

# ON THE QUANTUM THEORY OF MOLECULES

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## ABSTRACT

It is shown that the well-known contributions to the molecular terms corresponding to the energies of the motion of the electrons, the nuclear vibrations and the rotations of a molecule can be obtained systematically as the terms of a power expansion of the fourth root of the ratio of the electron mass to the (average) nuclear mass. The method yields, among other things, an equation for the rotations, which is a generalisation of the *ansatz* of *Kramers* and *Pauli* (top with built-in flywheel). Furthermore it provides a justification of the considerations by *Franck* and *Condon* on the intensities of the band lines. The situation is illustrated by the example of two-atomic molecules.

## 0. Introduction

It is well known that the terms of the molecular spectra are composed of contributions with different orders of magnitude. The largest contribution derives from the electronic motion around the nuclei, followed by the contribution from the nuclear vibrations, and lastly there are the contributions deriving from the nuclear rotations. The reason for the existence of such an ordering evidently lies in the size of the mass of the nuclei in comparison to that of the electrons. From the viewpoint of the old quantum theory, which computes stationary states with the help of classical mechanics, this idea has been developed by *Born* and *Heisenberg*;<sup>1</sup> it was shown that the enumerated energy contributions appear as terms of increasing order with regard to the ratio  $\sqrt{\frac{m}{M}}$ , where  $m$  is the electron mass and  $M$  the average nuclear mass. Nuclear vibrations and rotations occurred here in the same (second) order, which is in disagreement with the empirical findings for small rotational quantum numbers.

Here, the problem is taken up anew from the viewpoint of quantum mechanics.<sup>2</sup> Thereby it appears that one should not expand in  $\sqrt[2]{\frac{m}{M}}$  but in  $\sqrt[4]{\frac{m}{M}}$  in order to obtain the natural sequence of the energy contributions. Apart from this, the treatment becomes much simpler and more transparent than in the old theory. The nuclear vibrations represent the terms of second order, the rotations those of the fourth order in the expansion of the energy, while the terms of first and third order disappear. The cancellation of the first order terms is related to the existence of

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<sup>1</sup>M. Born and W. Heisenberg, *Ann. Phys.* **74**, 1 (1924).

<sup>2</sup>In the discussion of the principles of this work we have been assisted by the valuable comments of Dr. P. Jordan, to whom we express our thanks.

an “equilibrium configuration”, where the electronic energy with nuclei at rest is at a minimum. The fourth order terms for the rotational motion represent a generalisation of the well-known *ansatz* of *Kramers* and *Pauli*,<sup>3</sup> who have portrayed the behaviour of a molecule as a top with a flywheel. To determine the eigenfunctions and thereby also the transition intensities in the zeroth order approximation, the energy computation must be carried out through fourth order (rotations). One obtains expressions for the probabilities of simultaneous jumps of electronic, vibrational and rotational quantum numbers which give a precise formulation to the concepts developed by *Franck*<sup>4</sup> and formulated by *Condon*.<sup>5</sup>

The approximations higher than fourth order are not treated in this work; they will represent the couplings between the three basic types of motion. The calculation of these effects makes sense only when we consider at the same time all degeneracies of the electronic motion with the nuclei at rest, especially *Heisenberg’s* resonance degeneracy resulting from the equality of the electrons (and, should the occasion arise, also some nuclei) and for two-atomic molecules the degeneracy of the eigenrotation around the axis connecting the nuclei. We will forego these complicated considerations.

As an example two-atomic molecules will be considered more closely, not only following the general method, but also with another, in which the rotation is already taken into account in zeroth order by separation of variables, similar to the method of *Born* and *Hückel*<sup>6</sup> in the old quantum theory.

## 1. Terms and definitions

The mass and the Cartesian coordinates of the electron we indicate by

$$m, x_k, y_k, z_k,$$

those of the nuclei by

$$M_l, X_l, Y_l, Z_l.$$

If  $M$  is some mean value of the  $M_l$ , then we put

$$\kappa = \sqrt[4]{\frac{m}{M}} \quad (1)$$

and

$$M_l = M \frac{1}{\mu_l} = \frac{m}{\kappa^4 \mu_l}; \quad (2)$$

then  $\mu_l$  are pure numbers of order of magnitude 1. The potential energy of the system is

$$\begin{cases} U(x_1, y_1, z_1, x_2, y_2, z_2, \dots; X_1, Y_1, Z_1, X_2, Y_2, Z_2, \dots) \\ = U(x, X). \end{cases} \quad (3)$$

<sup>3</sup>H. A. Kramers, *Z. Phys.* **13**, 343 (1923); H. A. Kramers and W. Pauli Jr., **13**, 351 (1923).

<sup>4</sup>J. Franck, *Trans. Faraday Soc.* (1925).

<sup>5</sup>E. Condon, *Phys. Rev.* **28**, 1182 (1926); *Proc. Nat. Acad.* **13**, 462 (1927).

<sup>6</sup>M. Born and E. Hückel, *Phys. Z.* **24**, 1 (1923).

Here, as everywhere in what follows, we will represent the totality of the electronic coordinates by  $x$ , and the totality of the nuclear coordinates by  $X$ . The function  $U$  only depends on the relative positions of the particles, but we do not use its special form (Coulomb's law). The kinetic energy of the electrons is represented by the operator

$$\mathsf{T}_E = -\frac{h^2}{8\pi^2m} \sum_x \sum_k \frac{\partial^2}{\partial x_k^2}, \quad (4)$$

where the symbol  $\sum_x$  means the sum over the terms which emerge from the given equation through cyclic permutation of  $x, y, z$ .

The kinetic energy of the nuclei is

$$\mathsf{T}_K = -\kappa^4 \frac{h^2}{8\pi^2m} \sum_X \sum_l \mu_l \frac{\partial^2}{\partial X_l^2}. \quad (5)$$

The total energy corresponds to the operator

$$H = H_0 + \kappa^4 H_1 \quad (6)$$

where we have put

$$\left\{ \begin{array}{l} \mathsf{T}_E + U = H_0 \left( x, \frac{\partial}{\partial x}; X \right), \\ \mathsf{T}_K = \kappa^4 H_1 \left( \frac{\partial}{\partial X} \right). \end{array} \right. \quad (7)$$

Now instead of Cartesian nuclear coordinates we introduce new ones, namely the  $3N - 6$  functions

$$\xi_i = \xi_i(X), \quad (8)$$

which fix the *relative* positions of the nuclei with respect to each other, and 6 functions

$$\vartheta_i = \vartheta_i(X), \quad (9)$$

which determine the position of the nuclear framework in space. One can perform this in a symmetrical fashion, so that the Cartesian coordinates  $r_l, n_l, z_l$  are introduced relative to the instantaneous major axes of inertia. Between these we have the six equations

$$\sum_l M_l r_l = 0, \dots, \quad \sum_l M_l n_l z_l = 0, \dots$$

One can therefore express the  $r_l, \dots$  by  $3N - 6$  independent parameters  $\xi_1, \xi_2, \dots$ :

$$r_l = r_l(\xi), \dots$$

Thus there exist transformation equations of the form

$$X_l = X_0 + \sum_y \alpha_{xy}(\vartheta, \varphi, \psi) n_l(\xi), \quad (10)$$

between the original and the new coordinates. Here  $X_0, Y_0, Z_0$  are the coordinates of the centre of mass and  $\alpha_{xy}$  are the coefficients of the orthogonal rotation matrix and therefore known functions of the Euler angles  $\vartheta, \varphi, \psi$ . The quantities  $X_0, Y_0, Z_0, \vartheta, \varphi, \psi$  are the functions indicated by  $\vartheta_i$  in (9). By (10) the  $X_l$  are determined as functions of  $\vartheta_i, \xi_i$  solving [this equation] one obtains expressions (8) and (9).<sup>7</sup>

Through this transformation the energy  $H$  is of course not separated into contributions from translation, rotation and relative motion of the nuclei. But  $H_1$  can be separated into three parts, which will behave in the following characteristically different manner:

$$H_1 = H_{\xi\xi} + H_{\xi\vartheta} + H_{\vartheta\vartheta}. \quad (11)$$

$H_{\xi\xi}$  is homogeneous and linear in the  $\frac{\partial^2}{\partial\xi_i\partial\xi_j}$ ,  $H_{\xi\vartheta}$  contains the  $\frac{\partial}{\partial\xi_i}$ ;  $H_{\vartheta\vartheta}$  is free from all derivatives to  $\xi_i$ . One can make some general statements about these operators. If the whole operator  $H_1$  is applied to a function  $f(\xi)$  of the relative nuclear coordinates  $\xi_i$ , then the resulting quantity  $H_1f(\xi)$  must be independent of the position in space, and so of  $\vartheta_i$ . In  $H_{\xi\xi}$  in particular the coefficients of  $\frac{\partial^2}{\partial\xi_i\partial\xi_j}$  cannot be dependent on  $\vartheta_i$ . In contrast to this, in  $H_{\xi\vartheta}$ , in addition to  $\frac{\partial}{\partial\xi_i}$  the  $\xi_i, \vartheta_i$  and the  $\frac{\partial}{\partial\vartheta_i}$  appear; in  $H_{\vartheta\vartheta}$ , in addition to the  $\frac{\partial^2}{\partial\vartheta_i\partial\vartheta_j}$ , the  $\frac{\partial}{\partial\vartheta_i}, \xi_i$  and  $\vartheta_i$  appear.

