A new method is proposed, allowing to express the probability of radiationless transitions in the harmonic approximation for the zeroth vibrational level. The results coincide entirely with those obtained by the density matrix method.

The mathematical problem of finding the probability of radiationless transitions nonadiabatically generated was solved by a number of methods. These methods are reviewed in [1]. A correlation function method [2] has been recently added to them. In the present paper still another method is proposed, allowing to solve this problem in the special case of transitions with zeroth vibrational level in the harmonic approximation. At the same time we use the accurate values of the integrals

\[ \langle \Phi_{av'} | \Phi_{b0} \rangle \text{ and } \langle \Phi_{av'} | \frac{\partial}{\partial Q'} | \Phi_{b0} \rangle \]

and assume that \( \langle \phi_a | \delta / \delta Q' | \phi_b \rangle \) is independent of normal coordinates.

To find the radiationless transition probability we use the expression

\[ W_{b \rightarrow a} = \int \rho(E_a) \tilde{W}(E_a) dE_a, \]

where

\[ \tilde{W}(E_a) = \frac{2\pi}{\hbar} \sum_{\alpha} | \langle \alpha v' | H_{av} | b0 \rangle |^2 \delta(E_{av'} - E_{b0}). \]

and

\[ H_{av'} = -\hbar^2 \sum_i \frac{\partial^2}{\partial Q_i^2} \frac{\partial \Phi_{av'} \partial \Psi_{av}}{\partial Q_i}. \]

\( \rho(E_a) \) is the final state density of states (the level is determined by energy only).

The \( dE_a \) integration in (1) is performed by using the presence of the \( \delta \)-function. \( E_a \) is a continuous parameter, which can be chosen as the pure ground state electronic energy, and after removal of the singularity it is necessary to retain only the term corresponding to the given energy \( E_a \).

In the harmonic approximation

\[ \Phi_{av'} = \prod_{j=1}^{N} \chi_{av'} (Q_j), \]

\[ \chi_{av'} (Q_j) = \left( \frac{\beta_j}{\sqrt{\pi} 2^v j!} \right)^{1/2} \frac{H_{av'} (2v_j)}{H_{av'} (2v_j)} \exp \left( -\frac{\beta_j^2 Q_j^2}{2} \right). \]

Here \( \beta_j = (\omega_j / \hbar)^{1/2} \), \( H_{av'} \) are Hermite polynomials, and \( Q_j \) are normal coordinates. We assume that the normal coordinates and vibrational frequencies of both electronic states are related by

\[ Q_j = Q'_j - \delta Q_j^0, \quad \omega_j = \omega_j. \]
Using (3) and (5), we rewrite (2) as

\[
\tilde{W}_{b-a} = \frac{2\pi}{\hbar} \sum_{\nu_i} \left[ \sum_i |R_i(ab)|^2 \left( \frac{\partial}{\partial \Psi_i} \right)_b \left( \frac{\partial}{\partial \Psi_i} \right)_a \right]^* \left( \frac{\partial}{\partial \Psi_i} \right)_b \left( \frac{\partial}{\partial \Psi_i} \right)_a \times \prod_{j=1}^{N} \left< \alpha_j \left| \frac{\partial}{\partial Q_{j}} \left| \beta_0 \right. \right. \right. \\
= \prod_{j=1}^{N} \left< \alpha_j \right| \left. \frac{\partial}{\partial Q_{j}} \left. \left| \beta_0 \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \r