Q} = (Q_{1x}, Q_{1y}, Q_{1z}, \ldots, Q_{Nz}) \qquad (1\text{-}19)$$

The nuclear and electronic positions $(\mathbf{Q}, \mathbf{r})$ are measured in a laboratory-fixed coordinate system. The nuclear kinetic operators depends upon the $3N$ second-order derivatives with respect to these coordinates. In order to treat the vibrations of the nuclei the so-called normal coordinates are introduced.[4] This involves changing from the external coordinates $\mathbf{Q}$ to an internal molecular-coordinate system ξ.

Let us assume that we can find at least one point $\mathbf{Q}^0$ in the $3N$ dimensional coordinate system for which all the first derivatives of $W_t(\mathbf{Q})$, with respect to Q_{3N} are equal to zero. Thus for all μ

$$\left(\frac{\partial W(\mathbf{Q})}{\partial Q_{\mu x}}\right)_{\mathbf{Q}^0} = \left(\frac{\partial W(\mathbf{Q})}{\partial Q_{\mu y}}\right)_{\mathbf{Q}^0} = \left(\frac{\partial W(\mathbf{Q})}{\partial Q_{\mu z}}\right)_{\mathbf{Q}^0} = 0 \tag{1-20}$$

Obviously the function $W_t(\mathbf{Q})$ will have an extremum at the point $\mathbf{Q}^0$. Whether $\mathbf{Q}^0$ represents a minimum or a maximum depends, of course, upon the values of the second derivatives of $W_t(\mathbf{Q})$.

In the case where the conditions of Eq. (1-20) cannot be fulfilled, and at least one of the $3N$ derivatives is different from zero for all values of the nuclear coordinate, this simply means that the potential hypersurface cannot have a minimum with respect to this nuclear coordinate, and that the corresponding molecular state is unstable. However, if for some point $\mathbf{Q}^0$, Eq. (1-20) can indeed be fulfilled, $\mathbf{Q}^0$ will be taken to represent a stable configuration of the molecule in the state $\Psi_t(\mathbf{r}, \mathbf{Q})$.

We now introduce a set of $3N$ mass-weighted displacement coordinates $S_1, \ldots, S_{3N}$ defined as

$$\begin{aligned} S_1 &= \sqrt{M_1}(Q_{1x} - Q_{1x}^0) \\ S_2 &= \sqrt{M_1}(Q_{1y} - Q_{1y}^0) \\ S_3 &= \sqrt{M_1}(Q_{1z} - Q_{1z}^0) \\ &\vdots \\ S_{3N} &= \sqrt{M_N}(Q_{Nz} - Q_{Nz}^0) \end{aligned} \tag{1-21}$$

This transformation amounts to a translation of the Q-coordinate system followed by a change in scale on the axes. The first and second derivatives with respect to these displacement coordinates are seen to be

$$\frac{\partial}{\partial S_1} = \frac{1}{\sqrt{M_1}}\frac{\partial}{\partial Q_{1x}} \qquad \frac{\partial^2}{\partial S_1^2} = \frac{1}{M_1}\frac{\partial^2}{\partial Q_{1x}^2}$$

$$\vdots \qquad \text{and} \qquad \vdots$$

$$\frac{\partial}{\partial S_{3N}} = \frac{1}{\sqrt{M_N}}\frac{\partial}{\partial Q_{Nz}} \qquad \frac{\partial^2}{\partial S_{3N}^2} = \frac{1}{M_N}\frac{\partial^2}{\partial Q_{Nz}^2}$$

In this coordinate system the point S^0, for which all the first derivatives of the function $W_t(S)$ vanish, obviously lies at the origin $S^0 = (0, 0, \ldots, 0)$, and we can

expand $W_t(S)$ in a Taylor series retaining terms up to second order only:

$$W_t(S) = W_t^0 + \frac{1}{2}\sum_{k,l}\left(\frac{\partial^2 W_t(S)}{\partial S_k\,\partial S_l}\right)_0 S_k S_l + \cdots \tag{1-22}$$

where W_t^0 is the electronic energy evaluated at the origin (or equivalently at $\mathbf{Q}^0$) and where all terms containing the first derivatives of $W_t(S)$ are absent by virtue of Eq. (1-20). The second derivatives of $W_t(S)$ are to be evaluated at the origin, as indicated by the subscript 0.

