ON THE THEORY OF THE INTERACTION BETWEEN ELECTRONIC AND NUCLEAR MOTION FOR THREE-ATOMIC, BAR-SHAPED MOLECULES

By R. RENNER in Göttingen

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ABSTRACT

The vibrational structure of the Π-term is computed for molecules of the CO_2 type taking the interaction with the electronic motion into account.

1. Introduction and formulation of the problem

The usual route in the quantum-mechanical treatment of molecular states is to carry out a separation of electronic and nuclear motion. The justification for this procedure is that the nuclear motion is much slower than the electronic motion. Therefore we introduce only a small error, when we compute the electronic motion assuming that the nuclei are at rest in their instantaneous positions (multiple centre problem). The mathematical foundation for this has been given by Born and Oppenheimer.[1]

This separation into two types of motion *independent* of each other is justified only when the frequencies of the nuclear motion are small in comparison to the energy difference of the electronic levels of the molecule divided by h. An example of the fact that a more precise consideration of the interaction between nuclear and electronic motion can become essential is found in the Λ-doubling of two-atomic molecules.[2] At issue here is the interaction of the nuclear angular momentum for rotation of the molecule with the electronic angular momentum. At first, it must appear strange that the smaller rotational frequency and not the larger vibrational frequency is coupled to the electronic frequency. The reason for this is the high (cylindrical) *symmetry* with respect to the line connecting the two nuclei. This symmetry is, of course, conserved for the vibration and so inhibits a coupling between the vibrational and electronic frequencies.

In contrast, for more-atomic molecules the nuclear vibration can also interact with the electronic motion,[3] analogous to the rotation in two-atomic molecules.

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[1] M. Born and R. Oppenheimer, *Ann. Phys.* **84**, 457 (1927).

[2] F. Hund, *Z. Phys.* **42**, 93, (1927); R. de L. Kronig, *Loc. Cit.* **46**, 814 (1928); M. Born and S. Flügge, *Ann. Phys.* **16**, 768 (1933).

[3] G. Herzberg and E. Teller, *Z. Phys. Chem.* (B) **21**, 410 (1933).

Just as in the case of rotation of the molecule, here the vibration can lead to the splitting of degenerate electronic states, and just as the rotational structure becomes complicated through the decoupling of the electronic angular momentum from the axis of the molecule (*Figurenachse*), here we have to be prepared for a very complicated vibrational structure.

As an example of this situation, in this paper we will treat the CO_2 molecule, but it should be noted that the derivations and results that will follow can be transferred unaltered to other arbitrary bar-shaped three-atomic molecules. The three atoms of our molecule of the CO_2 type have a bar-shaped, symmetric configuration in their rest positions. This means that the molecule possesses cylindrical symmetry with respect to the line connecting the nuclei and furthermore a centre of symmetry. Therefore the electronic states can be classified in a fashion quite similar to those of a two-atomic molecule with equal atoms. For us, it is relevant only that the electronic states can be classified according to their angular momentum around the molecular axis as Σ-, Π-, Δ-terms and so forth, depending on the value of the angular momentum component being 0, ± 1, ± 2 (in units of $h/2\pi$). The Σ-states are not degenerate, while the Π-, Δ- and so forth states are doubly degenerate, representing the situation where the electronic angular momentum can represent a clockwise or counterclockwise rotation around the molecular axis. The CO_2 molecule has three *normal vibrations*, of which the first is totally symmetric, the second is antisymmetric around the symmetry centre (C-atom), and the third is degenerate. While for the first two vibrations the atoms move in the axis of the molecule, the last one is a *bending vibration*, which in general possesses an angular momentum. It therefore perturbs the strong linearity of the molecule. This has the consequence that the degeneracy of the Π-, Δ- and so forth terms will split. The size of the splitting can be of the order of magnitude of the electronic potential energy of the bending vibration, so that the requirement that the energy differences of the electronic states are large in comparison to the nuclear energy is no longer satisfied. This can be seen from the fact that the change in potential energy is largely effected by the same condition that leads to the splitting in electronic terms, namely the change in electronic eigenvalues when the molecule is deformed.

The only question now is how the *translation of the average value* of the electronic energy due to the deviation from the linear model relates to the *splitting of the electronic term*. The translation of the average will generally depend quadratically on the nuclear distortions in the neighbourhood of the equilibrium configuration. The size of the splitting, as we will see, will differ significantly for Π-, Δ-, etc. terms. For Σ-states, of course, no splitting is possible. This is also the reason why, for the ground state of the CO_2 molecule, the coupling we discuss here does not come into question. For Π-terms, the splitting depends quadratically on the coordinate r of the bending vibration and can, depending on the numerical behaviour, be larger or smaller than the average of the translation of the electronic terms. For Δ-terms the splitting is proportional to r^4, and can therefore be neglected for small amplitudes (harmonic approximation). Similar arguments hold even more strongly for higher

values of the electronic angular momentum. The complicated vibrational structure mentioned above will then appear, at least for small amplitudes, only for Π-terms. We therefore restrict ourselves to this case, since for large amplitudes the anharmonicities of the vibrations make the problem too complicated anyway. The goal of this work is to *compute the vibrational structure of the Π-term for molecules of the CO_2 type considering this interaction with the electronic motion.* We will here neglect the influence of electron spin.

2. Construction of the Schrödinger equation for the bending vibration of the three-atomic linear molecule

To simplify the problem, we assume that the translational and rotational motions, as well as the totally symmetric and anti-symmetric vibrational normal modes, have been separated from the total eigenfunction. These yield a multiplicative contribution to the desired eigenfunction of the electronic and bending vibrational motion; their contribution to the total energy eigenvalue of the molecule is additive. Next, we consider the electronic motion as a multi-centre problem.[4] Its major feature is that the relative spatial coordinates of the middle atom which interests us (the C-atom) enter the electronic eigenfunction as *parameters.* In our notation this dependence of the eigenfunctions and eigenvalues is denoted by an index k.

If we fix this atom on the molecular axis, then the molecule possesses rotational symmetry with respect to this axis, and the electronic eigenfunctions can be represented just as those of a two-atomic molecule:

$$f \cdot \cos \Lambda \vartheta, \tag{1a}$$

$$f \cdot \sin \Lambda \vartheta, \tag{1b}$$

where $\Lambda = 0, \pm 1, \pm 2, \dots$ indicates the quantum number of the angular momentum around the molecular axis for the "first" electron,[5] and ϑ its angle. The dependence of the other electron coordinates q_e is contained in f. The two functions (1) belong to the same energy value. The basis for this two-fold degeneracy of the electronic function, which obtains for $|\Lambda| \geq 1$, is, as we already indicated in Section 1, the fact that the electronic motion can rotate in a left or right hand fashion around the axis. Analogous to two-atomic molecules, we will designate the electronic states with $\Sigma, \Pi, \Delta, \dots$ corresponding to $\Lambda = 0, \pm 1, \pm 2, \dots$.