For two-atomic molecules we will state these operator functions explicitly.

The mechanical problem to be solved is

$$(H + \kappa^4 H_1 - W)\psi = 0. \quad (12)$$

We will show that the particular solution that represents nuclei and electrons combined into a stable molecule can be obtained through a power series in  $\kappa$ .

## 2. Electronic motion with fixed nuclei

When one puts  $\kappa = 0$  in (12), one obtains a differential equation in  $x_k$  alone, in which the  $X_l$  appear as parameters:

$$\left\{ H_0 \left( x, \frac{\partial}{\partial x}; X \right) - W \right\} \psi = 0. \quad (13)$$

This clearly represents the motion of the electrons with fixed nuclei. We assume that this eigenvalue problem is solved. The eigenvalues depend only on the connections  $\xi_i$  to  $X_i$ , since one can collapse the coordinate system with the system of the axes of inertia, wherein  $X_l = r_l(\xi)$ . In this axis system the eigenfunctions depend, except on the  $x_k$ , on the  $\xi_i$  only. If one transforms back to arbitrary space fixed axes, then the  $\vartheta_i$  appear as well.

We indicate the  $n$ th eigenvalue and the corresponding normalised eigenfunctions by

$$W = V_n(\xi), \quad \psi = \varphi_n(x; \xi, \vartheta) \quad (14)$$

<sup>7</sup>That this solution leads in general to multi-valued functions does not play a role here, but is physically important; cf. F. Hund, *Z. Phys.* **43**, 805 (1927).

so that the identity

$$\left\{ H_0 \left( x, \frac{\partial}{\partial x}; \xi, \vartheta \right) - V_n(\xi) \right\} \varphi_n(x; \xi, \vartheta) = 0 \quad (15)$$

is valid. Thereby we assume that  $V_n$  is a *simple* eigenvalue. In fact this will never be the case; because of the equivalence of the electrons the resonance degeneracy discovered by *Heisenberg* and *Dirac* comes into play, and for two-atomic molecules besides this there is also a degeneracy of the angular momentum around the axis. However, since we deal only with the system of the approximate process, we will neglect these degeneracies. Their consideration would lead to secular equations in higher approximations.

The most important goal of our investigation is the proof that the function  $V_n(\xi)$  plays the role of a potential energy for the motion of the nuclei. For this we need some auxiliary formulae, which we will now derive. The point is to show that the matrix, belonging to the derivative of  $H_0 \left( x, \frac{\partial}{\partial x}; \xi, \vartheta \right)$  with respect to  $\xi_i$  (so for fixed  $x, \frac{\partial}{\partial x}$ ) can be attributed to derivatives of  $V_n(\xi)$ .

Instead of taking the derivatives to  $\xi_i$  immediately, we replace  $\xi_i$  everywhere by  $\xi_i + \kappa\zeta_i$  and differentiate with respect to  $\kappa$ ; the coefficient of a power of  $\kappa$  is then a homogeneous polynomial in  $\zeta_i$ , of which the coefficients are the derivatives with respect to  $\xi_i$ . We thus write

$$V_n(\xi + \kappa\zeta) = V_n^0 + \kappa V_n^{(1)} + \kappa^2 V_n^{(2)} + \dots, \quad (16)$$

where

$$\begin{cases} \text{a)} & V_n^{(0)} = V_n(\xi), \\ \text{b)} & V_n^{(1)} = \sum_i \zeta_i \frac{\partial V_n}{\partial \xi_i}, \\ \text{c)} & V_n^{(2)} = \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 V_n}{\partial \xi_i \partial \xi_j}, \\ & \dots \end{cases} \quad (17)$$

and in a corresponding fashion

$$\begin{cases} H_0 = H_0^0 + \kappa H_0^{(1)} + \kappa^2 H_0^{(2)} + \dots, \\ \varphi_n = \varphi_n^0 + \kappa \varphi_n^{(1)} + \kappa^2 \varphi_n^{(2)} + \dots \end{cases} \quad (18)$$

One can now expand the quantities  $\varphi_n^{(1)}$ ,  $\varphi_n^{(2)}$  in terms of the eigenfunctions  $\varphi_n^0(x; \xi, \vartheta)$ ; we put

$$\begin{cases} \text{a)} & \varphi_n^{(1)} = \sum_{n'} u_{nn'}^{(1)} \varphi_{n'}^0, \\ \text{b)} & \varphi_n^{(2)} = \sum_{n'} u_{nn'}^{(2)} \varphi_{n'}^0, \\ & \dots \end{cases} \quad (19)$$

Here  $u_{nn'}^{(r)}$  is a polynomial of order  $r$  in  $\zeta_i$ , for instance<sup>8</sup>

$$\left\{ \begin{array}{l} u_{nn'}^{(1)} = \sum_i \zeta_i \int \overline{\varphi_n^0} \frac{\partial \varphi_{n'}^0}{\partial \xi_i} dx, \\ u_{nn'}^{(2)} = \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \int \overline{\varphi_n^0} \frac{\partial^2 \varphi_{n'}^0}{\partial \xi_i \partial \xi_j} dx. \end{array} \right. \quad (20)$$

The integrals appearing here, in which  $dx$  is the volume element in the configuration space of the electrons, are independent of the orientation of the nuclear framework in space, and hence independent of  $\vartheta_i$ ; so they can be computed for instance in the system of the major axes of inertia.

When  $F$  is an operator working on  $x_i$ , then

$$\int \overline{\varphi_{n'}^0} F \varphi_n^{(r)} dx = F_{nn'}^{(r)} \quad (21)$$

will be called the  $r$ th order matrix element of  $F$ . For  $r = 0$  it transforms into the normal matrix element

$$F_{nn'}^0 = F_{nn'} = \int \overline{\varphi_{n'}^0} F \varphi_n^0 dx. \quad (22)$$

Generally, according to (19)

$$F_{nn'}^{(r)} = \sum_{n''} u_{nn''}^{(r)} F_{n''n'} \quad (23)$$

Now from (15) it follows, for  $\kappa = 0$ , that

$$(H_0^0 - V_n^0)_{nn'}^{(r)} = u_{nn'}^{(r)} (V_{n'}^0 - V_n^0). \quad (24)$$

Furthermore through substitution of the expansions (16) and (18) into (15) we obtain the identities

$$\left\{ \begin{array}{l} \text{a) } (H_0^0 - V_n^0) \varphi_n^{(1)} + (H_0^{(1)} - V_n^{(1)}) \varphi_n^0 = 0, \\ \text{b) } (H_0^0 - V_n^0) \varphi_n^{(2)} + (H_0^{(1)} - V_n^{(1)}) \varphi_n^{(1)} \\ \quad + (H_0^{(2)} - V_n^{(2)}) \varphi_n^0 = 0, \\ \dots \end{array} \right. \quad (25)$$

On multiplication with  $\overline{\varphi_{n'}^0}$  and integration over  $x_i$ , one then obtains, using (24),

$$\left\{ \begin{array}{l} \text{a) } u_{nn'}^{(1)} (V_{n'}^0 - V_n^0) + (H_0^{(1)})_{nn'} - V_n^{(1)} \delta_{nn'} = 0, \\ \text{b) } u_{nn'}^{(2)} (V_{n'}^0 - V_n^0) + (H_0^{(1)} - V_n^{(1)})_{nn'} \\ \quad + (H_0^{(2)})_{nn'} - V_n^{(2)} \delta_{nn'} = 0, \\ \dots \end{array} \right. \quad (26)$$

<sup>8</sup> $\bar{z}$  is the conjugate complex of  $z$ .

From these one can compute the series of  $(H_0^{(1)})_{nn'}$ ,  $(H_0^{(2)})_{nn'}$ , ..., i.e. the matrix elements  $\left(\frac{\partial H_0}{\partial \xi_i}\right)_{nn'}$ ,  $\left(\frac{\partial^2 H_0}{\partial \xi_i \partial \xi_j}\right)_{nn'}$ , .... We will use these formulae later on.<sup>9</sup>

### 3. Construction of the approximate equations

An arbitrary configuration of electrons and nuclei cannot, of course, be treated with a general approximation scheme. We only want to consider here those configurations that represent a stable molecule. To this end, we put the following problem first:

Is there a system of values for the relative nuclear coordinates  $\xi_i$  such that the eigenfunctions  $\psi_n$  of the energy operator (6), insofar as they are dependent on the  $\xi_i$ , have values different from zero only in a small neighbourhood around this system of values?

This wave-mechanical requirement clearly represents the classical condition that the nuclei perform only small vibrations around an equilibrium configuration, since  $|\psi|^2$  is the probability for finding a particular configuration at a certain energy.

As the unperturbed system we consider the electronic motion for an almost arbitrary, but rigidly chosen, nuclear configuration  $\xi_i$ . Then we expand all quantities in small deviations of  $\xi_i$ , which we will call  $\kappa \zeta_i$ . We thereby assume that the "vibrational region" ["*Schwingungsbereich*"] decreases to zero with  $\kappa$ , an assumption which can only be justified by the result.

