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LETTER TO THE EDITOR

A generating function for the product of the Laguerre polynomials: Franck–Condon factor for multiphoton processes

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Abstract. We have formulated the generating function for the product of Laguerre polynomials and is used to determine the Franck–Condon factor for multiphoton transition between the electronic states on the adiabatic potential surfaces of the model displaced harmonic oscillator system. It is shown that for the multiphoton transition, the independent displacements from the successive adiabatic curves can be calculated from the experimental measurement of the Franck–Condon factor.

In this letter we draw attention to an important relation satisfied by the Laguerre polynomial which is used to determine the Franck–Condon factor [1] for multiphoton transition between the electronic states on the adiabatic potential surfaces of a model displaced harmonic oscillator system. Although to determine the Franck–Condon factor a good knowledge of the real potential surface is necessary, there are, however, a few models [2] where one can evaluate them explicitly.

The relation we propose here is the following generating function for the product of the Laguerre polynomial:

$$\begin{aligned} & \sum_{m_{j-1}=0}^{\infty} \dots \sum_{m_2=0}^{\infty} \sum_{m_1=0}^{\infty} (x_j)^m (x_1)^{-n} \left(\frac{x_{j-1}}{x_j}\right)^{m_{j-1}} \left(\frac{x_{j-2}}{x_{j-1}}\right)^{m_{j-2}} \dots \left(\frac{x_2}{x_3}\right)^{m_2} \left(\frac{x_1}{x_2}\right)^{m_1} \\ & L_{m_{j-1}}^{m-m_{j-1}}(x_j^2) L_{m_{j-2}}^{m_{j-1}-m_{j-2}}(x_{j-1}^2) \dots L_{m_1}^{m_2-m_1}(x_2^2) L_n^{m_1-n}(x_1^2) \\ & = \exp \left[\frac{\sum_{i=1}^j x_i^2 - \left(\sum_{i=1}^j x_i\right)^2}{2} \right] \left(\sum_{i=1}^j x_i\right)^{m-n} L_n^{m-n} \left[\left(\sum_{i=1}^j x_i\right)^2 \right] \end{aligned} \tag{1}$$

where L_m^k denote the Laguerre polynomial and m_i 's are positive integers including 0. j can be any integer where $j - 1$ will dictate the number of summation. m and n are two non-negative integers. x_i 's are real variables. Here we adopt the definition of a Laguerre polynomial as

$$L_n^{m-n}(x) = \sum_{k=\max(0, -(m-n))}^n (-1)^k \frac{m! x^k}{k!(n-k)!(m-n+k)!} \tag{2}$$

When $m - n \geq 0$, equation (2) corresponds to the Laguerre polynomial as given in [3]. However, equation (2) is valid for negative value of $m - n$. This gives a slight extension of the expression given in [3]. Formula (2) is equivalent to the expression used by Perelomov in [4] and in [5]. Thus, for example, one has,

$$L_2^{-1}(x) = \frac{x^2}{2} - x \quad (3a)$$

and

$$L_2^{-2}(x) = \frac{x^2}{2} \quad (3b)$$

in addition to the usual relations given in [3].

For $j = 2$, the formula (1) reduces to

$$\sum_{m_1=0}^{\infty} (x_2)^m (x_1)^{-n} \left(\frac{x_1}{x_2}\right)^{m_1} L_{m_1}^{m-m_1}(x_2^2) L_n^{m_1-n}(x_1^2) = \exp[-x_1 x_2] (x_1 + x_2)^{m-n} L_n^{m-n}[(x_1 + x_2)^2]. \quad (4)$$

Equation (4) can be proved by using the well known generating function [3]

$$\sum_{m_1=0}^{\infty} \left(\frac{x_1}{x_2}\right)^{m_1} L_{m_1}^{m-m_1}(x_2^2) = \exp[-x_1 x_2] \left(1 + \frac{x_1}{x_2}\right)^m \quad (5)$$

and the recurrence relation

$$(m+1)L_{m+1}^{n-1}(x) - (m+n)L_m^{n-1}(x) + xL_m^n(x) = 0 \quad (6)$$

where equation (6) directly follows from formula (2). Now, with repeated use of equation (6), the successive relations for higher j values, i.e. equation (1), can be proved by the method of induction.