The bending vibration with normal coordinate r takes place in a plane perpendicular to the molecular axis. We designate by φ its azimuth with respect to a fixed plane through the molecular axis. Because of the perturbation of the rotational

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[4]See, for the complete presentations of the quantum theory of the molecule, R. de L. Kronig, *Band Spectra and Molecular Structure*; W. Weizel, *Handb. Experimentalphysik*, Ergänzingsband Bandenspektren (1932); F. Hund, *Handb. Phys.*, 2nd ed., XXIV/1, 563 (1933); D. M. Dennisson, *Rev. Mod. Phys.* **3**, 280 (1931); E.Teller, *Handb. u. Jahrb.* 9/II, A2 (in press).
[5]See this description in Born and Flügge, *Op. Cit.*, p. 769.

symmetry with respect to this axis, a splitting of the two previously doubly degenerate levels appears. If E_k^e designates the average value of the two split values, then the single split levels can be written as

$$E_k^e + \sigma(r)\,, \tag{2a}$$

$$E_k^e - \sigma(r)\,. \tag{2b}$$

The half *splitting $\sigma(r)$, which represents a measure for the interaction between electronic and nuclear motion,* of course depends on the deviation of the rotational symmetry and not on φ. The eigenfunctions corresponding to (2a) and (2b) read in zeroth order

$$\psi_k^I(q_e) = f_k \cos \Lambda(\vartheta - \varphi)\,, \tag{3a}$$

$$\psi_k^{II}(q_e) = f_k \sin \Lambda(\vartheta - \varphi)\,, \tag{3b}$$

which means that $\psi_k^I(q_e)$ and $\psi_k^{II}(q_e)$ are the solutions of the following Schrödinger equations for the electronic motion:

$$\frac{h^2}{8\pi^2 m} \sum \Delta_e \psi_k^I(q_e) + (E_k^e + \sigma - V_k(q_e))\,\psi_k^I(q_e) = 0\,, \tag{4a}$$

$$\frac{h^2}{8\pi^2 m} \sum \Delta_e \psi_k^{II}(q_e) + (E_k^e - \sigma - V_k(q_e))\,\psi_k^{II}(q_e) = 0\,. \tag{4b}$$

In (4) the sum has to be extended over all electrons (mass $= m$); Δ_e represents the Laplace operator $\sum \frac{\partial^2}{\partial q_e^2}$ in perpendicular coordinates which describes the kinetic energy of a single electron. $V_k(q_e)$ is the potential energy of the electrons, which is composed of the Coulomb interactions of electrons with each other and with the nuclei of the molecule (index k).

From the total eigenfunction $\Psi(q_e q_k)(q \equiv r, \varphi)$ for the electron bending vibration we know that it has to satisfy the Schrödinger equation

$$\frac{h^2}{8\pi^2 m} \sum \Delta_e \Psi(q_e q_k) + \frac{h^2}{8\pi^2 \mu} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2} \right) \Psi(q_e q_k)$$

$$+ (E - V_k(q_e) + V(r))\Psi(q_e q_k) = 0\,. \tag{5}$$

Here μ is the nuclear mass, E the eigenvalue and $V(r)$ the potential energy of the nuclear motion, which of course depends only on r. $\Psi(q_e q_k)$ can be written in product form, if the dependence on r and φ is small, so that the derivatives of the electronic eigenfunction with respect to r and φ can be neglected.[6]

From the form of function (3) we see that this is no longer the case since the electronic functions are just as dependent on the nuclear coordinate φ as on the electronic coordinate ϑ. So the total eigenfunction cannot be written as a *simple*

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[6]See E. Teller, *Hand. u. Jahrb.* §8, *Loc. Cit.*

product of an electronic and a nuclear part. It should be added that this complication does not appear for the other coordinate r.

A way out of this problem is found when we note that generally every function of electrons and nuclei (because of the completeness of the electronic function) can be written in the form

$$\Psi(q_e q_k) = \sum_n c_n(q_k)\psi_n(q_e q_k) \,, \tag{6}$$

where the ψ_n represent the electronic functions with fixed nuclei. Normally in the development of the theory it appears that a good approximation is obtained when we choose only *one* term of the series (6). The $c_n(q_k)$ corresponding to that term then becomes the vibrational eigenfunction. It is now reasonable to try an *ansatz* of two functions from (6) which should correspond to the two degenerate eigenfunctions. The functions dependent on the nuclear coordinates will be designated as "vibrational functions". In a somewhat changed notation, we obtain the solution *ansatz*

$$\Psi(q_e q_k) = \psi^I(q_k) \cdot \psi_k^I(q_e) + \psi^{II}(q_k)\psi_k^{II}(q_e) \tag{7}$$

for the solution of the differential equation (5). If we substitute (7) into (5), then we succeed, in the first two rows of (8), in separating the electronic equations (4), since Δ_e does not operate on the nuclear functions and can be exchanged with these:

$$\psi^I(q_k)\left[\frac{h^2}{8\pi^2 m}\sum \Delta_e\psi_k^I(q_e) + (E_k^e + \sigma - V_k(q_e))\psi_k^I(q_e)\right]$$

$$+ \psi^{II}(q_k)\left[\frac{h^2}{8\pi^2 m}\sum \Delta_e\psi_k^{II}(q_e) + (E_k^e - \sigma - V_k(q_e))\psi_k^{II}(q_e)\right]$$

$$+ \frac{h^2}{8\pi^2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right)(\psi^I(q_k)\cdot\psi_k^I(q_e)$$

$$+ \psi^{II}(q_k)\cdot\psi_k^{II}(q_e)) - (E - E_k^e - \sigma - V(q_k))\psi^I(q_k)\cdot\psi_k^I(q_e)$$

$$+ (E - E_k^e + \sigma - V(q_k))\psi^{II}(q_k)\cdot\psi_k^{II}(q_e) = 0 \,. \tag{8}$$

From the first two rows of (8) we obtain zero because of (4). In the remainder we can put $\psi_k^I(q_e)$ and $\psi_k^{II}(q_e)$ in front of the differential operators. Because of the slow changes with r, the $\psi_k^I(q_e)$, $\psi_k^{II}(q_e)$ are interchangeable with $\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right)$; the effect of the operator $\frac{\partial^2}{\partial\varphi^2}$ can be computed from (3). We find that

$$\left.\begin{array}{ll}\frac{\partial}{\partial\varphi}\psi_k^I(q_e) = +\psi_k^{II}(q_e), & \frac{\partial}{\partial\varphi}\psi_k^{II}(q_e) = -\psi_k^I(q_e), \\[2mm] \frac{\partial^2}{\partial\varphi^2}\psi_k^I(q_e) = -\psi_k^I(q_e), & \frac{\partial^2}{\partial\varphi^2}\psi_k^{II}(q_e) = -\psi_k^{II}(q_e).\end{array}\right\} \tag{9}$$

Using (9), we find that

$$\psi_k^I(q_e)\left[\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right)\psi^I(r,\varphi)\right.$$

$$\left. - \frac{2}{r^2}\frac{\partial\psi^{II}(r,\varphi)}{\partial\varphi} + \frac{8\pi^2\mu}{h^2}(E - E_k^e - \sigma(r) - V(r))\psi^I(r,\varphi)\right]$$

$$+ \psi_k^{II}(q_e)\left[\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right)\psi^{II}(r,\varphi) + \frac{2}{r^2}\frac{\partial\psi^I(r,\varphi)}{\partial\varphi}\right.$$

$$\left. + \frac{8\pi^2\mu}{h^2}(E + E_k^e - \sigma(r) - V(r))\psi^{II}(r,\varphi)\right] = 0. \tag{10}$$

(10) can only be satisfied if the coefficients of $\psi_k^I(q_e)$ and $\psi_k^{II}(q_e)$ vanish identically.