Then from Section 2, (18), we have the expansion

$$H_0\left(x, \frac{\partial}{\partial x}; \xi + \kappa \zeta, \vartheta\right) = H_0^0 + \kappa H_0^{(1)} + \kappa^2 H_0^{(2)} + \dots, \quad (27)$$

where

$$\left\{ \begin{array}{l} \text{a) } H_0^0 = H_0\left(x, \frac{\partial}{\partial x}; \xi\right), \\ \text{b) } H_0^{(1)} = \sum_i \zeta_i \frac{\partial H_0}{\partial \xi_i}, \\ \text{c) } H_0^{(2)} = \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 H_0}{\partial \xi_i \partial \xi_j}, \\ \dots \end{array} \right. \quad (28)$$

and, following (11), since  $\frac{\partial}{\partial \xi} = \frac{1}{\kappa} \frac{\partial}{\partial \zeta}$ ,

<sup>9</sup>The classical analogue of the simplest conclusion of these formulae, namely the identity  $(H_0^{(1)})_{nn} = V_n^{(1)}$  following from (26a) for  $n = n'$ , is found in W. Pauli, *Ann. Phys.* **68**, 177 (1922); cf. especially §4, formula (11).

$$\left\{ \begin{aligned} \kappa^4 H_1 \left( X, \frac{\partial}{\partial X} \right) &= \kappa^4 \left( \frac{1}{\kappa^2} H_{\zeta\zeta} + \frac{1}{\kappa} H_{\zeta\vartheta} + H_{\vartheta\vartheta} \right) \\ &= \kappa^2 H_{\zeta\zeta}^0 + \kappa^3 (H_{\zeta\vartheta}^0 + H_{\zeta\zeta}^{(1)}) + \kappa^4 (H_{\vartheta\vartheta}^0 + H_{\zeta\vartheta}^{(1)} + H_{\zeta\zeta}^{(2)}) + \dots, \end{aligned} \right. \quad (29)$$

where

$$\left\{ \begin{aligned} \text{a)} \quad H_{\zeta\zeta}^0 &= H_{\zeta\zeta}^0 \left( \xi, \frac{\partial^2}{\partial \zeta_i \partial \zeta_j} \right), \\ \text{b)} \quad H_{\zeta\zeta}^{(1)} &= \sum_i \zeta_i \frac{\partial H_{\zeta\zeta}^0}{\partial \xi_i}, \\ &\dots \end{aligned} \right. \quad (30)$$

$$\left\{ \begin{aligned} \text{a)} \quad H_{\zeta\vartheta}^0 &= H_{\zeta\vartheta}^0 \left( \xi, \vartheta, \frac{\partial}{\partial \zeta}, \frac{\partial}{\partial \vartheta} \right), \\ \text{b)} \quad H_{\zeta\vartheta}^{(1)} &= \sum_i \zeta_i \frac{\partial H_{\zeta\vartheta}^0}{\partial \xi_i}, \\ &\dots \end{aligned} \right. \quad (31)$$

$$\left\{ \begin{aligned} \text{a)} \quad H_{\vartheta\vartheta}^0 &= H_{\vartheta\vartheta}^0 \left( \xi, \vartheta, \frac{\partial^2}{\partial \vartheta_i \partial \vartheta_j} \right), \\ \text{b)} \quad H_{\vartheta\vartheta}^{(1)} &= \sum_i \zeta_i \frac{\partial^2 H_{\vartheta\vartheta}^0}{\partial \xi_i}, \\ &\dots \end{aligned} \right. \quad (32)$$

The arguments  $\xi_i$  from here on have to be considered as constants.

The total energy operator thus becomes

$$\left\{ \begin{aligned} H &= H_0^0 + \kappa H_0^{(1)} + \kappa^2 (H_0^{(2)} + H_{\zeta\zeta}^0) \\ &+ \kappa^3 (H_0^{(3)} + H_{\zeta\vartheta}^0 + H_{\zeta\zeta}^{(1)}) \\ &+ \kappa^4 (H_0^{(4)} + H_{\vartheta\vartheta}^0 + H_{\zeta\vartheta}^{(1)} + H_{\zeta\zeta}^{(2)}) + \dots \end{aligned} \right. \quad (33)$$

The higher terms all have the same form and result from the terms with  $\kappa^4$  of the series by increasing the upper indices by 1.

Now we also write the desired eigenfunction and energy parameter in terms of  $\kappa$ :

$$\left\{ \begin{aligned} \psi &= \psi^0 + \kappa \psi^{(1)} + \kappa^2 \psi^{(2)} + \dots, \\ W &= W^0 + \kappa W^{(1)} + \kappa^2 W^{(2)} + \dots, \end{aligned} \right. \quad (34)$$

Then we obtain the following approximate equations:

$$\left\{ \begin{array}{l}
 \text{a) } (H_0^0 - W^0)\psi^0 = 0, \\
 \text{b) } (H_0^0 - W^0)\psi^{(1)} = (W^{(1)} - H_0^{(1)})\psi^0, \\
 \text{c) } (H_0^0 - W^0)\psi^{(2)} = (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0)\psi^0 \\
 \quad + (W^{(1)} - H_0^{(1)})\psi^{(1)}, \\
 \text{d) } (H_0^0 - W^0)\psi^{(3)} = (W^{(3)} - H_0^{(3)} - H_{\zeta\vartheta}^0 - H_{\zeta\zeta}^{(1)})\psi^0 \\
 \quad + (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0)\psi^{(1)} + (W^{(1)} - H_0^{(1)})\psi^{(2)}, \\
 \text{e) } (H_0^0 - W^0)\psi^{(4)} = (W^{(4)} - H_0^{(4)} - H_{\vartheta\vartheta}^0 - H_{\zeta\vartheta}^{(1)} - H_{\zeta\zeta}^{(2)})\psi^0 \\
 \quad + (W^{(3)} - H_0^{(3)} - H_{\zeta\vartheta}^0 - H_{\zeta\zeta}^{(1)})\psi^{(1)} \\
 \quad + (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0)\psi^{(2)} + (W^{(1)} - H_0^{(1)})\psi^{(3)}, \\
 \dots
 \end{array} \right. \quad (35)$$

#### 4. Solution of the approximate equations of zeroth and first order: nuclear equilibrium

The zeroth order equation (35a) represents the electronic motion with fixed nuclei as discussed in Section 2. From the *normalised* eigensolution  $\varphi_n^0(x; \xi, \vartheta)$ , introduced in Section 2, belonging to the eigenvalue  $V_n^0 = V_n(\xi)$ , one obtains the general solution in the form

$$\psi_n^0 = \chi_n^0(\zeta, \vartheta)\varphi_n^0(x; \xi, \vartheta), \quad (36)$$

where  $\chi_n^0$  is, first of all, an arbitrary function of the arguments  $\zeta_i, \vartheta_j$ ; it has to be available to attain the solution of the next approximate equation.

The next approximate equation (35b),

$$(H_0^0 - W_n^0)\psi_n^{(1)} = (W_n^{(1)} - H_0^{(1)})\psi_n^0, \quad (37)$$

has only a solution if the right hand side is orthogonal<sup>10</sup> (with respect to the electronic coordinates  $x_i$ ) to  $\psi_n^0$ . This yields the requirement

$$\{(H_0^{(1)})_{nn} - W^{(1)}\}\chi_n^0(\zeta, \vartheta) = 0, \quad (38)$$

where  $(H_0^{(1)})_{nn}$  is the diagonal element of the operator  $H_0^{(1)}$  with respect to  $x_i$  and thus, according to (28b), a homogeneous linear function of  $\zeta_i$ . According to (38) this should be constant, since  $\chi_n^0(\zeta, \vartheta)$  cannot vanish identically without  $\psi_n^0$  vanishing identically. From this it follows that

$$W^{(1)} = 0; \quad (H_0^{(1)})_{nn} = 0. \quad (39)$$

<sup>10</sup>We define the orthogonality of two functions  $f(x)$  and  $g(x)$  by  $\int \overline{f(x)}g(x)dx = 0$ .

According to (26a) and (17), however,

$$(H_0^{(1)})_{nn} = V_n^{(1)} = \sum_i \zeta_i \frac{\partial V_n}{\partial \xi_i}.$$

Thus one obtains

$$\frac{\partial V_n}{\partial \xi_i} = 0. \quad (40)$$

The continuation of our approximation procedure therefore requires that the relative nuclear coordinates  $\xi_i$  be not chosen arbitrarily, but represent an extremum value of the electronic energy  $V_n(\xi)$ . The existence of such an extremum is therefore the requirement for the existence of the molecule, a theorem which is usually assumed to be self-evident. We will show later that it is necessarily a minimum.

