

THE INTERACTION OF ELECTRONIC AND VIBRATIONAL MOTIONS IN COMPLEX MOLECULES

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IN the theory of the luminescence and absorption of complex molecules, the study of the vibrational energy of the molecule and the exchange of this energy with the surrounding medium plays a most important role.¹ However, it is as yet not clear to what degree and under what conditions the vibrational motion in a molecule may be considered independent of the electronic motion, their interaction being neglected. B. S. Neporent has even suggested (see, e.g., reference 2) that for a considerable fraction of the molecules, namely the molecules of the second class, the interaction of the electronic and vibrational motions is so great that the vibrational motion cannot in general be separated from the electronic motion. (For molecules of the second class, the law of mirror symmetry of the absorption and emission spectra is violated.) On the basis of this assumption, Neporent has divided the continuous spectra of complex molecules into "modulation spectra" and "decay spectra."

The problem of the interactions of electronic and vibrational motions in a complex molecule may be solved in principle by quantum-mechanical methods, but this is very difficult. Hence, it is essential to plan a program for the solution of a given problem, make correct estimates of the orders of magnitude of the corresponding interactions, and elucidate their role in various processes.

The quantum-mechanical problem of separating the energy of a polyatomic molecule into electronic, vibrational, and rotational energy was discussed in the classical paper of Born and Oppenheimer³ on the basis of the expansion of the energy operator in a power series in a small parameter β , which takes into account the difference in mass of the nuclei and electrons. This parameter was taken to be the fourth root of the ratio of the electronic mass m to the average nuclear mass M in the molecule:

$$\beta = \sqrt[4]{\frac{m}{M}} \tag{1}$$

Born and Oppenheimer showed that, by expressing the energy operator in the form

$$\hat{H} = \hat{H}_0 + \beta \hat{H}_1 + \beta^2 \hat{H}_2 + \beta^3 \hat{H}_3 + \beta^4 \hat{H}_4 + \dots \tag{2}$$

and analogously expanding the wave functions in a power series in

$$\Psi = \Psi_0 + \beta \Psi_1 + \beta^2 \Psi_2 + \dots, \tag{3}$$

we may derive the energy of the molecule in the form of the series

$$E = E_0 + \beta^2 E_2 + \beta^4 E_4 + \dots, \tag{4}$$

where the zero-order term $E_0 = E_{el}$ gives the electronic energy of the molecule, i.e., its energy when the nuclei are stationary. The second-order term $\beta^2 E_2 = E_{vib}$ is the vibrational energy of the molecule, while the fourth-order term $\beta^4 E_4$ contains the rotational energy E_{rot} (together with terms depending on the vibrations). An essential point is that there are no odd terms containing β, β^3, \dots , in the series in Eq. (4),* with the result that a series for the energy in terms of the parameter $\beta^2 = \sqrt{m/M}$ is obtained. The order of magnitude of the ratio E_{vib}/E_{el} is equal to $\beta^2 = \sqrt{m/M}$, while the order of magnitude of the ratio E_{rot}/E_{el} is equal to $\beta^4 = m/M$. This agrees with experiment, when we compare the differences $\Delta E_{el}, \Delta E_{vib}$, and ΔE_{rot} between the electronic, vibrational, and rotational energy levels.

The order of magnitude of the ratios E_{vib}/E_{el} and E_{rot}/E_{el} may be obtained also from elementary considerations.

In fact, in order of magnitude

$$\frac{E_{vib}}{E_{el}} = \frac{h\nu_{vib}}{h\nu_{el}} \cong \sqrt{\frac{k_{vib}}{M}} : \sqrt{\frac{k_{el}}{m}}, \tag{5}$$

where k_{vib} and k_{el} are the quasi-elastic constants for the oscillation of the nuclei with the frequency ν_{vib} and for the oscillation of the electrons (classically considered) with the frequency ν_{el} . The constants k_{vib} and k_{el} are of the same order of magnitude, since they are determined by the very same forces of interaction of the nuclei and electrons. Then, assuming $k_{vib} \cong k_{el}$, we obtain