	Σ	Π	Δ	Φ
Σ		a		
Π	a		1/2a	
			1/2a	
Δ		1/2a		1/2a
		1/2a		1/2a
Φ			1/2a	
			1/2a	

It remains for us to indicate the dependency of E_k^e, $\sigma(r)$ and $V(r)$ on r explicitly. Restricting ourselves to harmonic forces, and because of the equilibrium condition (vanishing of the first derivative of the potential), one can write

$$E_k^e + V(r) = \alpha r^2. \tag{11}$$

The r dependence of the interaction term $\sigma(r)$ is obtained with perturbation theory: the potential of the electron in the field of the nuclei in an undistorted state, where the nuclei are at rest on the molecular axis, is different from the potential where the middle nucleus has been displaced from its rest position as a result of the bending vibration. The difference between these potentials affects the perturbation and the splitting. This difference potential is given[7] as follows: the positive charge of the nucleus in the bar-shaped arrangement is neutralised by a negative charge of equal size and a positive charge is put on a position distorted from the equilibrium. This method leads to a description of the perturbation in terms of an electric dipole, of which the variable moment $= e \cdot r$; that is, it is equal to the product of the deviation of the middle nucleus and its (for the outer electrons, effective) nuclear charge. This dipole potential has, when we consider the "first" electron (with distance ρ from the dipole and azimuth ϑ), the value

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[7]See G. Herzberg and E. Teller, *Loc. Cit.*, p. 426.

$$U = \frac{er \cos \vartheta}{\rho^2}. \tag{12}$$

The following calculation of course applies to the other electrons in a similar fashion. We construct the perturbation energy matrix corresponding to (12) with the help of the two unperturbed electronic functions (1). We thereby restrict ourselves to two simply infinite series of states where Λ runs through the values $0, \pm 1, \pm 2, \ldots$ The construction of the complete perturbation matrix would change nothing in the qualitative conclusions we wish to draw. It possesses[8] the form above with

$$a = e \cdot r \cdot F \cdot \int_0^{2\pi} \cos^2 \vartheta d\vartheta.$$

The integration over the electron coordinates q_e is contained in F. Except for the two neighbouring diagonals, of which the elements are all equal, and the two elements a in the first row and column, all elements vanish; notably those in the squares along the diagonal. This means that for all terms the perturbation vanishes in first order. An influence only appears in second order. Because of the asymmetric positions of a mentioned before, it represents a *splitting of the Π-term*, while for the Δ-, Φ- and further terms it only leads to a simultaneous translation with an equal magnitude of the two degenerate terms. Because of the symmetric construction of the matrix the perturbation of neighbouring terms has the same effect on the two degenerate terms. Only in higher orders, through the intermediate influence of the split Π-term, do we find a splitting. Since the second order, and with it the splitting of the Π-term, depends quadratically on r, we may write

$$\sigma(r) = \sigma r^2. \tag{13}$$

The proportionality factor σ, which depends on F, and which represents *the measure for the coupling between the electron and bending vibrational motion*, can in principle be determined from perturbation theory, but remains practically unknown, since we do not know the eigenfunctions that depend on q_e which enter in F. So in our calculations σ will play the role of a *parameter*, which, due to its *dependency on the special construction of the electronic core* for different molecules of the CO_2 type and also for different electronic states of the same molecule, will be *different*. The perturbation will be particularly large when the Π-term lies very close to a Σ-term. The splitting of the Δ-, Φ- and higher terms will be proportional to r^4 or r^6 respectively. Since in (11) we have already restricted ourselves to a harmonic force *ansatz*, it makes sense only to treat the influence of the perturbation and splitting for a Π-term; we will therefore exclude the higher terms from our consideration.

If we substitute (11) and (13) in the two coupled differential equations ensuing from (10), we obtain the following two equations for the two bending vibrational functions $\psi^I(r, \varphi)$ and $\psi^{II}(r, \varphi)$ with the corresponding eigenvalue E:

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[8]The elements not given are 0.

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right)\psi^I(r,\varphi) - \frac{2}{r^2}\frac{\partial\psi^{II}(r,\varphi)}{\partial\varphi}$$

$$-\frac{\psi^I(r,\varphi)}{r^2} + \frac{8\pi^2\mu}{h^2}(E - (\alpha+\sigma)r^2)\psi^I(r,\varphi) = 0\,, \qquad (14a)$$

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right)\psi^{II}(r,\varphi) + \frac{2}{r^2}\frac{\partial\psi^I(r,\varphi)}{\partial\varphi}$$

$$-\frac{\psi^{II}(r,\varphi)}{r^2} + \frac{8\pi^2\mu}{h^2}(E - (\alpha-\sigma)r^2)\psi^{II}(r,\varphi) = 0\,. \qquad (14b)$$

They form the foundation for our further calculations.

The two functions ψ^I and ψ^{II} can be taken as the components of a two-dimensional vector Ψ. The product of two such vectors $\Psi' = \begin{pmatrix} \psi^{I'} \\ \psi^{II'} \end{pmatrix}$ and $\Psi'' = \begin{pmatrix} \psi^{I''} \\ \psi^{II''} \end{pmatrix}$ has the form

$$(\Psi', \Psi''^*) = \int \psi^{I'}\psi^{I''*} + \int \psi^{II'}\psi^{II''*}\,.$$

Then one can prove, with the help of (14), that vectors belonging to different eigen-values of (14) are orthogonal to each other. If we define the two operators

$$O = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\,, \qquad (15a)$$

$$Q = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\,, \qquad (15b)$$

which have to operate on the vector $\Psi = \begin{pmatrix} \psi^I \\ \psi^{II} \end{pmatrix}$ (matrix multiplication), then the two equations can be summarised in the operator equation

$$\left[\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial}{\partial\varphi} - O\right)^2\right]\Psi(r,\varphi) + \kappa^2[E - (\alpha - \sigma Q)r^2]\Psi(r,\varphi) = 0\,, \quad (16)$$

where $\kappa^2 = 8\pi^2\mu/h^2$.