The function  $\chi_n^0(\zeta, \vartheta)$  remains as yet undetermined. Substituting  $W_n^0 = V_n(\xi) = V_n^0$ ,  $W_n^{(1)} = 0$  and  $\psi_n^0 = \chi_n^0 \varphi_n^0$  in (37), then for  $\psi_n^{(1)}$  one obtains the defining equation

$$(H_0^0 - V_n^0)\psi_n^{(1)} = -H_0^{(1)}\varphi_n^0\chi_n^0. \quad (41)$$

A solution of this is, according to (25a),

$$\psi_n^{(1)} = \chi_n^0 \varphi_n^{(1)},$$

where  $\varphi_n^{(1)}$  is the function defined by (19a). The general solution is obtained from this by addition of a solution  $\varphi_n^0$  of the homogeneous equation with the as yet undetermined factor  $\chi_n^{(1)}(\xi, \vartheta)$ :

$$\psi_n^{(1)} = \chi_n^0 \varphi_n^{(1)} + \chi_n^{(1)} \varphi_n^0. \quad (42)$$

## 5. Solution of the approximate equations in second and third order: nuclear vibrations

We now approach the approximate equation (35c), which, on insertion of the previously found solutions of the lower order equations, reads

$$\begin{cases} (H_0^0 - V_n^0)\psi_n^{(2)} = (W_n^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0)\chi_n^0\varphi_n^0 \\ -H_0^{(1)}(\chi_n^0\varphi_n^{(1)} + \chi_n^{(1)}\varphi_n^0). \end{cases} \quad (43)$$

In order for this equation to be soluble, the right hand side must again be orthogonal to  $\varphi_n^0$ . With the terms introduced in Section 2, because of (39), this yields

$$\left\{ \left( H_0^{(2)} + H_{\zeta\zeta}^0 \right)_{nn} + \left( H_0^{(1)} \right)_{nn}^{(1)} - W_n^{(2)} \right\} \chi_n^0 = 0.$$

But from (26b) for  $V_n^{(1)} = 0$  it follows that

$$\left( H_0^{(2)} \right)_{nn} + \left( H_0^{(1)} \right)_{nn}^{(1)} = V_n^{(2)}. \quad (44)$$

Furthermore since  $H_{\zeta\zeta}^0$  is independent of  $x_k$ , according to (30a), we obtain

$$\{H_{\zeta\zeta}^0 + V_n^{(2)} - W_n^{(2)}\}\chi_n^0 = 0. \quad (45)$$

Taking into account the meaning of  $H_{\zeta\zeta}^0$  and  $V_n^{(2)}$  given by (17c), (30a), one sees that (45) is the equation of the harmonic nuclear vibrations,

$$\left\{ H_{\zeta\zeta}^0 \left( \xi, \frac{\partial^2}{\partial \zeta_i \partial \zeta_j} \right) + \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 V_n}{\partial \xi_i \partial \xi_j} - W_n^{(2)} \right\} \chi_n = 0. \quad (46)$$

The equation shows that the function  $V_n(\xi)$ , up to terms of the second order, indeed plays the role of the potential energy of the nuclei. For the existence of a stable molecule we now obtain the further requirement that the extreme value of  $V_n(\xi)$  determined through (40) be a minimum; since the quadratic form  $V_n^{(2)}$  must be positive definite, so that all degrees of freedom  $\zeta_i$  are stable and vibrations around the equilibrium position are possible. As is known, the vibrational equation (46) is separable into "normal coordinates"  $\eta_i$  by a linear transformation. If  $\sigma_{ns}^0(\zeta)$  is the eigensolution of (46) belonging to eigenvalue  $W_{ns}^{(2)}$ , then the general solution is

$$\begin{cases} \text{a) } W^{(2)} = W_{ns}^{(2)}, & \chi_n^0 = \chi_{ns}^0, & \text{where} \\ \text{b) } \chi_{ns}^0 = \rho_{ns}^0(\vartheta) \sigma_{ns}^0(\zeta). \end{cases} \quad (47)$$

The index  $s$  has to summarise the quantum numbers of the nuclear vibrations.  $\rho_{ns}^0(\vartheta)$  is an as yet undetermined function of  $\vartheta_i$ , the introduction of which is necessary for the continuation of the procedure.

As is well known,  $\sigma_{ns}^0(\zeta)$  is a linear combination of products of Hermitian orthogonal functions of the single normal coordinates  $\eta_i$ ; these functions have the property that they decrease to zero very fast (exponentially) outside the libration region of classical mechanics. With this, our approximation  $(\xi + \kappa\zeta)$  is justified in retrospect, since it is clear that it indeed leads to solutions which remain within boundaries that vanish with  $\kappa$  with respect to the  $\xi$ -oscillations. From the *Hermitian* orthogonal functions we further use the property that they are either even or odd functions of their arguments.

If  $\Phi$  is an arbitrary operator operating on  $\zeta_i$ , then we can form the corresponding matrix:

$$\Phi_{\substack{nn' \\ ss'}} = \int \overline{\sigma_{n's'}^0} \Phi \sigma_{ns}^0 d\zeta, \quad (48)$$

where  $d\zeta$  is the volume element in the space of the  $\zeta_i$ .

To solve Eq. (43) we place on the right hand side, following (45),

$$(W_{ns}^{(2)} - H_{\zeta\zeta}^0)\chi_{ns}^0 = V_n^{(2)}\chi_{ns}^0;$$

then (43) becomes

$$\begin{cases} (H_0^0 - V_n^0)\psi_n^{(2)} \\ = (V_n^{(2)} - H_0^{(2)})\chi_{ns}\varphi_n^0 - H_0^{(1)}(\chi_{ns}^0\varphi_n^{(1)} + \chi_{ns}^{(1)}\varphi_n^0). \end{cases} \quad (49)$$

Its general solution is

$$\psi_n^{(2)} = \chi_{ns}^0 \varphi_n^{(2)} + \chi_{ns}^{(1)} \varphi_n^{(1)} + \chi_{ns}^{(2)} \varphi_n^0, \quad (50)$$

where  $\chi_{ns}^{(2)}$  indicates a new undetermined function of  $\zeta_i, \vartheta_j$ . This is easily verified based on the identities (25).

Now we proceed to the investigation of the approximate equation of third order (35d), which reads, substituting the quantities already determined,

$$\left\{ \begin{array}{l} (H_0^0 - V_n^0) \psi_n^{(3)} = (W^{(3)} - H_0^{(3)} - H_{\zeta\vartheta}^0 - H_{\zeta\zeta}^{(1)}) \chi_{ns}^0 \varphi_n^0 \\ \quad + (W_{ns}^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0) (\chi_{ns}^0 \varphi_n^{(1)} + \chi_{ns}^{(1)} \varphi_n^0) \\ \quad - H_0^{(1)} (\chi_{ns}^0 \varphi_n^{(1)} + \chi_{ns}^{(1)} \varphi_n^{(1)} + \chi_{ns}^{(2)} \varphi_n^0). \end{array} \right. \quad (51)$$

The right hand side can be thought of as an expansion in  $\varphi_n^0$ , and thus we write

$$(H_0^0 - V_n^0) \psi_n^{(3)} = W^{(3)} \chi_{ns}^0 \varphi_n^0 - \sum_{n'} F_{nn'}^{(3)} \varphi_{n'}^0, \quad (52)$$

where

$$F_{nn'}^{(3)} = F_{nn'}^{(3,1)} \chi_{ns}^{(2)} + F_{nn'}^{(3,2)} \chi_{ns}^{(1)} + F_{nn'}^{(3,3)} \chi_{ns}^0. \quad (53)$$

Here the  $F$ 's are operators in  $\zeta$  and  $\vartheta$ , i.e.

$$\left\{ \begin{array}{l} \text{a) } F_{nn'}^{(3,1)} = (H_0^{(1)})_{nn'}, \\ \text{b) } F_{nn'}^{(3,2)} = \left( H_{\zeta\zeta}^0 - H_0^{(2)} - W_{ns}^{(2)} \right)_{nn'} + \left( H_0^{(1)} \right)_{nn'}^{(1)}, \end{array} \right. \quad (54)$$

while for  $F_{nn'}^{(3,3)}$  we can only state that it is a homogeneous function of the third degree in  $\zeta_i$  and  $\frac{\partial}{\partial \zeta_i}$ .

In order for (52) to be soluble, it must be the case that

$$W^{(3)} \chi_{ns}^0 - F_{nn}^{(3)} = 0;$$

because of (53) and (54a) this means that

$$F_{nn}^{(3,2)} \chi_{ns}^{(1)} = (W^{(3)} - F_{nn}^{(3,3)}) \chi_{ns}^0, \quad (55)$$

where according to (54b) and (44)

$$F_{nn}^{(3,2)} = H_{\zeta\zeta}^0 - V_n^{(2)} - W_{ns}^{(2)}.$$

(55) is thus the inhomogeneous equation corresponding to the vibrational equation (45); since (45) has the normalised solution  $\sigma_{ns}^0$  corresponding to the eigenvalue  $W_{ns}^{(2)}$ , (55) is soluble only if the right hand side has a vanishing integral over  $\zeta$ -space when multiplied with  $\overline{\sigma_{ns}^0}$ . Then, because of (47b) we obtain an integral equation for  $\rho_{ns}^0(\vartheta)$ :

$$\left( F_{ss}^{(3,3)} - W^{(3)} \right) \rho_{ns}^0 = 0.$$

But, as we saw, since  $F_{nn}^{(3,3)}$  is of odd order in  $\zeta_i$  and  $\frac{\partial}{\partial \zeta_i}$ , the diagonal element of the corresponding  $\zeta$ -matrix must vanish. This follows because if one transforms to the normal coordinates  $\eta_i$ , then  $\sigma_{ns}^0$  becomes a sum of products of Hermitian orthogonal functions, and  $F_{nn}^{(3,3)}$  a polynomial of odd order in  $\eta_i$  and  $\frac{\partial}{\partial \eta_i}$ , so that every term contains at least one of the  $\eta_i$  or  $\frac{\partial}{\partial \eta_i}$  of odd power. Therefore in the formation of the  $\zeta$ -matrix every term vanishes individually. So it follows that

$$W^{(3)} = 0, \tag{56}$$

and  $\rho_{ns}^0$  remains as yet undetermined.