Introducing this transformation of coordinates into the nuclear wave Eq. (1-18) leads to

$$\left[-\frac{\hbar^2}{2}\sum_k \nabla_k^2 + W_t^0 + \frac{1}{2}\sum_{k,l} f_{kl}^t S_k S_l - W_t\right]\chi_t(S) = 0 \tag{1-23}$$

The potential-energy term in Eq. (1-22) is a so-called quadratic form, containing all of the cross terms $S_k S_l$. Introducing a linear combination of all the displacement coordinates of Eqs. (1-21) we can, however, reduce the potential-energy terms to a form in which all of the cross terms have disappeared. Taking

$$\xi_u = \sum_k b_{ku} S_k \tag{1-24}$$

and introducing relative nuclear energies

$$\tilde{W}_t = W_t - W_t^0 \tag{1-25}$$

Eq. (1-23) can be written as

$$\sum_{u=1}^{3N}\left[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial\xi_u^2} + \frac{1}{2}a_u^t\xi_u^2\right]\chi_t(\xi_u) = \sum_{u=1}^{3N}\tilde{W}_t\chi_t(\xi_u) \tag{1-26}$$

The coordinates ξ_u represent all of the possible movements of the nuclei. Three of them will, therefore, describe the translations of the molecule as a whole, and three of them will characterize the rotations of the molecule. The translations and the rotations cannot, however, depend upon the intermolecular distances. The potential energy terms in Eq. (1-26) associated with the translations and the rotations, depending as they do upon the internuclear distances, must therefore be zero. This implies that for nonlinear molecules the coefficients a_1^t to a_6^t are zero. (For linear molecules only a_1^t to a_5^t are zero.) Equation (1-26) is thereby reduced to

$$\left[\sum_{u=1}^{6}\left(-\frac{\hbar^2}{2}\frac{\partial^2}{\partial\xi_u^2}\right) + \sum_{u=7}^{3N}\left(-\frac{\hbar^2}{2}\frac{\partial^2}{\partial\xi_u^2} + \frac{1}{2}a_u^t\xi_u^2\right) - \tilde{W}_t\right]\chi_t(\xi_u) = 0 \tag{1-27}$$

The $3N - 6$ linear combinations ξ_u of the cartesian nuclear displacement coordinates are called the normal coordinates of the molecule. They are of such a nature as to leave the center of mass of the nuclei unaltered, and the principal axes of inertia are likewise left unchanged. It is therefore natural to use, in the description of the molecule, a cartesian coordinate system with origin at the center of mass, and with the coordinate axes directed along the principal axes of inertia

for the nuclei in the equilibrium position. Hence, in the so-called *crude adiabatic approximation* we take for the molecular wave function

$$\Psi_{tv}(\mathbf{r}, \xi) = \chi_{tv}(\xi)\psi_t^0(\mathbf{r}) \tag{1-28}$$

where the static electronic wave function $\psi_t^0(\mathbf{r})$ is calculated at the equilibrium position of the nuclei, as indicated by the zero superscript, and v is the vibrational quantum number.

The totality of all the static electronic wave functions span what has been called a Longuet–Higgins space.[5] The completeness of this space implies that we can obtain a dynamic electronic wave function as a superposition of static electronic wave functions, that is

$$\Psi_j(\mathbf{r}, \xi) = \sum_t \psi_t^0(\mathbf{r})c_{tj}(\xi) \tag{1-29}$$

Such an expansion is encountered in the so-called Herzberg–Teller vibronic scheme.

When changing the electronic coordinates from an external to an internal coordinate system we must take care not to introduce translations and rotations into our space-fixed molecule. Calling the linear momentum $\mathbf{P}$ and the angular momentum $\mathbf{L}$ we have in the center-of-mass system with n electrons

$$\mathbf{P}_{\text{nuc}} + \sum_n \mathbf{p}_n = 0 \tag{1-30}$$

$$\mathbf{L}_{\text{nuc}} + \sum_n \mathbf{l}_n = 0 \tag{1-31}$$

The kinetic-energy terms of the hamiltonian are, with $M = \sum_\mu M_\mu$, the total nuclear mass,

$$T = \frac{1}{2M}\mathbf{P}_{\text{nuc}}^2 + \sum_n \frac{1}{2m}\mathbf{p}_n^2 \tag{1-32}$$