3. Solution of the kinetic vibrational equations in zeroth order and construction of the perturbation energy matrix

Our main task now consists in the calculation of the bending vibrational terms E of the bar-shaped molecule from (14) as a function of the interactions σ between the electronic and vibrational motion if the electronic state is a Π-state. In zeroth order we neglect the perturbation term σr^2 and solve the system of equations (index 0)

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right)\overset{(0)}{\psi^I} - \frac{2}{r^2}\frac{\partial\overset{(0)}{\psi^{II}}}{\partial\varphi} + \kappa^2\left(E^{(0)} - \frac{1}{\kappa^2 r^2} - \alpha r^2\right)\overset{(0)}{\psi^I} = 0\,, \quad (17a)$$

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right)\overset{(0)}{\psi}{}^{II} + \frac{2}{r^2}\frac{\partial \overset{(0)}{\psi}{}^{I}}{\partial \varphi} + \kappa^2\left(E^{(0)} - \frac{1}{\kappa^2 r^2} - \alpha r^2\right)\overset{(0)}{\psi}{}^{II} = 0 \quad (17b)$$

and then consider the coupling term σr^2 with perturbation theory. The solutions $\overset{(0)}{\psi}{}^{I}(r,\varphi)$ and $\overset{(0)}{\psi}{}^{II}(r,\varphi)$ and the eigenvalue $E^{(0)}$ are obtained immediately, since (17) must be based on the Schrödinger equation for the two-dimensional harmonic oscillator. Indeed, with the *ansatz* (index 1)

$$\overset{(0)}{\psi}{}^{I}_{1}(r,\varphi) = e^{+i\varphi}\Phi(r,\varphi)\,, \tag{18a}$$

$$\overset{(0)}{\psi}{}^{II}_{1}(r,\varphi) = -ie^{+i\varphi}\Phi(r,\varphi)\,, \tag{18b}$$

and (index 2)

$$\overset{(0)}{\psi}{}^{I}_{2}(r,\varphi) = e^{-i\varphi}\Phi(r,\varphi)\,, \tag{19a}$$

$$\overset{(0)}{\psi}{}^{II}_{2}(r,\varphi) = ie^{-i\varphi}\Phi(r,\varphi)\,, \tag{19b}$$

respectively, we obtain the equation of the two-dimensional harmonic oscillator

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right)\Phi + \kappa^2\left(E^{(0)} - \alpha r^2\right)\Phi = 0 \tag{20}$$

for the function $\Phi(r,\varphi)$. Since (18) and (19) represent linearly independent functions, the eigenvalue belonging to them is *two-fold degenerate*. Added to this is an additional *degeneracy with respect to the angular momentum* around the molecular axis. To see this, we solve (20). The *ansatz*

$$\Phi(r,\varphi) = e^{im\varphi} \cdot R(r)\,, \tag{21}$$

where $m = 0, \pm 1, \pm 2, \ldots$ represents the angular momentum (in units of $h/2\pi$) around the molecular axis, yields for the radial part $R(r)$ the differential equation

$$\frac{d^2 R}{dr^2} + \frac{1}{r}\frac{dR}{dr} - \frac{m^2}{r^2}R + \kappa^2(E^{(0)} - \alpha r^2)R = 0\,. \tag{22}$$

Its solutions can be found from the polynomial method

$$R_{Nm}(r) = e^{-1/2\kappa\sqrt{\alpha}r^2} \cdot r^m \sum_{\nu=0}^{N-m} c_\nu r^\nu\,, \tag{23}$$

where the coefficients c_ν have to be determined from a two-term recursion formula. m is subject to the condition $|m| \leq N$. The power series contains either even or

odd powers of r. The important result is that the eigenvalue $E^{(0)}$ depends only on N, but not on m.[9]

$$E_N^{(0)} = h\nu(N + 1). \tag{24}$$

$\nu = \frac{2}{\kappa}\sqrt{\alpha}$ is the frequency of the bending vibration.

With (18), (19) and (23) the bending vibrational functions belonging to (24) read

$$\Psi_{1Nm}^{(0)} \begin{cases} \overset{(0)}{\psi}{}^I{}_{1Nm} = e^{i(m+1)\varphi} \cdot R_{Nm}(r)\,, \\ \\ \overset{(0)}{\psi}{}^{II}{}_{1Nm} = -ie^{i(m+1)\varphi} \cdot R_{Nm}(r)\,, \end{cases} \tag{25a}$$

$$\Psi_{2Nm}^{(0)} \begin{cases} \overset{(0)}{\psi}{}^I{}_{2Nm} = e^{i(m-1)\varphi} \cdot R_{Nm}(r)\,, \\ \\ \overset{(0)}{\psi}{}^{II}{}_{2Nm} = ie^{i(m-1)\varphi} \cdot R_{Nm}(r)\,. \end{cases} \tag{25b}$$

It appears to be advantageous to make one more change in the designation, where we put for the factors $m + 1$ and $m - 1$ appearing in the exponents the capital M; so M is $m + 1$ or $m - 1$, depending on whether in $\Psi_{iNm}^{(0)}$ the index has the value 1 or 2. Because of the condition $|m| \leq N$ the exponents in $\Psi_{1Nm}^{(0)}$ assume the numerical values $N + 1$ to $-N + 1$, and in $\Psi_{2Nm}^{(0)}$ the numerical values $N - 1$ to $-N - 1$. Through this designation we discover that in the following perturbation energy matrix only those elements appear that are diagonal in M. The numerical values of M differ from the nuclear rotational momentum m by $+1$ or -1 and represent the total rotational momentum of the molecule with respect to its axis.

With the help of functions (25) and the introduction of the new quantum number M we represent the perturbation energy matrix elements P with respect to the coupling term $-Q\sigma r^2$; we retain the notation (16). The elements read, when we use primed quantum numbers for the final state and unprimed quantum numbers for the initial state,

$$P_{\substack{N\ N' \\ M\ M'}}^{11} = -\sigma\kappa^2 \int_0^\infty \int_0^{2\pi} \Psi_{1NM}^{(0)} Q r^2 \Psi_{1N'M'}^{*(0)} r\,dr\,d\varphi$$

$$= \sigma\kappa^2 \int_0^\infty \int_0^{2\pi} r^2 \left(\overset{(0)}{\psi}{}^I{}_{1NM} \cdot \overset{(0)}{\psi}{}^{I*}{}_{1N'M'} - \overset{(0)}{\psi}{}^{II}{}_{1NM} \cdot \overset{(0)}{\psi}{}^{II*}{}_{1N'M'} \right)$$

$$\times r\,dr\,d\varphi\,, \tag{26}$$

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[9](24) represents the energy levels of a two-dimensional oscillator with frequency ν, where $N = n_1 + n_2$ is equal to the sum of the quantum numbers of the single oscillators and $1 = 1/2 + 1/2$ is the sum of the zero-point energies (in units $h\nu$).

$$
P^{12}_{\substack{N\,N'\\M\,M'}} = -\sigma\kappa^2 \int_0^\infty \int_0^{2\pi} \Psi^{(0)}_{1NM} Q r^2 \Psi^{*(0)}_{2N'M'} r\,dr\,d\varphi
$$

$$
= \sigma\kappa^2 \int_0^\infty \int_0^{2\pi} r^2 \left(\overset{(0)}{\psi^I}_{1NM} \cdot \overset{(0)}{\psi^{I*}}_{2N'M'} - \overset{(0)}{\psi^{II}}_{1NM} \cdot \overset{(0)}{\psi^{II*}}_{2N'M'} \right)
$$

$$
\times\, r\,dr\,d\varphi\,, \tag{27}
$$

and the elements P^{22} and P^{21} go analogously. The calculation with the quantum numbers in (25) shows that few elements are different from zero. They are

$$
P^{11}_{\substack{N\,N'\\M\,M'}} = 0\,, \tag{28a}
$$

$$
P^{22}_{\substack{N\,N'\\M\,M'}} = 0\,, \tag{28b}
$$

$$
P^{12}_{\substack{N\,N'\\M\,M'}} = 4\pi\sigma\kappa^2 \int_0^\infty r^3 R_{NM} R_{N'M'}\,dr\,, \tag{28c}
$$

$$
P^{21}_{\substack{N\,N'\\M\,M'}} = 4\pi\sigma\kappa^2 \int_0^\infty r^3 R_{NM} R_{N'M'}\,dr\,. \tag{28d}
$$