Now (55) can be solved:

$$\chi_{ns}^{(1)} = S_{ns}^{(1)} \rho_{ns}^0, \tag{57}$$

where  $S_{ns}^{(1)}$  is the following operator relative to  $\vartheta_i$ :

$$S_{ns}^{(1)} = \sum_{s'}' \frac{F_{ss'}^{(3,3)} \sigma_{ns'}}{W_{ns}^{(2)} - W_{ns'}}. \tag{58}$$

Finally the solution of (52) becomes

$$\psi_n^{(3)} = \sum_{n'}' \frac{F_{nn'}^{(3)} \varphi_{n'}^0}{V_n^0 - V_{n'}^0}, \tag{59}$$

and this, following (53), has the form

$$\psi_n^{(3)} = \sum_{n'}' \left( G_{nn'}^{(3,1)} \chi_{ns}^{(2)} \varphi_{n'}^0 + G_{nn'}^{(3,2)} \chi_{ns}^{(1)} \varphi_{n'}^0 + G_{nn'}^{(3,3)} \chi_{ns}^0 \varphi_{n'}^0 \right), \tag{60}$$

where we put

$$G_{nn'}^{(3,2)} = \frac{F_{nn'}^{(3,2)}}{V_n^0 - V_{n'}^0}. \tag{61}$$

Following (54),  $G_{nn'}^{(3,1)}$  is a number,  $G_{nn'}^{(3,2)}$  a differential operator on  $\zeta_i$ , and  $G_{nn'}^{(3,3)}$  an operator on  $\zeta_i$  and  $\vartheta_j$ .

According to Section 2, (26a),

$$\begin{aligned} \sum_{n'}' G_{nn'}^{(3,1)} \chi_{ns}^{(2)} \varphi_{n'}^0 &= \sum \frac{(H_0^{(1)})_{nn'} \varphi_{n'}^0}{V_n^0 - V_{n'}^0} \chi_{ns}^{(2)} \\ &= \sum_{n'}' u_{nn'}^{(1)} \varphi_{n'}^0 \chi_{ns}^{(2)} \\ &= \varphi_n^{(1)} \chi_{ns}^{(2)}; \end{aligned}$$

so that

$$\psi_n^{(3)} = \varphi_n^{(1)} \chi_{ns}^{(2)} + \sum_{n'}' \left( G_{nn'}^{(3,2)} \chi_{ns}^{(1)} \varphi_{n'}^0 + G_{nn'}^{(3,3)} \chi_{ns}^0 \varphi_{n'}^0 \right). \tag{62}$$

## 6. Solution of the approximate equations of fourth and higher order: rotations and coupling effects

The approximate equations of fourth order (35e) read, after substituting the quantities already determined,

$$\left\{ \begin{aligned} (H_0^0 - V_n^0)\psi_0^{(4)} &= \left( W^{(4)} - H_0^{(4)} - H_{\vartheta\vartheta}^0 - H_{\zeta\vartheta}^{(1)} - H_{\zeta\zeta}^{(2)} \right) \chi_{ns}^0 \varphi_n^0 \\ &- \left( H_0^{(3)} + H_{\zeta\vartheta}^0 + H_{\zeta\zeta}^0 \right) \left( \chi_{ns}^{(0)} \varphi_n^0 + \chi_{ns}^0 \varphi_n^{(1)} \right) \\ &+ \left( W_{ns}^{(2)} - H_0^{(2)} + H_{\zeta\zeta}^0 \right) \left( \chi_{ns}^{(2)} \varphi_n^0 + \chi_{ns}^{(1)} \varphi_n^{(1)} + \chi_{ns}^0 \varphi_n^{(2)} \right) \\ &- H_0^{(1)} \left\{ \varphi_n^{(1)} \chi_{ns}^{(2)} + \sum_{n'}' \left( G_{nn'}^{(3,2)} \chi_{ns}^{(1)} \varphi_{n'}^0 + G_{nn'}^{(3,3)} \chi_{ns}^0 \varphi_{n'}^0 \right) \right\}. \end{aligned} \right. \quad (63)$$

We expand the right hand side again in orders of  $\varphi_n^0$ :

$$(H_0^0 - V_n^0)\psi_n^{(4)} = W^{(4)} \chi_{ns}^0 \varphi_n^0 - \sum_{n'} F_{nn'}^{(4)} \varphi_{n'}^0, \quad (64)$$

where

$$F_{nn'}^{(4)} = F_{nn'}^{(4,2)} \chi_{ns}^{(2)} + F_{nn'}^{(4,3)} \chi_{ns}^{(1)} + F_{nn'}^{(4,4)} \chi_{ns}^0; \quad (65)$$

here

$$F_{nn'}^{(4,2)} = \left( H_{\zeta\zeta}^0 - H_0^{(2)} - W_{ns}^{(2)} \right)_{nn'} + \left( H_0^{(1)} \right)_{nn'}^{(1)}, \quad (66)$$

which is identical to  $F_{nn'}^{(3,2)}$  (54b), while  $F_{nn'}^{(4,3)}$  is of odd order in  $\zeta_i$ ,  $\frac{\partial}{\partial \zeta_i}$ , but  $F_{nn'}^{(4,4)}$  of even order. The integrability condition of (64) reads

$$W^{(4)} \chi_{ns}^0 - F_{nn}^{(4)} = 0,$$

which, following (65), means that

$$F_{nn}^{(4,2)} \chi_{ns}^{(2)} = \left( W^{(4)} - F_{nn}^{(4,4)} \right) \chi_{ns}^0 - F_{nn}^{(4,3)} \chi_{ns}^{(1)}. \quad (67)$$

The left hand side again corresponds, because of (66), to the vibrational equation (45). The right hand side therefore must be normal to  $\sigma_{ns}^0$ . Substituting the values of  $\chi_{ns}^{(1)}$  and  $\chi_{ns}^{(2)}$  from (47b) and (57) and using the symbol

$$\left\{ \begin{aligned} (\Phi)_{ss'}^{(1)} &= \int \overline{\sigma_{ns'}^0} \Phi S_{ns}^{(1)} d\zeta \\ &= \sum_{s''}' \frac{(\Phi F_{nn}^{(3,3)})_{ss''}}{W_{ns}^{(2)} - W_{ns''}^{(2)}}, \end{aligned} \right. \quad (68)$$

one then obtains

$$\left\{ F_{nn}^{(4,4)} + \left( F_{nn}^{(4,3)} \right)_{ss}^{(1)} - W^{(4)} \right\} \rho_{ns}^0 = 0. \quad (69)$$

This equation finally determines the function  $\rho_{ns}^0(\vartheta)$  and thus the motion of the principal axes of inertia in space, or the translations and rotations. The main term of the operator in (69) is the one which contains the second derivatives with respect to  $\vartheta_i$ . One glance at (63) shows that its origin is in  $H_{\vartheta\vartheta}^0\chi_{ns}^0\varphi_n^0$ . In  $F_{nn}^{(4,4)}$  it is therefore represented by the term

$$\overline{(H_{\vartheta\vartheta}^0)} = \int \overline{\varphi_n^0} H_{\vartheta\vartheta}^0 (\varphi_n^0 \dots) dx, \quad (70)$$

where in place of the dots the function on which the operator operates must be substituted. Since the operator (70) is independent of the  $\zeta_i$ , the diagonal terms of its corresponding  $s$ -matrix are identical to it. Physically this fact means that in place of the simple operator  $H_{\vartheta\vartheta}^0$  the more complicated  $\overline{(H_{\vartheta\vartheta}^0)}$  appears, leading to a coupling of the rotational motion of the nuclei with the electronic motion. This problem is, as we will afterwards show in the example of two-atomic molecules, the treatment of the effects which *Kramers* and *Pauli*<sup>11</sup> tried to represent by the assumption of a flywheel built into the rotation. In (69), additional terms deriving from the operator  $H_{\zeta\vartheta}$  appear; they represent the coupling of the rotation with angular momenta that result from the vibrational motion of the nuclei. Finally there are also terms that do not operate on  $\vartheta_i$ ; they yield a contribution of order  $\kappa^4$  to the vibrational energy.

Since the translations can always be separated trivially, we consider only the rotations. When  $r$  is the corresponding quantum number, one must write for the solution of (70)

$$W^{(4)} = W_{nsr}^{(4)}; \quad \rho_{ns}^0 = \rho_{nsr}^0(\vartheta). \quad (71)$$

Therefore one can solve (67) and finally also (64). However, it is of little use to write out the formulae explicitly.

It is clear that the process can be continued without adding anything significantly new. The higher orders describe the couplings between rotations, vibrations and electronic motions. Quantum numbers additional to those already introduced will not appear.

