

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

E.D. Zhebrak

Moscow Institute of Physics and Technology  
el1holstein@phystech.edu

## Abstract

In the scope of the current research is introduced a new method to calculate Franck-Condon factors in polyatomic molecules that is based on the tomographic probability approach to quantum mechanics. This approach was implemented to calculate transition probabilities in various systems under an instantaneous shift of frequency and equilibrium position by an external force. The one-dimensional cases of harmonic oscillators and a case of a system with an arbitrary dimension and quadratic Hamiltonian were considered that provided explicit formulas for transition probabilities in these systems and also gave new integral relations for multidimensional Hermite polynomials.

## Introduction

Franck-Condon (FC) factors calculation is now the problem of great interest because of the numerous applications in different branches of physics [1]. For the case of a multidimensional system the FC factors were obtained first by Sharp and Rosenstock [2] and then by Doktorov et al. [3].

But these methods appeared not to be efficient for transition probabilities calculation in polyatomic molecules:

- ✗ FC integrals can't be factorized because of the Dushinsky effect [4]
- ✗ For a N-atomic molecule one needs to compute  $C_n^{3N-6+n-1}$  FC integrals, ( $n = E/\omega$ )
- ✗ The integrated expression is not fully positive.

➔

Huge dimension!

We propose a new method of FC factors calculation based on the tomographic probability approach to quantum mechanics.

## Transition probabilities in the tomographic approach

The formula for transition probability between an initial  $\varphi(x)$  and a final state  $\chi(x)$  is well known in terms of the wave functions:

$$P = \left| \int \varphi^*(x) \chi(x) dx \right|^2 \quad (1)$$

The function  $w(X, \mu, \nu)$  on the phase space having the meaning of probability distribution was first introduced in the work [5]. This function called the symplectic tomogram depends on three variables:  $X = \mu q + \nu p$  is the coordinate in a squeezed and rotated phase space and  $\mu, \nu$  are the parameters of this squeeze and rotation. The symplectic tomogram is related to wave function by the reversible transform:

$$w(X, \mu, \nu) = \frac{1}{2\pi|\nu|} \left| \int \psi(y) e^{\frac{i\mu}{\nu}y + \frac{iX}{\nu}y} dy \right|^2$$

Transition probability between two states defined by the tomograms  $w_1(X, \mu, \nu)$  and  $w_2(Y, \mu, \nu)$  can be expressed in the following form:

$$P_{1 \rightarrow 2} = \frac{1}{2\pi} \int w_1(X, \mu, \nu) w_2(Y, -\mu, -\nu) e^{i(X+Y)} dXdYd\mu d\nu \quad (2)$$

## Transition probabilities in an arbitrary multidimensional system with quadratic Hamiltonian

We consider an arbitrary N - dimensional system with a quadratic Hamiltonian determined by the wave function

$$\psi_{n_1 \dots n_N}(\vec{x}) = \frac{1}{\sqrt[2]{\pi^N} \sqrt{2^{n_1 + \dots + n_N} n_1! \dots n_N!}} \exp \left[ -\frac{1}{2} \vec{x}^T \sigma \vec{x} + \vec{\omega}^T \vec{x} + \varphi \right] H_n(\vec{x})$$

$\varphi$  is a normalizing factor.

The wave function of this system after an instantaneous shift of an equilibrium position and frequency will have the same form as the wave function of the initial state under a scaled and shifted argument:

$$\tilde{\psi}_{n_1 \dots n_N}(\Lambda \vec{x} + \vec{d}) = \frac{1}{\sqrt[2]{\pi^N} \sqrt{2^{n_1 + \dots + n_N} n_1! \dots n_N!}} \exp \left[ -\frac{1}{2} (\Lambda \vec{x} + \vec{d})^T \tilde{\sigma} (\Lambda \vec{x} + \vec{d}) + \vec{\tilde{\omega}}^T (\Lambda \vec{x} + \vec{d}) + \tilde{\varphi} \right] H_n(\Lambda \vec{x} + \vec{d})$$

Using the direct calculation scheme (1) we obtain symplectic tomograms for the state after a perturbation:

$$w_{n_1 \dots n_N}(\vec{X}, \vec{\mu}, \vec{\nu}) = \frac{1}{2^N \pi^{\frac{N}{2}} 2^{n_1 + \dots + n_N} n_1! \dots n_N! |\det \xi|} \left| \exp \left[ \frac{1}{4} \vec{K}^T \xi^{-1} \vec{K} - \frac{1}{2} \vec{d}^T \tilde{\sigma} \vec{d} + \vec{\tilde{\omega}}^T \vec{d} + \tilde{\varphi} \right] \right|^2 \times \left| H_n \left( \frac{1}{2} \tilde{\sigma} \Lambda \xi^{-1} \Lambda \tilde{\sigma} \right) \left( \tilde{\sigma} - \frac{1}{2} \tilde{\sigma} \Lambda \xi^{-1} \Lambda \tilde{\sigma} \right)^{-1} \left( \tilde{\sigma} \vec{d} + \frac{1}{2} \tilde{\sigma} \Lambda \xi^{-1} \vec{K} \right) \right|^2$$

where

$$\xi = \frac{\Lambda \sigma \Lambda}{2} - \Omega, \quad \vec{K} = \Lambda \vec{\omega} + \vec{\eta} - \Lambda \tilde{\sigma} \vec{d}, \quad \vec{\eta} = \left( -\frac{iX_1}{v_1}, \frac{iX_2}{v_2}, \dots, -\frac{iX_N}{v_N} \right), \quad (\Omega_{\mu}) = \frac{i\mu_{\mu}}{2v_{\mu}}, \quad (\Omega_{\nu})_{j \neq k} = 0.$$

The tomogram of the initial state has the same form under the following parameters:  $\tilde{\sigma} \rightarrow \sigma$ ,  $\tilde{\omega} \rightarrow \omega$ ,  $\vec{d} = 0$ ,  $\Lambda = 1$ .

