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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

\[ \langle \Phi_{a\nu'} | \Phi_{b\nu} \rangle \text{ and } \left< \Phi_{a\nu'} \right| \frac{\partial}{\partial Q_i} \left| \Phi_{b\nu} \right> \]

and assume that \( \langle \Phi_a | \partial/\partial Q | \Phi_b \rangle \) is independent of normal coordinates.

To find the radiationless transition probability we use the expression

\[ W_{b \rightarrow a} = \int \rho(E_a) \tilde{W}(E_a) dE_a, \quad (1) \]

where

\[ \tilde{W}(E_a) = \frac{2\pi}{\hbar} \sum_{\nu'} | \langle a \nu' | H_a | b0 \rangle |^2 \delta(E_a - E_{b0}). \quad (2) \]

and

\[ H_{a \nu' \nu} = -\hbar \sum_i \frac{\partial^2}{\partial Q_i^2} \frac{\partial \Phi_{b\nu'}}{\partial Q_i}; \quad (3) \]

\( \rho(E_a) \) 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

\[ \Phi_{b\nu'} = \prod_{j=1}^N \chi_{b\nu'}(Q_j), \quad (4) \]

\[ \chi_{b\nu'}(Q_j) = \left( \frac{\beta_j}{\sqrt{\pi} 2^{\nu_j} \nu_j!} \right)^{1/2} H_{\nu_j}'(\beta_j Q_j) \exp \left( -\frac{\beta_j^2 Q_j^2}{2} \right). \]

Here \( \beta_j = (\omega_j/\hbar)^{1/2} \), \( H_{\nu_j}' \) 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

\[ Q_j = Q_j' - \Delta Q_j, \quad \omega_j = \omega_j'. \quad (5) \]

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\[ Q_j = Q_j' - \Delta Q_j, \quad \omega_j = \omega_j'. \quad (5) \]
Using (3) and (5), we rewrite (2) as

\[
\tilde{W}_{b-a} = \frac{2\pi}{\hbar} \sum v_i \left[ \sum R_i(ab)^2 \langle \psi_i | \frac{\partial}{\partial Q_i} | \psi_b \rangle \langle \psi_i | \frac{\partial}{\partial Q_i} | \psi_0 \rangle \right. \\
\times \left. \prod_{j=1}^N \langle \psi_j | \psi_0 \rangle \langle \psi_j | \psi_b \rangle \right] \delta \left( E_b - E_a + \sum v_j w_j \right)
\]

\[
\times \left[ \prod_{j=1}^N \langle \psi_j | \psi_0 \rangle \langle \psi_j | \psi_b \rangle \right] \delta \left( E_a - E_b + \sum v_j h_j \right) .
\]

(6)

Here

\[
R_i(ab) = -\frac{\hbar^2}{2} \left( \frac{\partial}{\partial Q_i} \psi_b \right).
\]

Using (4') and (5), we easily obtain for the integrals arising

\[
\langle \chi_{\psi_i} (Q_i) | \chi_{\psi_0} (Q_i) \rangle = \frac{S_i^{\psi_i} \exp \left( -\frac{S_i}{2} \right)}{[\psi_i !]^{1/2}}.
\]

(7)

\[
| \langle \chi_{\psi_i} (Q_i) | \chi_{\psi_0} (Q_i) \rangle |^2 = \frac{S_i^{\psi_i} \exp \left( -\frac{S_i}{2} \right)}{\psi_i !}
\]

(8)

\[
\left( \frac{\partial}{\partial Q_i} \chi_{\psi_0} (Q_i) \right) = -\beta_i \left( \frac{S_i^{\psi_i} \exp \left( -\frac{S_i}{2} \right)}{\psi_i !} \right) \exp \left( -\frac{S_i}{2} \right),
\]

(9)

\[
\left| \left( \frac{\partial}{\partial Q_i} \chi_{\psi_0} (Q_i) \right) \right|^2 = \frac{\beta_i \left( \frac{1}{2} \left( S_i^{\psi_i-1} + S_i^{\psi_i+1} \right) - \psi_i S_i^{\psi_i} \right) \exp \left( -\frac{S_i}{2} \right)}{\psi_i !}.
\]

(10)

Substituting these integrals into (6) leads to

\[
\tilde{W}_{b-a} = \frac{2\pi}{\hbar} \sum v_i \left[ \sum R_i(ab)^2 \langle \psi_i | \frac{\partial}{\partial Q_i} | \psi_b \rangle \langle \psi_i | \frac{\partial}{\partial Q_i} | \psi_0 \rangle \right. \\
\times \exp \left( -\frac{S_i}{2} \right) \prod_{j=1}^N \frac{S_j^{\psi_j}}{\psi_j !} \exp \left( -\frac{S_j}{2} \right) + \sum R_i R_j \beta_i \beta_j \\
\times \left[ \frac{S_i^{\psi_i-1}}{V^2} - \frac{S_i^{\psi_i+1}}{V^2} \right] \left[ \frac{S_j^{\psi_j-1}}{V^2} - \frac{S_j^{\psi_j+1}}{V^2} \right] \exp \left( -\frac{S_i + S_j}{2} \right) \right] \\
\times \left[ \prod_{j=1}^N \langle \psi_j | \psi_0 \rangle \langle \psi_j | \psi_b \rangle \right] \delta \left( E_a - E_b + \sum v_j h_j \right) .
\]

(11)

After some simple transformations Eq. (11) can be reduced to the form

\[
\tilde{W}_{b-a} = \frac{2\pi}{\hbar} \sum v_i \left[ \sum R_i(ab)^2 \langle \psi_i | \frac{\partial}{\partial Q_i} | \psi_b \rangle \langle \psi_i | \frac{\partial}{\partial Q_i} | \psi_0 \rangle \right. \\
\times \exp \left( -\frac{S_i}{2} \right) \prod_{j=1}^N \frac{S_j^{\psi_j}}{\psi_j !} \left[ \delta (h w_{ab} + h w_i) \\
+ \sum v_j h w_j \right] + S_i \left( \frac{1}{2} (h w_{ab} + 2 h w_i) + \sum v_j h w_j \right) \\
- 2\delta \left( h w_{ab} + h w_i + \sum v_j h w_j \right) + \delta \left( h w_{ab} + \sum v_j h w_j \right) \right] \\
+ \sum_{j=1}^N \frac{2\pi R_i R_j \beta_i \beta_j V S_j V S_i}{2} \sum \frac{S_j^{\psi_j}}{\psi_j !} \left[ \delta (h w_{ab}) \\
+ \sum v_j h w_j + \sum v_j h w_j \right].
\]

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