Here for the non-vanishing terms the numerical value of M must be equal to that of M'. (28) predicts that only *states* which have *equal total angular momentum* and where the nuclear angular momentum differs by 2, *perturb each other*. The important fact that the perturbation matrix (28) reduces to irreducible parts with respect to the total angular momentum, allows us to treat the perturbation calculations separately for each value of $M = 0, \pm1, \pm2, \ldots$ To evaluate (28) numerically we only have to compute the integrals dependent on r and determine the selection rules with respect to N. This becomes a calculation of the matrix elements of r^2 for a two-dimensional harmonic oscillator, which can be performed by squaring the matrix for r. As selection rules for N we obtain $N' = N, N \pm 2$. The matrix elements different from zero become

$$
P^{12}_{\substack{N\,N\\M\,M}} = \frac{1}{2}\varepsilon h\nu \sqrt{(N+M+1)(N-M+1)}\,, \tag{29a}
$$

$$
P^{21}_{\substack{N\,N\\M\,M}} = \frac{1}{2}\varepsilon h\nu \sqrt{(N-M+1)(N+M+1)}\,, \tag{29b}
$$

$$
P^{12}_{\substack{N\,N-2\\M\,M}} = \frac{1}{4}\varepsilon h\nu \sqrt{(N+M+1)(N+M-1)}\,, \tag{29c}
$$

$$
P^{21}_{\substack{N\,N-2\\M\,M}} = \frac{1}{4}\varepsilon h\nu \sqrt{(N-M+1)(N-M-1)}\,, \tag{29d}
$$

$$
P^{12}_{\substack{N\,N+2\\M\,M}} = \frac{1}{4}\varepsilon h\nu \sqrt{(N-M+1)(N-M+3)}\,, \tag{29e}
$$

$$
P^{21}_{\substack{N\,N+2\\M\,M}} = \frac{1}{4}\varepsilon h\nu \sqrt{(N+M+1)(N+M+3)}\,. \tag{29f}
$$

We have introduced the shorthand notation $\varepsilon = \sigma/\alpha = \sigma/2\pi^2\mu\nu^2$, where ε is the ratio of the interaction energy to the nuclear potential, and ν is the unperturbed frequency of the nuclear vibration.

We present the perturbation energy matrices for each value of the total angular momentum M separately. For the case where M is zero, the matrix reads

$$
P_0 = \begin{pmatrix}
0 & P^{12}_{11\atop 00} & 0 & P^{12}_{13\atop 00} & & \\
P^{21}_{11\atop 00} & 0 & P^{21}_{13\atop 00} & 0 & & \\
0 & P^{12}_{31\atop 00} & 0 & P^{12}_{33\atop 00} & 0 & P^{12}_{35\atop 00} \\
P^{21}_{31\atop 00} & 0 & P^{21}_{33\atop 00} & 0 & P^{21}_{35\atop 00} & 0 \\
& & 0 & P^{12}_{53\atop 00} & 0 & P^{12}_{55\atop 00} \\
& & P^{21}_{53\atop 00} & 0 & P^{21}_{55\atop 00} &
\end{pmatrix}.
\tag{30}
$$

The matrices corresponding to a positive value of the total angular momentum $(M > 0)$ read

$$
P_M = \begin{pmatrix}
0 & P^{21}_{M-1\,M+1\atop M\;\;M} & 0 & & \\
P^{12}_{M+1\,M-1\atop M\;\;M} & 0 & P^{12}_{M+1\,M+1\atop M\;\;M} & 0 & P^{12}_{M+1\,M+3\atop M\;\;M} \\
0 & P^{21}_{M+1\,M+1\atop M\;\;M} & 0 & P^{21}_{M+1\,M+3\atop M\;\;M} & 0 \\
& 0 & P^{12}_{M+3\,M+1\atop M\;\;M} & 0 & P^{12}_{M+3\,M+3\atop M\;\;M} \\
& P^{21}_{M+3\,M+1\atop M\;\;M} & 0 & P^{21}_{M+3\,M+3\atop M\;\;M} & 0
\end{pmatrix}.
\tag{31a}
$$

The lower vibrational quantum numbers N (middle index on P) which appear for a fixed value of M are (because $|m| \le N$) $M - 1$ and $M + 1$ respectively. In a similar fashion one obtains for the case $M < 0$

$$
P_{-M} = \begin{pmatrix}
0 & 0 & P^{12}_{M-1\,M+1\atop -M\;-M} & & \\
0 & 0 & P^{12}_{M+1\,M+1\atop -M\;-M} & & P^{12}_{M+1\,M+3\atop -M\;-M} \\
P^{21}_{M+1\,M+1\atop -M\;-M} & P^{21}_{M+1\,M+1\atop -M\;-M} & 0 & P^{21}_{M+1\,M+3\atop -M\;-M} & 0 \\
& 0 & P^{12}_{M+3\,M+1\atop -M\;-M} & 0 & P^{12}_{M+3\,M+3\atop -M\;-M} \\
& P^{21}_{M+3\,M+1\atop -M\;-M} & 0 & P^{21}_{M+3\,M+3\atop -M\;-M} & 0
\end{pmatrix}.
\tag{31b}
$$

The three matrices (30), (31a) and (31b) are different from each other only in the construction of the upper-left part. All elements left open are zero. As the dotted lines indicate, the infinite matrices (30) and (31) can be constructed from quadratic, two-by-two sub-matrices; the corresponding states are two terms degenerate in the bending vibration in zeroth order.

4. Calculation of the bending vibrational terms as a function of the interaction and the selection rules

We now concentrate on our main task, which is the calculation of the dependence of the bending vibrational terms on the interaction $\varepsilon = \sigma/\alpha$. The problem is to find the eigenvalues of the perturbation energy matrices (30) and (31) through a canonical transformation S. They represent the corrections to the eigenvalues in zeroth order (24) (major axis transformation). While for smaller values of ε (up to about 0.4) a perturbation calculation through second order in ε is sufficient, for larger values of ε a numerical procedure leads to the goal.