To calculate the Franck–Condon factor of transition we describe the molecular system which is situated in the external radiation field $E(R, t)$ with an interaction potential as $V_{\text{int}} = -d \cdot E(R, t)$, where d is the dipole moment of the molecule. The total electronic Hamiltonian can be written as

$$H_e(r, R) = T_e + V_{ee}(r) + V_{NN}(R) + V_{eN}(r, R) \quad (7)$$

with V_{ee} , $V_{NN}(R)$ and $V_{eN}(r, R)$ as the electron–electron, nuclear–nuclear and electron–nuclear interactions, respectively. r and R are the electronic and nuclear coordinates, respectively, and T_e is the electronic kinetic energy operator. In the electronic Hamiltonian we have neglected the kinetic energy part, T_N , of the nuclear motion. Thus taking the nuclear coordinate as a parameter the corresponding eigenstate and eigenvalues can be given as

$$H_e|\phi_n\rangle = U_n(R)|\phi_n\rangle \quad (8)$$

where the energy eigenvalues $U_n(R)$ are the adiabatic potential surfaces, $\{|\phi_n\rangle\}$ forms a complete orthonormal set of electronic states. The time-dependent state of the total system can be given by

$$|\Psi(t)\rangle = \sum_n \psi_n(R, t)|\phi_n\rangle. \quad (9)$$

The coefficients $\psi_n(R, t)$ can be regarded as the wavefunctions for the nuclear motion. Thus the time-dependent Schrodinger equation becomes

$$H|\Psi(t)\rangle = i\hbar \sum_n \dot{\psi}_n(R, t)|\phi_n\rangle \quad (10)$$

and the equation of the nuclear wavefunction is given by

$$[T_N + U_m(R)]\psi_m(R, t) - \sum_n \langle \phi_m | d \cdot E(R, t) | \phi_n \rangle \psi_n(R, t) = i\hbar \frac{\partial}{\partial t} \psi_m(R, t). \quad (11)$$

This neglect of nuclear kinetic energy operator on the electronic wavefunction is precisely the Born–Oppenheimer approximation [1].

We introduce the vibrational eigenfunctions on the adiabatic energy surfaces by the eigenvalue equations

$$[T_N + U_m(R)]u_v^m(R) = \Omega_v^m u_v^m(R) \quad (12)$$

where $u_v^m(R)$ are the vibrational eigenfunctions of an electronic state m .

Now writing the nuclear wavefunction in terms of the vibrational eigenfunction as

$$\psi_m(R, t) = \sum_v C_v^m(t) u_v^m(R) \quad (13)$$

we obtain

$$i\hbar \frac{\partial}{\partial t} C_\xi^m(t) = \Omega_\xi^m C_\xi^m(t) + \sum_{v,n} \mu_{nm} E_0 \langle u_\xi^m | u_v^n \rangle C_v^n(t) \quad (14)$$

where the overlap integral element $\langle u_\xi^m | u_v^n \rangle$ is the Franck–Condon factor determining the coupling between the levels.

Thus the Franck–Condon coupling requires the knowledge of the detailed structure of the energy surface. For a two-state displaced oscillator model we have

$$H_1 = \frac{P^2}{2M} + \frac{1}{2} M \Omega_1^2 R^2 \quad (15a)$$

$$H_2 = \Delta E + \frac{P^2}{2M} + \frac{1}{2} M \Omega_1^2 (R - R_0)^2 \quad (15b)$$

where H_1 (H_2) is the vibrational Hamiltonian corresponding to electronic level 1(2). P , M , ΔE and Ω_1 are the momentum, mass, energy difference between level 1 and 2 and frequency of the oscillators, respectively. R is the coordinate of the oscillators and R_0 is the displacement of the excited state potential from the ground state.

One can define the displacement operator [6] $D(\xi) = e^{-i\frac{R_0 P}{\hbar}}$ such that

$$D(\xi) R D^\dagger(\xi) = R - R_0 \quad (16)$$

with $\xi = R_0$. Starting from the eigenvalue equation

$$H_1 |u_v^1\rangle = \hbar \Omega_1 v |u_v^1\rangle \quad (17)$$

we obtain

$$(H_2 - \Delta E) |u_v^2\rangle \equiv D(\xi) H_1 D^\dagger(\xi) |u_v^2\rangle = \hbar \Omega_1 v |u_v^2\rangle. \quad (18)$$