$$\frac{E_{vib}}{E_{el}} \cong \sqrt{\frac{m}{M}} = \beta^2. \tag{6}$$

On taking into account the fact that the total electronic energy is of the same order of magnitude as the kinetic energy T_{el} of the revolution of the electrons about the nuclei, we find for the ratio E_{rot}/E_{el}

$$\frac{E_{rot}}{E_{el}} = \frac{h\nu_{rot}}{h\nu_{el}} \cong \frac{T_{rot}}{T_{el}} \cong \frac{M_{rot}^2}{2I_{rot}} : \frac{M_{el}^2}{2I_{el}}, \tag{7}$$

where M_{rot}^2 and M_{el}^2 are the squares of the rotational and electronic angular momenta, while $I_{rot} = MR^2$ (R denotes the dimensions of the molecules) and $I_{el} = mr^2$ (where r denotes the distance of the electrons from the nuclei) are the corresponding moments of inertia.

*When the operator of Eq. (2) is averaged over the functions of Eq. (3), thus leading to Eq. (4), these terms vanish.

If we assume that $M_{\text{rot}}^2 \cong M_{\text{el}}^2$ (they are of the order of magnitude of $\hbar^2 = \hbar^2/4\pi^2$) and that $R = r$, we obtain

$$\frac{E_{\text{rot}}}{E_{\text{el}}} \cong \frac{m}{M} = \beta^4. \quad (8)$$

The possibility of performing the expansion in Eq. (4), based physically on the slowness of the motion of the nuclei in comparison with that of the electrons, is the basis of the ordinary approximate quantum-mechanical treatment of molecules (see, e.g., reference 4), in which the wave function of the molecule is written in the form (neglecting rotation)

$$\Psi = \psi_{\text{el}}(x, \rho) \psi_{\text{vib}}(\rho). \quad (9)$$

where $\psi_{\text{el}}(x, \rho)$ and $\psi_{\text{vib}}(\rho)$ are the wave functions describing the electronic and vibrational motions, x denotes the set of electronic coordinates, and ρ the relative coordinates of the nuclei (changes in these coordinates represent the vibrational coordinates).

$\psi_{\text{el}}(x, \rho)$ is the solution of the wave equation for electronic motion with the nuclei taken to be stationary, i.e., in the so-called adiabatic approximation:

$$\hat{H}_{\text{el}}(x, \rho) \psi_{\text{el}}(x, \rho) = \epsilon_{\text{el}}(\rho) \psi_{\text{el}}(x, \rho), \quad (10)$$

where

$$\hat{H}_{\text{el}}(x, \rho) = \hat{T}_{\text{el}}(\rho) + V(x, \rho) \quad (11)$$

is the operator for the electronic energy, equal to the sum of the kinetic energy operator for the electrons \hat{T}_{el} and the energy of interaction of the electrons and nuclei (the latter being stationary) $V(x, \rho)$. $\epsilon_{\text{el}}(\rho)$ is the electronic energy as a function of the relative coordinates of the nuclei; for stable molecules, this has a minimum at certain values $\rho = \rho_e$.

$\psi_{\text{vib}}(\rho)$ is the solution of the wave equation for vibrational motion. It may be obtained from the wave function

$$[\hat{H}_{\text{el}}(x, \rho) + \hat{T}_{\text{vib}}(\rho)] \Psi = E \Psi, \quad (12)$$

where E is an eigenvalue of the energy operator $\hat{H}_{\text{el}}(x, \rho) + T_{\text{vib}}(\rho)$, which includes the operator for the kinetic energy of the vibrations $\hat{T}_{\text{vib}}(\rho)$. The solution is found by substituting in the form of Ψ in Eq. (9), and averaging over the electronic motion. Then, in fact, we have

$$\int \psi_{\text{el}}^*(x, \rho) [\hat{H}_{\text{el}}(x, \rho) + \hat{T}_{\text{vib}}(\rho)] \psi_{\text{el}}(x, \rho) \psi_{\text{vib}}(\rho) dx = E \psi_{\text{vib}}(\rho). \quad (13)$$