It is not necessary to apply the procedure to $M = 0$, i.e. to (30), because here it is possible to find an exact solution of the system of differential equations (14). From (25) we observe that in this case the functions ψ^I and ψ^{II} do not depend on φ and that therefore the coupling terms $\partial \psi^{II}/\partial \varphi$ and $\partial \psi^I/\partial \varphi$ vanish, so that two uncoupled wave equations result. Each of these equations represents the motion of an oscillator, the first with potential energy $(\alpha + \sigma)r^2$, the second with $(\alpha - \sigma)r^2$. Analogously to (24) one obtains for the energy terms that are characterised with an index $+$ and $-$ respectively

$$E_{N,0}^{+(-)} = \frac{2}{\kappa}\sqrt{\alpha \, {}^{+}_{(-)}\sigma}(N+1) = \frac{2\sqrt{\alpha}}{\kappa}\sqrt{1 \, {}^{+}_{(-)}\sigma/\alpha}(N+1) = h\nu\sqrt{1 \, {}^{+}_{(-)}\varepsilon}(N+1). \quad (32)$$

$E_{N,0}^{+}$ and $E_{N,0}^{-}$ are the two bending vibrational terms into which the original value $E_N^{(0)}$ splits when the interaction is taken into account. The index 0 indicates that the total angular momentum M vanishes in this case. The eigenfunctions belonging to the two energy values (32) differ with respect to their character under a reflection through a plane through the molecular axis in that one retains its sign under this symmetry operation, and the other changes its sign. This situation corresponds exactly to that for the Σ^+- and Σ^--states of two-atomic molecules. The curves drawn in Fig. 1 represent the two energy levels $E_{N,0}^{+(-)}/h\nu$ as a function of ε in the interval $0 \leq \varepsilon \leq 1$;[10] the different pairs of curves (designated with i in the figure) represent the vibrational quantum numbers $N = 0, 1, 2, \ldots$ Both curves start for the case of vanishing coupling at $E_N^{(0)}/h\nu = (N+1)$. The curves $E_{N,0}^{-}$ go to zero for all values of N for $\varepsilon = 1$ (nuclear potential = interaction) and do not possess discrete solutions for $\varepsilon > 1$; while the curves $E_{N,0}^{+}$ increase parabolically for all values of ε. The essential result is that the energy curves representing both term systems intersect for total angular momentum 0, i.e. a mutual influence of $E_{N,0}^{+}$ and $E_{N,0}^{-}$ does not take place. The reason for this is that, as we have seen above, the eigenfunctions belonging to $E_{N,0}^{+}$ and $E_{N,0}^{-}$ have different symmetry properties.[11]

---

[10]The frequency ν of the unperturbed vibration cannot be calculated within the framework of this work , so we present the dimensionless quantity $E/h[\nu]$ as a function of ε.

[11]According to F. Hund, *Z. Phys.* **40**, 742 (1927) and J. v. Neumann and E. Wigner, *Phys. Z.* **30**, 467 (1929), no intersections of terms can appear; but, as above, it has to be required by a symmetry property.
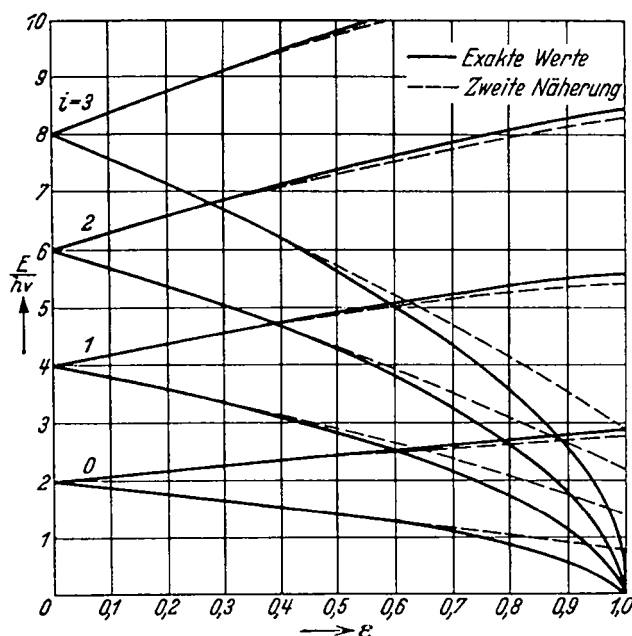
Fig. 1. Bending vibrational structure of the Π-term for the total momentum $M = 0$ as a function of the interaction ϵ.

This situation differs for the case where the total angular momentum is different from zero. There is no decomposition in two independent term systems here, since there is no symmetry relationship that could require this.

We first solve (31) for small ε by perturbation theory. We obtain the energy perturbations through first order in ε if we transform the small two-by-two matrices in the diagonal of (31) to major axes; the diagonal terms represent the energy corrections to first order in the previously degenerate vibrational levels $E_N^{(0)}$. The splitting of the matrices P (31) takes place through the canonical transformation $S^{-1}PS$ with the help of the unitary matrix

$$S = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 & 0 \\ 0 & -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 & \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \\ 0 & 0 & 0 & -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \end{pmatrix}, \tag{33a}$$

$$S^{-1} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 & 0 \\ 0 & \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 & \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} \\ 0 & 0 & 0 & \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \end{pmatrix}. \tag{33b}$$

The result of the transformation (33) reads, when S is applied to (31a) and (31b) respectively,

$$S^{-1}PS = \begin{pmatrix} 0 & \dfrac{1}{\sqrt{2}}P^{21}_{\substack{M-1\,M+1 \\ M \quad M}} & \dfrac{1}{\sqrt{2}}P^{21}_{\substack{M-1\,M+1 \\ M \quad M}} \\[2ex] \dfrac{1}{\sqrt{2}}P^{21}_{\substack{M+1\,M-1 \\ M \quad M}} & -P^{12}_{\substack{M+1\,M+1 \\ M \quad M}} & 0 \\[2ex] \dfrac{1}{\sqrt{2}}P^{21}_{\substack{M+1\,M-1 \\ M \quad M}} & 0 & P^{21}_{\substack{M+1\,M+1 \\ M \quad M}} \\[2ex] & -\dfrac{1}{2}(P^{12}-P^{21})_{\substack{M+3\,M+1 \\ M \quad M}} & \dfrac{1}{2}(P^{12}+P^{21})_{\substack{M+3\,M+1 \\ M \quad M}} \\[2ex] & \dfrac{1}{2}(-P^{12}+P^{21})_{\substack{M+3\,M+1 \\ M \quad M}} & \dfrac{1}{2}(P^{12}+P^{21})_{\substack{M+3\,M+1 \\ M \quad M}} \end{pmatrix}$$

$$\left. \begin{matrix} -\dfrac{1}{2}(P^{12}+P^{21})_{\substack{M+1\,M+3 \\ M \quad M}} & \dfrac{1}{2}(P^{12}-P^{21})_{\substack{M+1_M\,M+3 \\ \quad M}} \\[2ex] \dfrac{1}{2}(-P^{12}+P^{21})_{\substack{M+1\,M+3 \\ M \quad M}} & \dfrac{1}{2}(P^{12}+P^{21})_{\substack{M+1\,M+3 \\ M \quad M}} \\[2ex] -P^{12}_{\substack{M+3\,M+3 \\ M \quad M}} & 0 \\[2ex] 0 & -P^{21}_{\substack{M+3\,M+3 \\ M \quad M}} \end{matrix} \right) \tag{34a}$$