Substituting Eq. (1-30) into Eq. (1-32) leads to

$$T = \frac{1}{2M}\left(\sum_n \mathbf{p}_n\right)^2 + \frac{1}{2m}\sum_n \mathbf{p}_n^2 = \frac{1}{2\eta_r}\sum_n \mathbf{p}_n^2 + \frac{1}{M}\sum_{n'>n} \mathbf{p}_n \cdot \mathbf{p}_{n'} \tag{1-33}$$

where $\eta_r = mM/(m + M)$, the reduced mass. The cross terms which appear in Eq. (1-33) constitute the so-called mass-polarization term. Due to the presence of $1/M$ it is very small and may be neglected in the present context. Similar, though more complicated, are the coupling terms which appear in the preservation of the angular momentum. However, these may also be safely ignored.

Using the crude adiabatic approximation the equations which govern the nuclear vibrations are then given by the last part of Eq. (1-27)

$$\sum_{u=1}^{3N-6}\left(-\frac{\hbar^2}{2}\frac{\partial^2}{\partial \xi_{tu}^2} + \frac{1}{2}a_u^t \xi_{tu}^2 - w_{vu}^t\right)\chi_{tv}(\xi_{tu}) = 0 \tag{1-34}$$

where v is a vibrational quantum number and t specifies the electronic state. The eigenvalues and eigenfunctions are those of the harmonic oscillator with unit mass and force constant a_u^t:

$$w_{vu}^t = (v + \tfrac{1}{2})\hbar\sqrt{a_u^t} = (v + \tfrac{1}{2})h\nu_u^t \qquad v = 0, 1, 2, \ldots \tag{1-35}$$

$$\chi_{tv}(\xi_{tu}) = C_v \exp\left(-\frac{\xi_{tu}^2}{2}\right) H_v(\xi_{tu}) \tag{1-36}$$

where C_v is a normalization constant and the functions $H_v(x)$ are Hermite polynomials. The first polynomials are

$$H_0(x) = 1$$
$$H_1(x) = 2x$$
$$H_2(x) = 4x^2 - 2$$
$$H_3(x) = 8x^3 - 12x$$

Notice that when v is even, only even powers of x occur in the Hermite polynomials, whereas for odd values of v, the Hermite polynomials are made up solely of odd powers.

1-4 SYMMETRY CLASSIFICATIONS AND COUPLING COEFFICIENTS

In classical mechanics there are constants of motion, such as the energy, the linear momentum **p**, and others. In quantum mechanics any operator represented by $\hat{A}$ which commutes with $\mathscr{H}$ will be a constant of the motion. This we write

$$[\mathscr{H}, \hat{A}] = \mathscr{H}\hat{A} - \hat{A}\mathscr{H} = 0$$

Hence

$$\hat{A}(\mathscr{H}\Psi) = \mathscr{H}(\hat{A}\Psi)$$
$$\| \qquad\qquad \|$$
$$\hat{A}(W\Psi) = W(\hat{A}\Psi)$$

Notice that $(\hat{A}\Psi)$ is a solution to the Schrödinger equation whenever Ψ is, and it has the same eigenvalue W.

For any molecule there are a certain number of symmetry operations that commute with $\mathscr{H}$. These include the operations which rotate, reflect, or invert the molecule into itself. Of all of these operations (including that which leaves the molecule as it was, $\hat{E}$) we have that any two of them are equivalent to a third. Such a set of symmetry operations constitutes a group.[6] The eigenfunctions of $\mathscr{H}$ form a basis for the so-called irreducible representations of the group. The molecular states can therefore be characterized by their irreducible representations in the point group of the molecule.

A set of functions spanning an irreducible representation is described by its transformation properties under the symmetry operations of the molecule. Since the traces of the transformation matrices are independent of the choice of coordinate system, it is the various traces, called the *characters*, which are used as indicators. To take an example: in the molecular symmetry O the symmetry operators are $\hat{E}$, $8\hat{C}_3$, $3\hat{C}_2$, $6\hat{C}_4$, and $6\hat{C}'_2$. The set of functions (xz), (yz), and (xy)

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