Thus we find

$$|u_v^2\rangle = D(\xi) |u_v^1\rangle \quad (19)$$

and the Franck–Condon factor now becomes

$$|\langle u_v^2 | u_\mu^1 \rangle|^2 = |\langle u_v^1 | D(\xi) | u_\mu^1 \rangle|^2. \quad (20)$$

Now we consider a multiphoton transition, say a k -photon process, through the displaced oscillator model where each potential surface is harmonic with its centre displaced from the successive lower electronic state as R_1 , R_2 , $R_3 \dots R_k$ respectively, and the successive

differences in energy become $\Delta E_1, \Delta E_2 \dots \Delta E_k$ etc. Thus the adiabatic curves of the electronic states are

$$H_1 = \frac{P^2}{2M} + \frac{1}{2}M\Omega_1^2 R^2 \tag{21a}$$

$$H_2 = \Delta E_1 + \frac{P^2}{2M} + \frac{1}{2}M\Omega_1^2 (R - R_1)^2 \tag{21b}$$

$$H_3 = \Delta E_2 + \frac{P^2}{2M} + \frac{1}{2}M\Omega_1^2 (R - R_1 - R_2)^2 \tag{21c}$$

...

$$H_{k+1} = \Delta E_k + \frac{P^2}{2M} + \frac{1}{2}M\Omega_1^2 (R - R_1 - R_2 - \dots - R_{k-1} - R_k)^2. \tag{21d}$$

In what follows we construct the unitary displacement operators as $D(\xi_1), D(\xi_2), \dots D(\xi_k)$ with $\xi_1 = R_1, \xi_2 = R_2 - R_1, \xi_k = R_k - R_{k-1}$,

$$D(\xi_i)RD^\dagger(\xi_i) = R - R_i + R_{i-1} \tag{22}$$

where $D(\xi_i) = e^{-\frac{i}{\hbar}\xi_i P}$.

To obtain the Franck–Condon factor for a k -photon transition one needs to calculate the quantity $|\langle u_\nu^k | u_\mu^1 \rangle|^2$. The final state can be obtained as

$$|u_\nu^k\rangle = D(\xi_k)D(\xi_{k-1}) \dots D(\xi_2)D(\xi_1)|u_\nu^1\rangle. \tag{23}$$

By using the relation [7] $d(\xi, m, n) = \langle u_\nu^m | D(\xi) | u_\nu^n \rangle = e^{-\frac{|\xi|^2}{2}} \left(\frac{n!}{m!}\right)^{\frac{1}{2}} \xi^{m-n} L_n^{m-n}(|\xi|^2)$ we find

$$D(\xi_k)D(\xi_{k-1}) \dots D(\xi_1)|u_\nu^1\rangle = \sum_{m_k=0}^{\infty} \sum_{m_{k-1}=0}^{\infty} \dots \sum_{m_2=0}^{\infty} \sum_{m_1=0}^{\infty} d(\xi_k, m_k, m_{k-1}) \tag{24}$$

$$d(\xi_{k-1}, m_{k-1}, m_{k-2}) \dots d(\xi_2, m_2, m_1)d(\xi_1, m_1, n)|u_{m_k}^1\rangle.$$

Now using the summation relation as given in equation (1) in the above equation one can find

$$\langle u_m^k | u_n^1 \rangle = \exp \left[\sum_{i=1}^k \xi_i^2 - \left(\sum_{i=1}^k \xi_i \right)^2 \right] \left(\sum_{i=1}^k \xi_i \right)^{m-n} L_n^{m-n} \left[\left(\sum_{i=1}^k \xi_i \right)^2 \right] \tag{25}$$

from which the Franck–Condon factor, F can be calculated.

For example, for a three-state system with the two-photon transition, F can be given by

$$F = |\exp[-2R_1 R_2](R_1 + R_2)^{m-n} L_n^{m-n} [(R_1 + R_2)^2]|^2. \tag{26}$$

Thus the independent displacements from the successive adiabatic curves characterize the factor F in a nontrivial way and can be found explicitly from the experimental measurement of the factor F .

In conclusion, in this letter we have proposed the generating function for the product of the Laguerre polynomials and discussed its application to calculate the Franck–Condon factor for multiphoton transition of a model displaced harmonic oscillator system. In this context, we have given a slightly generalized form of the Laguerre polynomial. We hope that the relation will be more applicable elsewhere.

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