$$S^{-1}PS = \begin{pmatrix} 0 & -\dfrac{1}{\sqrt{2}}P^{12}_{\substack{M-1\,M+1 \\ -M \;\; -M}} & \dfrac{1}{\sqrt{2}}P^{21}_{\substack{M-1\,M+1 \\ -M \;\; -M}} \\[2ex] \dfrac{1}{\sqrt{2}}P^{21}_{\substack{M+1\,M-1 \\ -M \;\; -M}} & -P^{12}_{\substack{M+1\,M+1 \\ -M \;\; -M}} & 0 \\[2ex] \dfrac{1}{\sqrt{2}}P^{21}_{\substack{M+1\,M-1 \\ -M \;\; -M}} & 0 & P^{21}_{\substack{M+1\,M+1 \\ -M \;\; -M}} \\[2ex] & -\dfrac{1}{2}(P^{12}-P^{21})_{\substack{M+3\,M+1 \\ M \quad M}} & \dfrac{1}{2}(P^{12}+P^{21})_{\substack{M+3\,M+1 \\ M \quad M}} \\[2ex] & \dfrac{1}{2}(-P^{12}+P^{21})_{\substack{M+3\,M+1 \\ M \quad M}} & \dfrac{1}{2}(P^{12}+P^{21})_{\substack{M+3\,M+1 \\ M \quad M}} \end{pmatrix}$$

$$
\left.
\begin{array}{cc}
-\dfrac{1}{2}(P^{12}+P^{21})_{\substack{M+1\,M+3\\M\quad M}} & \dfrac{1}{2}(P^{12}-P^{21})_{\substack{M+1\,_M\,M+3\\ \quad M}} \\[2ex]
\dfrac{1}{2}(-P^{12}+P^{21})_{\substack{M+1\,M+3\\M\quad M}} & \dfrac{1}{2}(P^{12}+P^{21})_{\substack{M+1\,M+3\\M\quad M}} \\[2ex]
-P^{12}_{\substack{M+3\,M+3\\-M\,-M}} & 0 \\[2ex]
0 & -P^{21}_{\substack{M+3\,M+3\\-M\,-M}}
\end{array}
\right)
\tag{34b}
$$

Introducing the values (29) we obtain for the two non-degenerate energy corrections $E^{(1)-}$ and $E^{(1)+}$ through first order

$$
E^{(1)\,{}^{+}_{(-)}}_{\substack{M+2i-1,\pm M}} = {}^{+}_{(-)}P^{12}_{\substack{M+2i-1\,M+2i-1\\\pm M\qquad \pm M}} = {}^{+}_{(-)}h\nu\varepsilon\sqrt{i(i+M)}\,.
\tag{35}
$$

In (35) the first index $(M+2i-1)$ gives the vibrational quantum number and the second index $M > 0$ the total angular momentum; the allowed values for the vibrational levels $i = 0, 1, 2, \ldots$ For $i = 0$ the perturbation disappears in first order. While the perturbation in first order leads to a splitting of the energy terms E^{+} and E^{-}, the perturbation through second order in ε for both cases yields the same value as the same sign. In general

$$
E^{(2)\,{}^{+}_{(-)}}_{\substack{M+2i-1,\pm M}} = \frac{1}{4(E^{(0)}_{M+2i-1} - E^{(0)}_{M+2i-3})}
$$

$$
\times \left[(P^{12}+P^{21})^{2}_{\substack{M+2i-3\,M+2i-1\\\pm M\qquad \pm M}} + (P^{21}-P^{12})^{2}_{\substack{M+2i-3\,M+2i-1\\\pm M\qquad \pm M}}\right]
$$

$$
+ \frac{1}{4(E^{(0)}_{M+2i-1} - E^{(0)}_{M+2i+1})}
$$

$$
\times \left[(P^{12}+P^{21})^{2}_{\substack{M+2i-1\,M+2i+1\\\pm M\qquad \pm M}} + (P^{12}+P^{21})^{2}_{\substack{M+2i-1\,M+2i+1\\\pm M\qquad \pm M}}\right]\,.
\tag{36}
$$

With $E^{(0)}_{M+2i-1} = h\nu(M+2i)$ we obtain from this, after squaring the powers,

$$
E^{(2)\,{}^{+}_{(-)}}_{\substack{M+2i-1,\pm M}} = \frac{1}{h\nu}\left\{[(P^{12})^{2}+(P^{21})^{2}]_{\substack{M+2i-3,\,M+2i-1\\\pm M\qquad \pm M}}\right.
$$

$$
\left. - [(P^{12})^{2}+(P^{21})^{2}]_{\substack{M+2i-1\,M+2i+1\\\pm M\qquad \pm M}}\right\}\,.
\tag{37}
$$

If we substitute the value of the matrix elements of (29) into (37), then after some minor algebra we obtain the result

$$
E^{(2)\,{}^{+}_{(-)}}_{\substack{M+2i-1,\pm M}} = -\frac{1}{8}h\nu\varepsilon^{2}(M+2i)\,.
\tag{38}
$$

(38) is valid for all values of $i = 1, 2, \ldots$. The case $i = 0$ forms an exception. There

$$
E^{(2)\,{}^{+}_{(-)}}_{\substack{M-1,\pm M}} = -\frac{1}{h\nu}(P^{21})^{2}_{\substack{M-1\,M\\\pm M\,\pm M}} = -\frac{1}{8}h\nu\varepsilon^{2}M(M+1)\,.
\tag{38a}
$$

The total eigenvalue is constructed from (35) and (38). For $i \neq 0$ we have

$$E^{(-)}_{M+2i+1, \pm M} \overset{+}{{}_{(-)}} = h\nu \left[M + 2i \overset{+}{{}_{(-)}} \varepsilon \sqrt{i(i+M)} - \frac{1}{8} \varepsilon^2 (2i+M) \right], \quad i = 1, 2, \ldots ; \quad (39)$$

similarly, for $M = 0$, where we have no splitting,

$$E_{M-1, \pm M} = h\nu \left[M - \frac{1}{8} \varepsilon^2 M(M+1) \right]. \tag{39a}$$

According to (39) for a fixed value of M we would obtain curves analogous to those in Fig. 1 for different i-values. In this approximation the decomposition and intersection corresponding to the two split term systems of Fig. 1 could be obtained as well; there the E-branches (*Zweige*) for $\varepsilon \leq 1$ would remain above the abscissa representing the energy value 0 (cf. the dotted curve parts in Fig. 2).
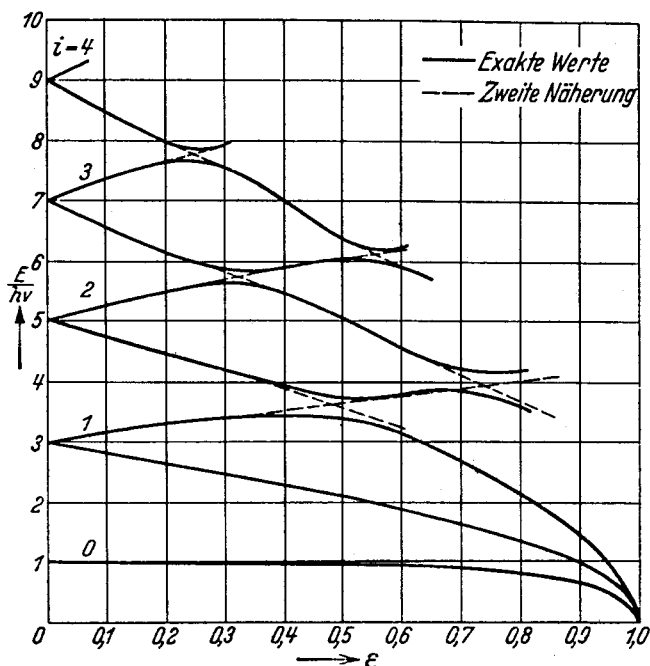

Fig. 2. Bending vibrational structure of the Π-term for the total momentum $|M| = 1$ as a function of the interaction ϵ.

