EVALUATION OF THE NUCLEAR FACTOR OF THE PROBABILITY OF A RADIATIONLESS TRANSITION BY INTEGRATION OVER THE DOMINANT REGIONS IN PHASE SPACE

Alexey Sergeev and Bilha Segev
Dept. of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

Introduction
We study a radiationless transition in a polyatomic molecule. The molecule originally vibrates around the minimum of Born – Oppenheimer surface corresponding to some excited electronic state. During the transition the electronic energy transfers to vibrational degrees of freedom of nuclei moving on the lower surface corresponding to the ground electronic state.

The subject of this study is the Franck – Condon integral, or an overlap integral between nuclear components of the molecular wavefunctions in the initial (I) and final (F) states. It is the dominant factor of the transition rate, and it could vary by many orders of magnitude because of the tunneling nature of the transition.

\[
f_{\nu} = \int [\Psi_I(q)]^* \Psi_F(q) dq = \int [\Psi_{\nu}^I(q)]^* \Psi_{\nu}^F(q) dq
\]

Wigner function
\[
\rho(q, p) = \langle q | \rho \psi(q) \rangle = \frac{1}{\sqrt{2\pi \hbar}} \int e^{-i\frac{p}{\hbar}q} \psi(q) dq
\]

Transition rate
\[
\Gamma(E) = \frac{1}{\hbar} \sum_{\nu \to \nu'} f_{\nu'}^2
\]

Initial distribution
\[
\rho_{\nu}(q, p) = \frac{1}{(2\pi \hbar)^{3N}} f_{\nu}(q, p) e^{-\frac{q^2 + p^2}{2\hbar}}
\]

Harmonic approximation:
\[
\nu^I(q) = \frac{1}{2} \sum_{i=1}^{N} \omega_i q_i^2
\]

\[
h, \nu(q, p) = \frac{1}{2} \sum_{i=1}^{N} \left( \frac{1}{\omega_i} p_i^2 + \alpha_i q_i^2 \right)
\]

\[
C(q, p) = 1.
\]

Final distribution
\[
\rho_{\nu}(q, p) = \frac{1}{(2\pi \hbar)^{3N}} f_{\nu}(q, p) e^{-\frac{q^2 + p^2}{2\hbar}}
\]

Leading order:
\[
\rho_{\nu}(q, p) = \delta(E - H^I(q, p))
\]

First order correction:
\[
\rho_{\nu}(q, p) = H^I(q, p) + \sum_{\nu'} \rho_{\nu'}(q, p) e^{i\theta_{\nu'}}(H^F - H^I)
\]

\[
\rho_{\nu}(q, p) = \sum_{\nu'} f_{\nu'}(q, p) e^{i\theta_{\nu'}}(W - H^I)
\]

Jumps point (\(q^*, p^*)
\[
W(q^*, p^*) = \Delta H^I(q^*, p^*)
\]

Results

Acknowledgments
This research was supported by a Grant from the United States - Israel Binational Science Foundation (BSF), Jerusalem, Israel.