We now summarise the characteristic features of the found solution. The most conspicuous result is that, for the complete determination of the eigenfunctions even in zeroth order, the solution of the approximation differential equation up to fourth order is necessary, namely

$$\psi_{nsr}(x, \zeta, \vartheta) = \varphi_n^0(x, \zeta, \vartheta) \sigma_{ns}^0(\zeta) \rho_{nsr}^0(\vartheta) + \dots, \quad (72)$$

where  $\varphi_n^0$  is the eigenfunction of the electronic motion with fixed nuclei,  $\sigma_{ns}^0$  that of the nuclear vibrations, and  $\rho_{nsr}^0$  that of the nuclear rotation. Here the vibrational coordinates  $\zeta_i$  have to be taken relative to the equilibrium position  $\xi_i$ , which is determined by the requirement that the energy of the electronic motion  $V_n(\xi)$  be a

<sup>11</sup>H.A. Kramers and W. Pauli, *Z. Phys.* **13**, 343, 351 (1923).

minimum there. The determination of the functions  $\varphi_n^0$ ,  $\sigma_{ns}^0$ ,  $\rho_{nsr}^0$  simultaneously yields the energy up to fourth order inclusive,

$$W_{nsr} = V_n^0 + \kappa^2 W_{ns}^{(2)} + \kappa^4 W_{nsr}^{(4)} + \dots, \quad (73)$$

where  $V_n^0$  is the minimum value of the electronic energy, which characterises the molecule considered when it is at rest,  $W_{ns}^{(2)}$  is the energy of the nuclear vibrations and  $W_{nsr}^{(4)}$  contains (as well as the additional terms in the vibrational energy) the energy of the rotations. In this approximation (up to  $\kappa^4$ ), the three basic types of motion appear “separated”. If one wants to investigate their couplings, then higher powers of  $\kappa$  have to be taken into account.

Based on (72) we can make some statements on transition probabilities (intensities of band lines).

The electric moment of the molecule  $M$  is composed of a contribution from the nuclei  $B$  and a contribution from the electrons  $p$ ; one component is

$$M_x = B_x + p_x, \quad \begin{cases} B_x = \sum_l e_l X_l, \\ p_x = e \sum_k x_k. \end{cases} \quad (74)$$

From this one forms the matrix elements related to  $x_k$ ,  $\zeta_i$  and  $\vartheta_j$  in the orders of the series. First is

$$(p_x)_{n'} = \int p_x \varphi_n^0 \overline{\varphi_{n'}^0} dx, \quad (75)$$

a function of  $\zeta_i$ ,  $\vartheta_j$ . Subsequently,

$$(p_x)_{n's'} = \int (p_x)_{n'} \sigma_{ns}^0 \overline{\sigma_{n's'}^0} d\zeta, \quad (B_x)_{n's'} = \int B_x \sigma_{ns}^0 \overline{\sigma_{n's'}^0} d\zeta \quad (76)$$

are functions only of  $\vartheta_j$ , and finally

$$\begin{cases} (p_x)_{n's'r'} = \int (p_x)_{n's'} \rho_{nsr}^0 \overline{\rho_{n's'r'}^0} d\vartheta, \\ (B_x)_{n's'r'} = \int (B_x)_{n's'} \rho_{nsr}^0 \overline{\rho_{n's'r'}^0} d\vartheta \end{cases} \quad (77)$$

are numerical constants, which determine the radiation and transition probability for  $nsr \rightarrow n's'r'$ . This step-by-step construction can be interpreted as follows: to every electronic jump  $n \rightarrow n'$  there belongs a virtual oscillator with moment  $(p_z)_{n'}$ , from which one obtains the matrix  $(p_z)_{n'n'}$  representing a system of vibrational bands (transitions  $s \rightarrow s'$ ), according to a rule deviating from the usual one, since we use one eigenfunction from the lower, and one from the upper level [formula (76)]. The equivalent repeats itself in the lines of a band (transitions  $r \rightarrow r'$ ). Estimates of the intensities first stated by *Franck*<sup>12</sup> and elaborated by *Condon*<sup>13</sup>

<sup>12</sup>J. Franck, *Trans. Faraday Soc.* (1925).

<sup>13</sup>E. Condon, *Phys. Rev.* **28**, 1182 (1926); *Proc. Nat. Acad.* **13**, 462 (1927).

are contained herein. Namely, this is determined by the trend in the functions  $V_n(\xi)$  and  $V_{n'}(\xi)$ ; only in the neighbourhood of their minima are the functions  $\sigma_{ns}^0$  and  $\sigma_{n's'}^0$ , notably different from zero, their product therefore only [differs from zero] when these neighbourhoods overlap. If the function  $V_n(\xi)$  in the electronic jump  $n \rightarrow n'$  is therefore only changed a little in its trend, the bands with small changes in  $s$  will be strong, but as soon as  $V_n(\xi)$  shifts strongly on the electronic jump  $n \rightarrow n'$ , an overlap in the interval where  $\sigma_{ns}^0$  and  $\sigma_{n's'}^0$  do not vanish will only be possible for larger differences,  $s - s'$ . These conditions have been discussed in a quantitative fashion by *Condon*. Similar considerations can be construed for the rotations *mutatis mutandis*.

## 7. Special case of two-atomic molecules

As an example we will now briefly treat the two-atomic molecules. For these we have, except for a resonance degeneracy originating from the identity of the electrons, a further degeneracy, since to each energy value belong two motions, in which the angular momenta around the line connecting the nuclei are opposite and equal. But since our present problem is not the true fine structure of the bands, we will forego a discussion of this degeneracy. We therefore restrict ourselves to cases where the angular momentum around the axis vanishes, or those where the energy of the electronic motion does not or only weakly depends on it.

For two nuclei we have only *one*  $\xi$  coordinate, the nuclear distance  $\xi$ , and five  $\vartheta$  coordinates, namely the coordinates of the centre of mass  $X_0, Y_0, Z_0$  and the polar coordinates  $\vartheta, \omega$  of the line between the nuclei (the axis).

The kinetic energy of the nuclei becomes

$$T_K = -\kappa^4 \frac{h^2}{8\pi^2 m} \left\{ \Delta_0 + \frac{\mu}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial}{\partial \xi} \right) + \frac{\mu}{\xi^2} \Delta_\vartheta \right\}, \quad (78)$$

where we put

$$\kappa = \sqrt[4]{\frac{m}{M_1 + M_2}}, \quad \mu = \frac{(M_1 + M_2)^2}{M_1 M_2} \quad (79)$$

and

$$\begin{cases} \Delta_0 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}, \\ \Delta_\vartheta = \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \omega^2} + \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right). \end{cases} \quad (80)$$

So we have

$$\begin{cases} H_{\xi\xi} = -\frac{h^2}{8\pi^2 m} \mu \frac{\partial^2}{\partial \xi^2}, \\ H_{\xi\vartheta} = -\frac{h^2}{8\pi^2 m} \frac{2\mu}{\xi} \frac{\partial}{\partial \xi}, \\ H_{\vartheta\vartheta} = -\frac{h^2}{8\pi^2 m} \left( \Delta_0 + \frac{\mu}{\xi^2} \Delta_\vartheta \right). \end{cases} \quad (81)$$

Replacing  $\xi$  here by  $\xi + \kappa\zeta$  and expanding in  $\kappa$  then yields

$$\begin{cases} H_{\zeta\zeta}^0 = -\frac{\hbar^2}{8\pi^2m}\mu\frac{\partial^2}{\partial\zeta^2}, \\ H_{\zeta\zeta}^{(p)} = 0, \quad p = 1, 2, \dots, \end{cases} \quad (82)$$

$$\begin{cases} H_{\zeta\vartheta}^0 = -\frac{\hbar^2}{8\pi^2m}\frac{2\mu}{\xi}\frac{\partial}{\partial\zeta}, \\ H_{\zeta\vartheta}^{(1)} = \frac{\hbar^2}{8\pi^2m}\frac{2\mu}{\xi^2}\zeta\frac{\partial}{\partial\zeta}, \\ \dots \end{cases} \quad (83)$$

$$\begin{cases} H_{\vartheta\vartheta}^0 = -\frac{\hbar^2}{8\pi^2m}\left(\Delta_0 + \frac{\mu}{\xi^2}\Delta_\vartheta\right), \\ H_{\vartheta\vartheta}^{(1)} = \frac{\hbar^2}{8\pi^2m}\frac{2\mu}{\xi^3}\zeta\Delta_\vartheta. \\ \dots \end{cases} \quad (84)$$

The nuclear distance is determined by the equation

$$V'_n = \frac{dV_n}{d\xi} = 0. \quad (85)$$

The equation of the nuclear vibrations here reads

$$\left\{ -\frac{\hbar^2}{8\pi^2}\frac{\mu}{m}\frac{d^2}{d\zeta^2} + \frac{1}{2}\zeta^2V''_n(\xi)W_n^{(2)} \right\} \chi_n^0 = 0. \quad (86)$$

On putting

$$\begin{cases} a = \frac{8\pi^2}{\hbar}\frac{m}{\mu}W_n^{(2)}, & b = \frac{8\pi^2}{\hbar^2}\frac{m}{2\mu}V''_n, \\ \eta = \zeta\sqrt[4]{b}, \end{cases} \quad (87)$$

one obtains<sup>14</sup>

$$\left\{ \frac{d^2}{d\eta^2} + \left( \frac{a}{\sqrt{b}} - \eta^2 \right) \right\} \chi_n^0 = 0.$$

The eigenvalues are

$$\frac{a}{\sqrt{b}} = 2s + 1 \quad (s = 0, 1, 2, \dots),$$

the eigenfunctions

$$\sigma_{ns}^0 = e^{-\frac{\eta^2}{2}} H_s(\eta),$$

where  $H_s$  is the  $s$ th Hermite polynomial.

