A method to calculate Franck-Condon factors in terms of the tomographic probability representation

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Franck-Condon (FC) factors calculation is now the problem of great interest because of the numerous applications in molecular vibrational spectra analysis, investigation of crystals' optical properties, in radiationless processes study etc. The most frequently used method to obtain FC factors is to calculate an overlapping integral of initial and final wave functions of a system under consideration [1], [2]. But this approach comes across various difficulties if there is a need to obtain FC factors in polyatomic molecules.

In the present work a method based on the tomographic probability approach [3] is introduced. Previously this method was represented for some particular one-mode cases in [4].

An arbitrary multidimensional system with quadratic Hamiltonian including a polyatomic molecule in the Franck-Condon approximation is defined by the following wave function:

$$\psi_{n_1 \ldots n_N}(\vec{x}) = \frac{1}{\sqrt[4]{\pi^N}\sqrt{2^{n_1+\ldots+n_N} n_1! \ldots n_N!}} \times \exp\left[-\frac{1}{2}\vec{x}^T \sigma \vec{x} + \vec{\varpi}^T \vec{x} + \varphi\right] H_{\vec{n}}(\vec{x}) \qquad (1)$$

Taking into account the Dushinsky effect [5] and the formula for transition probability in terms of symplectic tomograms [6] we obtain an integral expression for FC factors in polyatomic molecules with fully real and positive integrated function:

$$\begin{aligned} P_{n_1 \ldots n_N m_1 \ldots m_N} = & \frac{1}{4^N \pi^N 2^{n_1+\ldots+n_N+m_1+\ldots+m_N} n_1! \ldots n_N! m_1! \ldots m_N!} \\ & \times \int \frac{1}{|\nu_1 \ldots \nu_N|^2 \left|\det \xi \det \tilde{\xi}\right|} \exp\left[i\left(\vec{X}-\vec{Y}\right)\right] \\ & \times \left| e^{\frac{1}{4}(\vec{\varpi}+\vec{\eta})^T \left(\frac{\sigma}{2}-\Omega\right)^{-1} (\vec{\varpi}+\vec{\eta}) + \frac{1}{4}\tilde{\vec{\kappa}}^T \xi^{-1} \tilde{\vec{\kappa}} - \frac{1}{2}\vec{d}^T \tilde{\sigma} \vec{d} + \tilde{\vec{\varpi}}^T \vec{d} + \varphi + \tilde{\varphi}} \right|^2 \\ & \times \left| H_{\vec{n}}^{\{\sigma-\sigma(\sigma-2\Omega)^{-1}\sigma\}}(\vec{z}) \, H_{\vec{m}}^{\{\tilde{\sigma}-\frac{1}{2}\tilde{\sigma}\Lambda\xi^{-1}\Lambda\tilde{\sigma}\}}\left(\tilde{\vec{z}}\right) \right|^2 \\ & \times d\vec{X} \, d\vec{Y} \, d\vec{\mu} \, d\vec{\nu}, \end{aligned} \qquad (2)$$

where $\vec{z} = \left(\sigma - \sigma(\sigma-2\Omega)^{-1}\sigma\right)^{-1} \left(\sigma(\sigma-2\Omega)^{-1}(\vec{\varpi}+\vec{\eta})\right)$,
$\tilde{\vec{z}} = \left(\tilde{\sigma} - \frac{1}{2}\tilde{\sigma}\Lambda\xi^{-1}\Lambda\tilde{\sigma}\right)^{-1} \left(\tilde{\sigma}\vec{d} + \frac{1}{2}\tilde{\sigma}\Lambda\xi^{-1}\tilde{\vec{\kappa}}\right)$,
$\xi = \frac{\sigma}{2} - \Omega$, $\tilde{\xi} = \frac{\Lambda\sigma\Lambda}{2} - \Omega$, $\vec{\kappa} = \vec{\varpi} + \vec{\eta}$, $\tilde{\vec{\kappa}} = \Lambda\tilde{\vec{\varpi}} + \tilde{\vec{\eta}} - \Lambda\tilde{\sigma}\vec{d}$,
$\vec{\eta}$ and $\tilde{\vec{\eta}}$ are N -dimensional vectors determined by the tomogram parameters
$\vec{\eta} = \left(-\frac{iX_1}{\nu_1}, -\frac{iX_2}{\nu_2}, \ldots, -\frac{iX_N}{\nu_N}\right)$ and $\tilde{\vec{\eta}} = \left(\frac{iY_1}{\nu_1}, \frac{iY_2}{\nu_2}, \ldots, \frac{iY_N}{\nu_N}\right)$,
Ω is a $N \times N$ diagonal matrix with $(\Omega_{kk}) = \frac{i\mu_k}{2\nu_k}$, $\left(\Omega_{jk}\right)_{j \neq k} = 0$ and Λ is a Dushinsky matrix.

Comparing (2) with the results calculated in terms of wave functions we have also obtained new integral relations for an absolute square of Hermite polynomials.

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