Taking Eq. (10) into account, and neglecting the effect of the operator $\hat{T}_{\text{vib}}(\rho)$ on the electronic wave function $\psi_{\text{el}}(x, \rho)$ [which varies slowly as a function of ρ in comparison with the vibrational function $\psi_{\text{vib}}(\rho)$], we obtain the equation

$$[\epsilon_{\text{el}}(\rho) + \hat{T}_{\text{vib}}(\rho)] \psi_{\text{vib}}(\rho) = E \psi_{\text{vib}}(\rho), \quad (14)$$

which, if we assume that $E = \epsilon_{\text{el}}(\rho_e) + E_{\text{vib}}$, may be written in the form

$$\hat{H}_{\text{vib}} \psi_{\text{vib}}(\rho) = [\hat{T}_{\text{vib}}(\rho) + \{\epsilon_{\text{el}}(\rho) - \epsilon_{\text{el}}(\rho_e)\}] \psi_{\text{vib}}(\rho) = E_{\text{vib}} \psi_{\text{vib}}(\rho). \quad (15)$$

This equation is an approximate wave equation for the vibrational motion, in which the electronic energy with stationary nuclei $\epsilon_{\text{el}}(\rho) - \epsilon_{\text{el}}(\rho_e) = U_{\text{vib}}(\rho)$ [as calculated from the electronic level $\epsilon_{\text{el}}(\rho_e) = E_{\text{el}}$] plays the role of the potential energy of vibration, while the value of the vibration energy E_{vib} is obtained as an eigenvalue of the vibrational energy operator $\hat{H}_{\text{vib}} = \hat{T}_{\text{vib}}(\rho) + U_{\text{vib}}(\rho)$.

A separation of the electronic and vibrational motions takes place in the approximation under study. The interaction of the electronic and vibrational motions is determined by the non-adiabatic terms which were dropped in going from Eq. (12) to Eq. (14). These terms take into account the influence of the operator $T_{\text{vib}}(\rho)$ on the electronic wave-functions $\psi_{\text{el}}(x, \rho)$. The order of magnitude of the non-adiabatic terms determines the order of magnitude of the energy of interaction of the electronic and vibrational motions; these terms contain the derivatives of $\psi_{\text{el}}(x, \rho)$ with respect to ρ , and require a more detailed study.

The operator $\hat{T}_{\text{vib}}(\rho)$ is the sum of quadratic terms of the type

$$\frac{\hat{p}_i^2}{2M_i} = -\frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial \rho_i^2}, \quad (16)$$

where \hat{p}_i is the momentum operator corresponding to the i -th vibrational coordinate, and the coefficient M_i is of the order of magnitude of the mass of the nuclei.*

We note that the mean value of the operators $(\hat{p}_i^2/2M_i)$ in Eq. (15), which give the mean kinetic energy of the vibrations (for one degree of freedom) will be of the order of $\beta^2 = \sqrt{m/M}$ in comparison with the electronic energy. That is, $(\hat{p}_i^2)^{1/2}$ will be of the order of $\beta M^{1/2} = (m/M)^{1/4} M^{1/2} = (mM)^{1/4}$. The matrix elements of the type $\int \psi_{\text{vib}}^*(\rho) \hat{p}_i \psi_{\text{vib}}(\rho) d\rho$ will be of the same order of magnitude. The order of magnitude of the electronic energy will be determined by that of the mean kinetic energy $(\hat{p}_\lambda^2/2m)$ of the individual electrons, where \hat{p}_λ is the momentum operator for an electron.† When $(\hat{p}_\lambda^2/2m) \cong 1$, $(\hat{p}_\lambda^2)^{1/2}$ is of the order of magnitude of $m^{1/2}$, and the same order of magnitude is found for the matrix elements of the type $\int \psi_{\text{el}}^*(x, \rho) \hat{p}_\lambda \psi_{\text{el}}(x, \rho) dx$.

The application of the operator of Eq. (16) to the wave function of Eq. (9) gives

*With a suitable choice of the coordinates ρ , the operator $\hat{T}_{\text{vib}}(\rho)$ will not contain terms of the type $(\hat{p}_i \hat{p}_j/2M_{ij}) = (\hbar^2/2M_{ij})(\partial/\partial \rho_i)(\partial/\partial \rho_j)$ ($i \neq j$). In the general case, there are also mixed terms with $i \neq j$. The same treatment may be applied to these terms as to the purely quadratic terms of the type in Eq. (16).