<sup>14</sup>E. Schrödinger, *Ann. Phys.* **79**, 361, Sec. 3 (1926).

The vibrational energy is therefore

$$\begin{aligned}\kappa^2 W_{ns}^{(2)} &= a \frac{h^2}{8\pi^2} \frac{\kappa^2 \mu}{m} = (2s+1) \sqrt{b} \frac{h^2}{8\pi^2} \frac{\kappa^2 \mu}{m} \\ &= \left(s + \frac{1}{2}\right) h \cdot \frac{1}{4\pi} \sqrt{\kappa^4 \frac{\mu}{m} V_n''}\end{aligned}$$

or

$$\kappa^2 W_{ns}^{(2)} = \left(s + \frac{1}{2}\right) h \nu_0, \quad (88)$$

where

$$\frac{1}{4\pi} \sqrt{\kappa^4 \frac{\mu}{m} V_n''} = \frac{1}{4\pi} \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right) V_n''} = \nu_0 \quad (89)$$

is the frequency of the oscillator.

We now construct Eq. (69) for the rotations, but forego the detailed evaluation of the correction to the vibrational energy. Since in this case  $H_{\zeta\vartheta}$  according to (81) does not contain the derivatives with respect to  $\vartheta_j$ , we have, in (69), only the term  $\overline{(H_{\vartheta\vartheta}^0)_n}$  to consider; all remaining terms we summarise in the constant  $C_{ns}$ . The rotational equation (69) then reads

$$\left\{\overline{(H_{\vartheta\vartheta}^0)_n} + C_{ns} - W^{(4)}\right\} \rho_{ns}^0 = 0. \quad (90)$$

If we discard the translational part in  $H_{\vartheta\vartheta}^0$ , then according to (70) and (84) we obtain for an arbitrary function  $f(\vartheta)$

$$\overline{(H_{\vartheta\vartheta}^0)_n} f(\vartheta) = -\frac{h^2 \mu}{8\pi^2 m \xi^2} \int \overline{\varphi_n^0} \Delta_{\vartheta} (\varphi_n^0 f) dx$$

and according to (80)

$$\Delta_{\vartheta} (\varphi_n^0 f) = \varphi_n^0 \Delta_{\vartheta} f + f \Delta_{\vartheta} \varphi_n^0 + 2 \left( \frac{1}{\sin^2 \vartheta} \frac{\partial \varphi_n^0}{\partial \omega} \frac{\partial f}{\partial \omega} + \frac{\partial \varphi_n^0}{\partial \vartheta} \frac{\partial f}{\partial \vartheta} \right).$$

Therefore

$$\begin{aligned}\overline{H_{\vartheta\vartheta}^0} f &= -\frac{h^2 \mu}{8\pi^2 m \xi^2} \left\{ \Delta_{\vartheta} f + f \cdot \int \overline{\varphi_n^0} \Delta_{\vartheta} \varphi_n^0 dx \right. \\ &\quad \left. + 2 \frac{1}{\sin^2 \vartheta} \frac{\partial f}{\partial \omega} \int \overline{\varphi_n^0} \frac{\partial \varphi_n^0}{\partial \omega} dx + 2 \frac{\partial f}{\partial \vartheta} \int \overline{\varphi_n^0} \frac{\partial \varphi_n^0}{\partial \vartheta} dx \right\}.\end{aligned}$$

When we write  $\Delta_{\vartheta}$  in the form

$$\Delta_{\vartheta} = \frac{\partial^2}{\partial \vartheta^2} + \text{ctg} \vartheta \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \vartheta^2}$$

we see that it is appropriate to introduce the following shorthand notation:

$$\left\{ \begin{array}{l} \overline{\Theta}_n = \int \frac{\overline{\varphi}_n^0}{\varphi_n^0} \frac{\partial \varphi_n^0}{\partial \vartheta} dx, \quad \overline{\Omega}_n = \int \frac{\overline{\varphi}_n^0}{\varphi_n^0} \frac{\partial \varphi_n^0}{\partial \omega} dx, \\ \overline{\Theta}_n^2 = \int \frac{\overline{\varphi}_n^0}{\varphi_n^0} \frac{\partial^2 \varphi_n^0}{\partial \vartheta^2} dx, \quad \overline{\Omega}_n^2 = \int \frac{\overline{\varphi}_n^0}{\varphi_n^0} \frac{\partial^2 \varphi_n^0}{\partial \omega^2} dx. \end{array} \right. \quad (91)$$

These quantities are the diagonal elements of matrices of  $p_\vartheta$ ,  $p_\omega$ , or  $p_\vartheta^2$ ,  $p_\omega^2$  (neglecting a factor  $\frac{h}{2\pi x}$ , or  $-\frac{h^2}{4\pi x}$ ), and can be interpreted as the average value of the angular momentum of the electronic motion corresponding to the Euler angles, or the average values of their squares. Then, in detail, Eq. (90) reads

$$\left\{ \begin{array}{l} \left\{ \left( \frac{\partial^2}{\partial \vartheta^2} + 2\overline{\Theta}_n \frac{\partial}{\partial \vartheta} + \overline{\Theta}_n^2 \right) + \text{ctg} \vartheta \left( \frac{\partial}{\partial \vartheta} + \overline{\Theta}_n \right) \right. \\ \quad \left. + \frac{1}{\sin^2 \vartheta} \left( \frac{\partial^2}{\partial \omega^2} + 2\overline{\Omega}_n \frac{\partial}{\partial \omega} + \overline{\Omega}_n^2 \right) \right. \\ \quad \left. + \frac{8\pi^2 m \xi^2}{h^2 \mu} (W^{(4)} - C_{ns}) \right\} \rho_{ns}^0 = 0. \end{array} \right. \quad (92)$$

This is very similar to the equation construed by *Kramers* and *Pauli* for the rotator with a built-in flywheel; the difference is mainly that these authors, instead of the averages of squares  $\overline{\Theta}_n^2$ ,  $\overline{\Omega}_n^2$ , obtain the squares of averages  $\overline{\Theta}_n^2$ ,  $\overline{\Omega}_n^2$ .

Incidentally, the dependencies of the factors (91) on the angles  $\vartheta$ ,  $\omega$  can be determined in a quite elementary fashion, by the assumption that to this end the diagonal elements of the quantum-mechanical matrices can be replaced by the corresponding classical average values. The motion of the angular momentum vector of the electronic motion can be separated into an irregular fluctuation with no mean rotation and a superimposed uniform rotation around the molecular axis. The fluctuation we replace on average by a fixed vector, which then rotates uniformly around the axis. So the same situation as in the case of a symmetric top is obtained, where the angular momentum related to a coordinate system fixed to the top can have components  $L$ ,  $M$  and  $N$ . From this, the components of the angular momentum belonging to the angles  $\vartheta$ ,  $\omega$  can be expressed as follows:<sup>15</sup>

$$\begin{aligned} \Theta &= L \cos \gamma - M \sin \gamma, \\ \Omega &= L \sin \vartheta \sin \gamma + M \sin \vartheta \cos \gamma + N \cos \gamma, \end{aligned}$$

where  $\gamma$  is the angle of the eigenrotation around the axis. On averaging over  $\gamma$  there follows

$$\begin{aligned} \overline{\Theta} &= 0, & \overline{\Omega} &= N \cos \vartheta, \\ \overline{\Theta}^2 &= \frac{1}{2}(L^2 + M^2), & \overline{\Omega}^2 &= \frac{1}{2}(L^2 + M^2) \sin^2 \vartheta + N^2 \cos^2 \vartheta. \end{aligned}$$

<sup>15</sup>See e.g. F. Klein and A. Sommerfeld: *Theorie des Kreisels 1*, p. 108.

Here  $N$  has to be identified with the quantum number  $p$ , which gives the angular momentum around the axis, and  $\frac{1}{2}(L^2 + M^2)$ ,  $\frac{1}{2}N^2$  with the average of the squares  $\overline{p_\perp^2}$ ,  $\overline{p_\parallel^2}$  of the total electronic angular momentum perpendicular and parallel to the axis. Since  $N$  is constant,  $\overline{p_\parallel} = p^2$ . One obtains, finally,

$$\begin{cases} \overline{\Theta}_n = 0, & \overline{\Omega}_n = p \cos \vartheta, \\ \overline{\Theta}_n^2 = \overline{p_\perp^2}, & \overline{\Omega}_n^2 = \overline{p_\perp^2} \sin^2 \vartheta + \overline{p_\parallel^2} \cos^2 \vartheta. \end{cases} \quad (93)$$

This result, however, needs a rigorous quantum-mechanical proof; presumably  $p^2$  has to be replaced by  $p(p+1)$ .

