LETTER TO THE EDITOR

An operator approach to the construction of generating functions for the product of Laguerre polynomials: the thermal average bandshape function of a molecule

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Abstract. We introduce two different forms of mathematical identities, involving the product of Laguerre polynomials. These identities are a direct reflection of an operator identity. It is shown that these relations are useful in calculating the thermal average bandshape function of a molecular system. For a model displaced-oscillator system we derive how the displacement between two adiabatic potential surfaces affects the bandshape function.

In this work we present an operator approach to construct some new identities involving the product of Laguerre polynomials. The derivation came from a physical argument for the multiphoton transition between different adiabatic electronic states (see, for example, [1]) of a molecule. The adaiabatic potentials are treated as harmonic oscillators but they may be displaced and the frequency parameters can also change. In our recent work we calculated an exact expression for the Franck–Condon factor for multiphoton processes in a molecule [2]. In this letter we generalize our approach to work on a quantum open system by introducing some identities of nonunitary operators and thereby construct new mathematical identities involving Laguerre polynomials.

Recently, femtosecond time-resolved spectroscopy [3] has become very popular in elucidating the fast dynamics of molecular vibration and rotation. In this letter we have calculated a useful quantity, i.e. the thermal average bandshape function of a molecule. The molecule is modelled by Born–Oppenheimer adiabatic potential surfaces of electronic states [4]. We consider that the potential surfaces are displaced harmonic oscillators. For example, in a time-resolved absorption experiment, we assume the system is in the vibronic manifold $\{a, v\}$ in thermal equilibrium and a short-pulse laser excites the system to a vibronic manifold $\{b, u\}$. Our aim here is to calculate the thermal average bandshape function. For short-time approximation the expression we have derived is amenable to classical interpretation of the bandshape function, as is usually done in the coherent state description [5, 6] of a quantum system.

In what follows we present the operator identities and their relation with the generating functions of the product of the Laguerre polynomials. First, we introduce a nonunitary displacement operator where the number of parameters is doubled with respect to the coherent state displacement operator [6] of a harmonic oscillator. Say,

$$\mathcal{D} = \mathrm{e}^{Xa^{\dagger}-Ya} \tag{1}$$

where $[a, a^\dagger] = 1$, corresponds to boson algebra with $X, Y \in \mathbb{C}$. Thus, one can obtain

$$\langle m|\mathcal{D}|n\rangle = e^{-\frac{XY}{2}} X^{m-n} \left(\frac{n!}{m!}\right)^{\frac{1}{2}} L_n^{m-n}(XY) \tag{2}$$

where $L_m^k(x)$ denotes the Laguerre polynomial [7] and m and n are positive integers including zero.

Using Glauber's identity [8] one can show that

$$\prod_{i=1}^p e^{x_i a^\dagger - y_i a} = e^{Xa^\dagger - Ya} e^{Z/2} \tag{3}$$

where

$$X = \sum_{i=1}^p x_i \tag{4}$$

$$Y = \sum_{i=1}^p y_i \tag{5}$$

$$Z = \sum_{i,j=1; i<j}^p (x_i y_j - x_j y_i) \tag{6}$$

where $x_i, y_i \in \mathbb{C}$.

Taking the (m, n) matrix element in both sides of equation (3) and assuming that x_i and y_i are real variables and with $y_i = x_i$ for all i, one can prove the following:

$$\sum_{m_{p-1}=0}^\infty \cdots \sum_{m_2=0}^\infty \sum_{m_1=0}^\infty (x_p)^m (x_1)^{-n} \left(\frac{x_{p-1}}{x_p}\right)^{m_{p-1}} \left(\frac{x_{p-2}}{x_{p-1}}\right)^{m_{p-2}} \cdots \left(\frac{x_2}{x_3}\right)^{m_2} \left(\frac{x_1}{x_2}\right)^{m_1}$$

$$\times L_{m_{p-1}}^{m-m_{p-1}}(x_p^2) L_{m_{p-2}}^{m_{p-1}-m_{p-2}}(x_{p-1}^2) \dots L_{m_1}^{m_2-m_1}(x_2^2) L_n^{m_1-n}(x_1^2)$$

$$= \exp\left[\frac{\sum_{i=1}^p x_i^2 - (\sum_{i=1}^p x_i)^2}{2}\right] \left(\sum_{i=1}^p x_i\right)^{m-n} L_n^{m-n}\left[\left(\sum_{i=1}^p x_i\right)^2\right] \tag{7}$$

where p can be any integer where $p - 1$ dictates the number of the summation. m and n are two non-negative integers. This is reported in [2].