†Our treatment deals with the outer electrons, the binding energy of which determines the order of magnitude of the electronic energy of the molecule in which we are interested.

$$\frac{\hat{p}_i^2}{2M_i} \psi_{e1}(x, \rho) \psi_{vib}(\rho) = \psi_{e1}(x, \rho) \frac{\hat{p}_i^2}{2M_i} \psi_{vib}(\rho) + \frac{\hat{p}_i \psi_{e1}(x, \rho)}{V 2M_i} \frac{\hat{p}_i \psi_{vib}(\rho)}{V 2M_i} + \psi_{vib}(\rho) \frac{\hat{p}_i^2 \psi_{e1}(x, \rho)}{2M_i} \quad (17)$$

While the first term (averaged over the electronic and vibrational motions) is of the order of β^2 , the second and third terms, which take into account the interactions of electronic and vibrational motion due to failure of the adiabatic approximation, lead to interaction energies of a higher order of magnitude. On multiplying by $\Psi' = \psi'_{e1}(x, \rho) \psi'_{vib}(\rho)$ and integrating, the second term gives the matrix element

$$\int \Psi' \left[\frac{\hat{p}_i \psi_{e1}(x, \rho)}{\sqrt{2M_i}} \frac{\hat{p}_i \psi_{vib}(\rho)}{V 2M_i} \right] dx d\rho, \quad (18)$$

which may be represented in the form

$$\int \psi_{e1}^*(x, \rho) \frac{\hat{p}_i \psi_{e1}(x, \rho)}{V 2M_i} dx \int \psi_{vib}^*(\rho) \frac{\hat{p}_i \psi_{vib}(\rho)}{V 2M_i} d\rho.$$

The derivative expression $\hat{p}_i \psi_{e1}(x, \rho) = (\hbar/i)(\partial/\partial \rho_i) \times \psi_{e1}(x, \rho)$ will be of the same order of magnitude as $\hat{p}_\lambda \psi_{e1}(x, \rho) = (\hbar/i)(\partial/\partial x_\lambda) \psi_{e1}(x, \rho)$, since the electronic wave function depends on the relative coordinates of the electrons and the nuclei. Hence, the matrix element $\int \psi_{e1}^*(x, \rho) [\hat{p}_i \psi_{e1}(x, \rho)/(2M_i)^{1/2}] dx$ is of the same order of magnitude as the matrix element $(2M_i)^{-1/2} \int \psi_{e1}^*(x, \rho) \hat{p}_\lambda \psi_{e1}(x, \rho) dx$, which is of the order of $m^{1/2}/M^{1/2} = \beta^2$. Since the order of magnitude of the matrix element $\int [\psi'_{vib}(\rho) \hat{p}_i \psi_{vib}(\rho)/(2M_i)^{1/2}] d\rho$ will be $(mM)^{1/4}/M^{1/2} = (m/M)^{1/4} = \beta$, the order of magnitude of expression (18) is β^3 . Analogously, the following matrix element corresponds to the third term in Eq. (17):

$$\int \psi_{e1}^*(x, \rho) \psi_{vib}^*(\rho) \frac{\hat{p}_i^2 \psi_{e1}(x, \rho)}{2M_i} \psi_{vib}(\rho) dx d\rho = \int \frac{\psi_{e1}^*(x, \rho) \hat{p}_i^2 \psi_{e1}(x, \rho)}{2M_i} dx, \quad (19)$$

This is of the order of $m/M = \beta^4$ (if we take into account the fact that $\hat{p}_i^2 \psi_{e1}(x, \rho)$ is of the order of magnitude of $\hat{p}_\lambda^2 \psi_{e1}(x, \rho)$, and that $\int \psi_{e1}^*(x, \rho) \times \hat{p}_\lambda^2 \psi_{e1}(x, \rho) dx$ is of the order of m).