According to (2) the transition probability between the state before the perturbation  $|n_1 \dots n_N\rangle$  and the state after it  $|m_1 \dots m_N\rangle$  is defined in terms of symplectic tomograms by the integral relation:

$$P_{n_1 \dots n_N, m_1 \dots m_N} = \frac{1}{4^N \pi^N 2^{n_1 + \dots + n_N + m_1 + \dots + m_N} n_1! \dots n_N! m_1! \dots m_N! |\det \xi| |\det \tilde{\xi}|} \left| \exp \left[ \frac{1}{4} (\vec{\omega} + \vec{\eta})^T \left( \frac{\sigma}{2} - \Omega \right)^{-1} (\vec{\omega} + \vec{\eta}) + \frac{1}{4} \vec{K}^T \xi^{-1} \vec{K} - \frac{1}{2} \vec{d}^T \tilde{\sigma} \vec{d} + \vec{\tilde{\omega}}^T \vec{d} + \varphi \right] \right|^2 \exp \left[ i(\vec{X} - \vec{Y}) \right] \times \left| H_n^{(\sigma - \sigma(\sigma - 2\Omega)^{-1} \sigma)} \left( (\sigma - \sigma(\sigma - 2\Omega)^{-1} \sigma)^{-1} (\sigma(\sigma - 2\Omega)^{-1} (\vec{\omega} + \vec{\eta})) \right) \right|^2 \times \left| H_m^{(\tilde{\sigma} - \frac{1}{2} \tilde{\sigma} \Lambda \xi^{-1} \Lambda \tilde{\sigma})} \left( (\tilde{\sigma} - \frac{1}{2} \tilde{\sigma} \Lambda \xi^{-1} \Lambda \tilde{\sigma})^{-1} \left( \tilde{\sigma} \vec{d} + \frac{1}{2} \tilde{\sigma} \Lambda \xi^{-1} \vec{K} \right) \right) \right|^2 d\vec{X} d\vec{Y} d\vec{\mu} d\vec{\nu}$$

By the wave function method:

According to the integral property of multidimensional Hermite polynomials firstly derived in [6] one gets the following relation for transition probabilities in polyatomic molecules:

$$P_{n_1 \dots n_N, m_1 \dots m_N} = \frac{1}{2^{n_1 + \dots + n_N + m_1 + \dots + m_N} n_1! \dots n_N! m_1! \dots m_N! |\det(\sigma + \Lambda \tilde{\sigma} \Lambda)|} \left| H_{\vec{n}}^{(K)}(\vec{y}) \right|^2 \times \left| \exp \left[ \frac{1}{2} (\vec{\omega} + \Lambda \tilde{\omega} - \Lambda \tilde{\sigma} \vec{d})^T (\sigma + \Lambda \tilde{\sigma} \Lambda)^{-1} (\vec{\omega} + \Lambda \tilde{\omega} - \Lambda \tilde{\sigma} \vec{d}) - \frac{1}{2} \vec{d}^T \tilde{\sigma} \vec{d} + \vec{\tilde{\omega}}^T \vec{d} + \varphi \right] \right|^2$$

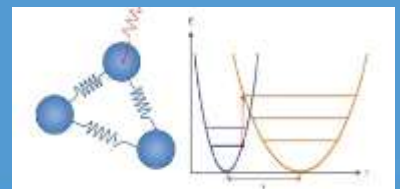
$$\vec{y} = R^{-1} \begin{pmatrix} \vec{z}_1 \\ \vec{z}_2 \end{pmatrix}, \quad \vec{z}_1 = \frac{1}{4} (\sigma + \Lambda \tilde{\sigma} \Lambda)^{-1} + (\sigma + \Lambda \tilde{\sigma} \Lambda)^{-1} \sigma (\vec{\omega} + \Lambda \tilde{\omega} - \Lambda \tilde{\sigma} \vec{d}),$$

$$\vec{z}_2 = \frac{1}{4} (\tilde{\sigma} \Lambda (\sigma + \Lambda \tilde{\sigma} \Lambda)^{-1} + (\sigma + \Lambda \tilde{\sigma} \Lambda)^{-1} \Lambda \tilde{\sigma}) (\vec{\omega} + \Lambda \tilde{\omega} - \Lambda \tilde{\sigma} \vec{d}) + \vec{\tilde{\omega}}$$

$$R_{11} = \sigma - \frac{1}{2} \sigma (\sigma + \Lambda \tilde{\sigma} \Lambda)^{-1} \sigma,$$

$$R_{22} = \tilde{\sigma} - \frac{1}{2} \tilde{\sigma} \Lambda (\sigma + \Lambda \tilde{\sigma} \Lambda)^{-1} \Lambda \tilde{\sigma},$$

$$R_{12} = -\frac{1}{2} \tilde{\sigma} \Lambda (\sigma + \Lambda \tilde{\sigma} \Lambda)^{-1} \sigma,$$



1. Huh, J., and R. Berger. *Journal of Physics: Conference Series* 380. 1 (2012).
2. Sharp, T. E., and H. M. Rosenstock. *The Journal of Chemical Physics* 41. 11 (1964): 3453
3. E. V. Doktorov, I. A. Malkin, and V. I. Man'ko, *J. Mol. Spectrosc.* 56 (1975): 1.

4. Dushinsky, F. *Acta Physicochim.* (1937): 551.
5. Mancini, S., V. I. Man'ko, and P. Tombesi. *Physics Letters A* 213:1 (1996): 1.
6. Man'ko V.I., Wunsche A. *Quantum Semiclass. Opt.* 9 (1997): 381.