By virtue of the eigenvalue problem (92) the quantity  $\frac{8\pi^2 m \xi^2}{h^2 \mu} W^{(4)}$  becomes identical to a numerical function of the rotational quantum number  $r$ , and thus identical to  $g_{ns}(r)$ . For the rotational energy it therefore follows that

$$\kappa^4 W_{nsr}^{(4)} = \frac{h^2 \mu \kappa^4}{8\pi^2 m \xi^2} g_{ns}(r) = \frac{h^2}{8\pi^2 J} g_{ns}(r), \quad (94)$$

where

$$J = \frac{m}{\mu \kappa^4} \xi^2 = \frac{M_1 M_2}{M_1 + M_2} \xi^2 \quad (95)$$

is the moment of inertia of the nuclei in the equilibrium position.

A discussion of the higher approximations without considering the degeneracies is of no value and we will forego this discussion here.

Instead we wish to show briefly that the two-atomic molecule can be treated by a completely different perturbation treatment, of which the classical analogue has been worked out by *Born* and *Hückel*.<sup>16</sup> Here we take as the unperturbed motion not the electronic motion with fixed nuclei, but with uniform rotation of the nuclei.

## 8. Independent treatment of two-atomic molecules

We return to Eq. (12) and write it, substituting (11):

$$\{H_0 + \kappa^4(H_{\xi\xi} + H_{\xi\vartheta} + H_{\vartheta\vartheta}) - W\} \psi = 0.$$

For two-atomic molecules the specialty is that  $H_{\xi\vartheta}$  is completely independent of  $\vartheta$ . In this case, the method leads to the goal of separate translations and rotations immediately. Following (81), one obtains (neglecting of the translational term)

$$\left\{ H_0 - \frac{h^2 \mu}{8\pi^2 m} \kappa^4 \left( \frac{\partial^2}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial}{\partial \xi} + \frac{1}{\xi^2} \Delta_\vartheta \right) - W \right\} \psi = 0. \quad (96)$$

On putting

$$\psi = Y_r(\vartheta, \omega) \Psi_r(x; \xi), \quad (97)$$

<sup>16</sup>M. Born and E. Hückel, *Phys. Z.* **24**, 1 (1923).

where  $Y_r$  is a spherical function of  $r$ th order, which therefore satisfies the equation

$$\Delta_{\vartheta} Y_r + r(r+1)Y_r = 0,$$

we obtain for  $\Psi_r$  the requirement

$$\left\{ H_0 - \frac{h^2 \mu}{8\pi^2 m} \kappa^4 \left( \frac{\partial^2}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial}{\partial \xi} - \frac{r(r+1)}{\xi^2} \right) - W \right\} \Psi_r = 0. \quad (98)$$

Now again we replace  $\xi$  by  $\xi + \kappa\zeta$ ; we therefore investigate vibrations for the state of uniform rotation. Indicating the energy of this state by

$$R = \frac{h^2 \mu \kappa^2}{8\pi^2 m} \frac{r(r+1)}{\xi^2} = \frac{h^2}{8\pi^2 J} r(r+1) \quad (99)$$

and putting

$$W = E + R, \quad (100)$$

Eq. (98) becomes

$$(\mathbf{H}^0 + \kappa \mathbf{H}^{(1)} + \kappa^2 \mathbf{H}^{(2)} + \dots - E) \Psi_r = 0, \quad (101)$$

where

$$\left\{ \begin{array}{l} \mathbf{H}^0 = H_0^0, \\ \mathbf{H}^{(1)} = H_0^{(1)} + \zeta R', \\ \mathbf{H}^{(2)} = H_0^{(2)} + \frac{1}{2} \zeta^2 R'' - \frac{h^2 \mu}{8\pi^2 m} \frac{\partial^2}{\partial \zeta^2}, \\ \mathbf{H}^{(3)} = H_0^{(3)} + \frac{1}{6} \zeta^3 R''' - \frac{h^2 \mu}{8\pi^2 m} \frac{2}{\zeta} \frac{\partial}{\partial \zeta}, \\ \dots \end{array} \right. \quad (102)$$

$H_0^0, H_0^{(1)}$  indicate the operators given before, with the same interpretation. All formulae of Section 2 are valid unchanged. The approximate equations read

$$\left\{ \begin{array}{l} \text{a) } (\mathbf{H}^0 - E^0) \Psi_r^0 = 0, \\ \text{b) } (\mathbf{H}^0 - E^0) \Psi_r^{(1)} = (E^{(1)} - \mathbf{H}^{(1)}) \Psi_r^0, \\ \text{c) } (\mathbf{H}^0 - E^0) \Psi_r^{(2)} = (E^{(2)} - \mathbf{H}^{(2)}) \Psi_r^0 + (E^{(1)} - \mathbf{H}^{(1)}) \Psi_r^{(1)}, \\ \dots \end{array} \right. \quad (103)$$

The first one has the solution

$$E^0 = V_n(\xi), \quad \Psi_r^0 = \Psi_{rn}^0 = \sigma_{rn}^0(\zeta) \varphi_n^0(x; \xi), \quad (104)$$

where  $V_n(\xi), \varphi_n^0(x; \xi)$  are the previously introduced functions and  $\sigma_{rn}^0(\zeta)$  is as yet arbitrary. The integrability condition for (103b) reads

$$(E^{(1)} - \mathbf{H}^{(1)}) \sigma_{rn}^0(\zeta) = 0.$$

Now, according to Section 2, (26a),

$$H_{nn}^{(1)} = \left( H_0^{(1)} \right)_{nn} + \zeta R' = V_n^{(1)} + \zeta R' = \zeta \frac{d}{d\xi} (V_n + R).$$

Therefore it follows, as earlier (Section 4), that

$$E^{(1)} = 0, \quad \frac{d}{d\xi} (V_n + R) = 0. \quad (105)$$

This condition obviously implies that in the unperturbed rotation an equilibrium must exist between the centrifugal force and the quasi-electric force, which resists a displacement of the nuclei as a consequence of the electronic motion. The centrifugal force is explicitly

$$-\left( \frac{1}{M_1} + \frac{1}{M_2} \right) \frac{p_r^2}{\xi^3} = -\left( \frac{1}{M_1} + \frac{1}{M_2} \right) \frac{h^2}{4\pi^2} \frac{r(r+1)}{\xi^3},$$

where the quantum-mechanical value  $\frac{h}{2\pi} \sqrt{r(r+1)}$  has been substituted for the angular momentum  $p_r$ . According to (99) and (95) this agrees with  $R'$ .

From the relation (105) the equilibrium distance  $\xi_r$  has to be computed, which still depends on the rotational quantum number  $r$ . For small values of the rotational energy  $R$ ,  $\xi_r$  can be expanded in powers of

$$\beta = \kappa^4 \frac{\mu}{m} \frac{h^2}{4\pi^2} r(r+1) = \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \frac{h^2}{4\pi^2} r(r+1), \quad (106)$$

whence one obtains<sup>17</sup>

$$\xi_r = \xi + \frac{1}{\xi^3 V_n''} \beta - \frac{3}{\xi^7 V_n''^2} \left( 1 + \frac{\xi}{6} \frac{V_n'''}{V_n''} \right) \beta^2 + \dots \quad (107)$$

Since  $\beta$  is of order  $\kappa^4$ , one will, in a systematic procedure, use only as many terms of the series as is consistent with the order of the approximation in the perturbational treatment.

If we now consider this perturbation treatment again, we wish to state briefly that the method is the same as earlier, but rather simplified by the anticipation of the rotations. The solution of (103b) reads, corresponding to (42),

$$\Psi_{rn}^{(1)} = \sigma_{rn}^0 \varphi_n^{(1)} + \sigma_{rn}^{(1)} \varphi_n^0 \quad (108)$$

and the integrability condition on (102c) yields

$$\left\{ H_{nn}^{(2)} + \left( H^{(1)} \right)_{nn}^{(1)} - E_n^{(2)} \right\} \sigma_{rn}^0 = 0.$$

<sup>17</sup>This formula can be taken simply from the cited work of Born and Hückel.

This, however, is the vibrational equation

$$\left\{ -\frac{\hbar^2 \mu}{8\pi^2 m} \frac{\partial^2}{\partial \zeta^2} + \frac{1}{2} \zeta^2 (V_n'' + R'') - E_n^{(2)} \right\} \sigma_{rn}^0 = 0. \quad (109)$$

So, just as in Section 7,

$$\kappa^2 E_{rns}^{(2)} = \left( s + \frac{1}{2} \right) h\nu_r, \quad (110)$$

where the frequency

$$\nu_r = \frac{1}{4\pi} \sqrt{\left( \frac{1}{M_1} + \frac{1}{M_2} \right) (V_N'' + R'')} \quad (111)$$

still depends on the rotational quantum number, which is contained in  $R$ .

Furthermore, as in Section 7,

$$\sigma_{rns}^0 = e^{-\frac{\eta^2}{2}} H_s(\eta), \quad (112)$$

with

$$\eta = \xi \sqrt[4]{b}, \quad b = \frac{8\pi^2}{h^2} \frac{m}{2\mu} (V_n'' + R''). \quad (112a)$$

The procedure can be continued in the known fashion. We find that  $E^{(3)} = 0$ , while  $E^{(4)}$  also contains, except for a deviation from the harmonic vibrational law, a coupling with the electronic motion. But the detailed specification of these formulae falls outside the scope of this paper, which only has to make explicit the principle of the expansion. Furthermore, the derivation of the higher approximations is useful only when the degeneracies are considered at the same time.