For a given electronic state, averaging over the electronic wave function of the term in Eq. (17) containing $\hat{p}_i \psi_{e1}(x, \rho) \hat{p}_i \psi_{vib}(\rho)$ gives the value zero:

$$\left(\int \psi_{e1}^*(x, \rho) \hat{p}_i \psi_{e1}(x, \rho) dx = 0 \right),$$

whereas the corresponding averaging of the term in Eq. (17) containing $\hat{p}_i^2 \psi_{e1}(x, \rho)$ gives a contribution of the order of β^4 to $\epsilon_{e1}(\rho)$ in Eq. (14) [see Eq. (19)]. This results only in a certain change in $\psi_{vib}(\rho)$ and E_{vib} . However, the non-adiabatic terms result in the non-vanishing of matrix elements of the type

$$\int \psi_{e1}^* \hat{T}_{vib}(\rho) \Psi dx d\rho = \int \psi_{e1}^*(x, \rho) \psi_{vib}^*(\rho) \hat{T}_{vib}(\rho) \psi_{e1}(x, \rho) \psi_{vib}(\rho) dx d\rho, \quad (20)$$

taken with regard to differing electronic states. The largest terms in such matrix elements, derived from the terms in Eq. (17) containing $\hat{p}_i \psi_{e1}(x, \rho) \hat{p}_i \psi_{vib}(\rho)$, will be of the order of β^3 . Now, if the distances between the electronic levels are of the order of unity, these terms will lead only to a small interaction of these levels. That is, they give rise to a slight mixing of the corresponding wave functions, which will not have an appreciable influence on the separation of the electronic and vibrational motions. The role of the terms in Eq. (17) containing $\hat{p}_i^2 \psi_{e1}(x, \rho)$ will be even smaller; these terms will make a contribution of the order of β^4 to the matrix elements of (20). Thus, the non-adiabatic terms will not interfere with the separation of the electronic and vibrational motions. This conclusion is valid both for diatomic and polyatomic molecules. For the latter, the essential factor will be not the total amount of vibrational energy, but rather, the mean amount per degree of freedom, which will be determined fundamentally by the order of magnitude of the ratio of velocities of motion of the nuclei to the electrons. Because of the smallness of the magnitudes of β^3 and β^4 , even a considerable increase in the number of non-adiabatic terms occurring with an increase in the number of degrees of freedom will not affect the possibility of separating the vibrational and electronic motions. Here we must take into account the fact that some of the terms may be very small, and that even a partial compensation of different terms may also take place. Hence, there are no grounds for expecting that an appreciable fraction of the complex molecules will show very large interactions of the electronic and vibrational motions, or that "modulation spectra" might be observed. The classification of complex molecules into molecules obeying the law of mirror symmetry (molecules of the first class) and those not obeying this law (molecules of the second class) must be related to the degree of difference of the vibrational structures of the electronic states combining in the spectrum.

The possibility of separating the vibrational motion from the electronic motion for complex molecules does not imply that the problem of the adiabatic approximation does not play a role in the theory of complex molecules and might be completely neglected. Even a relatively small mixing of electronic states due to the non-adiabatic terms may lead to the possibility of radiationless transitions. Such transitions will be determined by the non-vanishing of the matrix elements of types (17) and (18) upon approach of the electronic-vibrational levels of two different electronic states [when $E' - E'' = (E'_{e1} + E'_{vib}) - (E''_{e1} + E''_{vib})$ is small]. The corresponding matrix elements will be rather large when the potential-energy surfaces for the electronic states in question intersect. This is analogous to the situation which occurs when the potential energy curves for a diatomic molecule intersect (cf., e.g.,

references 5 and 6 on the theory of predissociation). For complex molecules, the number of such intersections will increase with the number of vibrational degrees of freedom. Hence, radiationless transitions may become highly probable. When the probability of such transitions is of the order of $10^9 - 10^{10} \text{ sec}^{-1}$, the excited molecules will not luminesce.

The conceptions presented above are qualitative; a more detailed analysis is needed of the question of the interaction of electronic and vibrational motions in polyatomic molecules. This analysis must be based on the taking into account of the terms determining the deviation from the adiabatic approximation. For this purpose, it should be expedient to make quantum-mechanical calculations with an estimation of the order of magnitude of the various interactions for the simplest models of molecules. The models must reflect the peculiarities of complex molecules, and must take into account the possibility of vibrations of various types, in particular, the deformation vibrations. Of great significance will be the study of radiationless transitions associated with the existence of non-

adiabatic terms. The carrying out of systematic studies of the interactions of electronic and vibrational motion in complex molecules is very important in the further development of the theory of the luminescence and absorption of these molecules.

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