To correct the energy curves for fairly high values of ε and especially to investigate them for larger values of ε, where (39) loses its validity, we use a numerical procedure. This will also decide how the branches E^+ and E^- behave where they should intersect according to second order perturbation theory. It is only possible here to present the line of thought and the results of the process: it consists of

constructing the linear system of equations belonging to the secular equation of the perturbation energy matrix (31) and substituting the matrix elements P by numerical values. For each value of the total angular momentum M we obtain a separate infinite system of linear equations, just as with the decomposition of the energy matrix. The solution of this system proceeds in the following fashion: starting from the approximations already obtained, we choose the eigenvalues and eigenvectors such that they obey the system of linear equations as well as possible. Here we have a simplifying factor which makes the calculation possible at all, namely that it is approximately possible to solve a limited number of linear equations only. The influence of further equations is small. The result of the calculation is that there, where in second order an intersection of the two energy curves would occur, a mutual avoidance occurs. This fact is in accordance with the already cited considerations of Hund and von Neumann and Wigner, since for $M \neq 0$ no symmetry property that would require intersection exists. A further result is that the curves representing the E^--branches go to zero for $\varepsilon = 1$. The latter fact, which we recognise from the case $M = 0$, can also be justified from the system of differential equations (14): if we neglect the coupling term $\frac{2}{r^2} \frac{\partial \psi^I}{\partial \varphi}$ [12] in (14b), then we obtain an equation analogous to (17), for which the eigenvalues read, in analogy to (32),

$$E_{2i+1,M} = \frac{2}{\kappa}\sqrt{\alpha - \sigma}\left(\sqrt{M^2 + 1} - M + 2i + 1\right). \tag{40}$$

The eigenvalues of the energy vanish for $\sigma = \alpha$, and (40) yields an asymptotic representation around $\sigma \approx \alpha$ of the energy curve representing the E^--branch.

   The curves obtained in this fashion are presented in Fig. 2 for $M = 1$ as a function of the interaction between electron and nuclear motion $\varepsilon = \sigma/\alpha$ in the interval $0 \leq \varepsilon \leq 1$. The dotted parts on the avoided crossings clarify the behaviour in second order. An essential point, represented in Fig. 1 as well as Fig. 2, is that the splittings for sufficiently large interactions are of the same order of magnitude as the differences between the separate degenerate energy levels. Curves analogous to the ones in Fig. 2, where the avoided crossings of the different branches occur, and for which the E^--branches go to zero for $\varepsilon = 1$, are also obtained for the further cases $M = \pm 2, \pm 3, \ldots$

   At the end of this section we add a small remark about the case $M = 0$, which we treated exactly, and which can serve as an indication of the quality of our approximation procedure: this case can also be treated with perturbation theory. The important result here is that after the principal axis transformation (because of the equality $P_{kk'}^{12}\big|_{00} = P_{kk'}^{21}\big|_{00}$) a decomposition of the transformed matrix into two submatrices appears. This represents the fact that the two term systems E^+ and E^- do not mutually influence each other, but intersect. The result of the perturbation

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[12]This is allowed for the case $\sigma \approx \alpha$, since in this case (14b) represents the motion in a very flat potential $(\alpha - \sigma_2)r^2$ and (14a) the motion in a strongly curved potential $(\alpha + \sigma)r^2$. The difference between the eigenvalues corresponding to (14a) and (14b) respectively is then large, so that the mutual perturbation (coupling term $\partial \psi^I / \partial \varphi$) can be neglected.

theory up to second order in ε is presented by the dotted lines in Fig. 1. The deviation of the values found from perturbation theory from the exact values yields a measure for the quality of the approximation and allows the conclusion that it would be useful for E^+ in the whole interval $0 \leq \varepsilon \leq 1$, while for E^- it would hold only for small ε. This has been ascertained as well by the numerical procedure.

As a last point in this section there remains the discussion of the selection rules which can be found analogous to the two-atomic molecule. On the one hand we have to consider the ||-transitions (components of the radiation parallel to the molecule) with $\Delta\Lambda = 0$ (Π–Π transition) and on the other hand the $\perp$-transitions (radiation perpendicular to the molecular axis) with $|\Delta\Lambda| = 1$ (Π–Σ or Π–Δ transitions). On the basis of the symmetry properties of the eigenfunction (25) one recognizes that the selection rules for the total angular momentum read $\Delta M = 0$ when we deal with a Π–Π transition, and $|\Delta M| = 1$ when the electronic transition leads from a Π- to a Σ- or Δ-state. On the behaviour of the quantum number i for small values of ε, especially where no noteworthy mutual influence of the term levels takes place, we can say that the selection rule $|\Delta i| = 0, 2, 4, \ldots$ is valid, where higher $|\Delta i|$-values appear with less intensity.[13] For larger values of the interaction the meaning of the quantum number i is lost altogether, and also this selection rule loses its meaning.

5. Discussion

Unfortunately there is no experimental material, by which we can *directly* compare our theoretical result with the experiment. If this were the case one should attempt to fit the measured vibrational structure of the molecule, for instance in a Π–Σ transition of the electrons into our scheme of Fig. 1 or Fig. 2 with respect to the selection rules, and find a value for the interaction ε which fits in.

Strong series		Weak series		Difference in terms of both series
$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	cm^{-1}
91870		92330		460
93060	1190	93600	1270	540
94250	1190	94840	1240	590
95410	1160	96090	1250	680
96560	1150	97330	1240	770
		(98630)	1300	

Instead Rathenau[14] has performed absorption measurements on CO_2, and has found, among others, the series given in the table. A direct interpretation in terms of our scheme cannot be undertaken with certainty. With some probability, however, it

[13]See G. Herzberg and E. Teller, *Op. Cit.*, §6.
[14]G. Rathenau, *Z. Phys.* **87**, 32 (1933).

can be assumed that the strong series is an excitation of a series of totally symmetric vibrations of the Π-term from a vibrationless ground state of the Σ-state. Also the second weak series can be ascribed to a transition from a vibrationless Σ-state to a series of totally symmetric vibrations of the Π-term, but with the distinction that here the bending vibration is two-fold (because of the selection rule) excited ($i = 2$), which yields the difference with the first series. The small value of the difference between the series, which should represent the double value of the bending vibration, can be explained from our theory when we assume that the lower $i = 2$ bending vibrational level has been depressed as a result of the interaction. It should be added here that except for these two series in the indicated region a large number of further weak lines were recorded, which up to now could not be ascribed.

Göttingen, Institut für theoretische Physik der Universität