Now we define a nonunitary generalized displacement operator

$$\mathcal{D}(z, \alpha, \beta) = z^{a^\dagger a} e^{\alpha a^\dagger - \beta a} \tag{8}$$

where $z, \alpha, \beta \in \mathbb{C}$.

We construct the product operator

$$\mathcal{P} = \prod_{i=1}^p \mathcal{D}_i(z_i, \alpha_i, \beta_i). \tag{9}$$

Making a transformation

$$\mathcal{D}'_{n+1} = e^{-\sum_{i=1}^n u_i a^\dagger a} \mathcal{D}_{n+1} e^{\sum_{i=1}^n u_i a^\dagger a} \tag{10}$$

which means

$$\mathcal{D}'_{n+1} = e^{\alpha_n (\prod_{i=1}^n z_i^{-1}) a^\dagger - \beta_n (\prod_{i=1}^n z_i) a} \tag{11}$$

where $u_i = \ln(z_i)$. Thus, one can write $\mathcal{P}$ as

$$\mathcal{P} = \left(\prod_{i=1}^p z_i\right)^{a^\dagger a} \prod_{n=1}^{p-1} \mathcal{D}'_{n+1} \mathcal{D}_1. \tag{12}$$

This can be simplified to

$$\mathcal{P} = \left(\prod_{i=1}^{p} z_i\right)^{a^\dagger a} \prod_{i=1}^{p} e^{\gamma_i a^\dagger - \delta_i a} \tag{13}$$

where $\gamma_i = \alpha_i \prod_{j=i+1}^{p} z_j^{-1}$ and $\delta_i = \beta_i \prod_{j=i+1}^{p} z_j$.

Therefore, we construct the operator identity

$$\prod_{i=1}^{p} z_i^{a^\dagger a} e^{\alpha_i a^\dagger - \beta_i a} = \exp[-\tfrac{1}{2}(\mathcal{X}\mathcal{Y} - \mathcal{Z})]\left(\prod_{i=1}^{p} z_i\right)^{a^\dagger a} e^{\mathcal{X} a^\dagger} e^{-\mathcal{Y} a} \tag{14}$$

where $\mathcal{X} = \sum_{i=1}^{p} \gamma_i$ and $\mathcal{Y} = \sum_{i=1}^{p} \delta_i$. Here we have also defined

$$A_i = \frac{z_i \alpha_i}{\alpha_{i-1}} \tag{15}$$

where $i = 1$ and p are cyclic boundary values, i.e. when $i = 1, i - 1 = p$. Using the definition A_i, $\mathcal{X}$ and $\mathcal{Y}$ one can write

$$\mathcal{X}\mathcal{Y} = \sum_{j=1}^{p} \alpha_j \beta_j + \sum_{l=1}^{p-1} \frac{\alpha_{l+1}\beta_{l+1}}{\prod_{j=1}^{l+1} A_j} \sum_{i=1}^{l} \prod_{k=1}^{i} A_k + \sum_{l=1}^{p-1} \frac{\alpha_l \beta_l}{\prod_{j=1}^{l} A_j} \sum_{i=l+1}^{p} \prod_{k=1}^{i} A_k \tag{16}$$

and

$$\mathcal{Z} = \sum_{l=1}^{p-1} \frac{\alpha_{l+1}\beta_{l+1}}{\prod_{j=1}^{l+1} A_j} \sum_{i=1}^{l} \prod_{k=1}^{i} A_k - \sum_{l=1}^{p-1} \frac{\alpha_l \beta_l}{\prod_{j=1}^{l} A_j} \sum_{i=l+1}^{p} \prod_{k=1}^{i} A_k. \tag{17}$$

Now, the first class of identities can be constructed by taking the matrix element of both sides of equation (14) in a particular basis. If we choose the occupation number basis $\{|n\rangle\}$, then one obtains

$$\sum_{k_1=0}^{\infty} \cdots \sum_{k_2=0}^{\infty} \sum_{k_{p-1}=0}^{\infty} A_1^m A_2^{k_1} A_3^{k_2} \ldots A_p^{k_{p-1}}$$

$$\times L_{k_1}^{m-k_1}(\alpha_1\beta_1) L_{k_2}^{k_1-k_2}(\alpha_2\beta_2) \ldots L_{k_{p-1}}^{k_{p-2}-k_{p-1}}(\alpha_{p-1}\beta_{p-1}) L_n^{k_{p-1}-n}(\alpha_p\beta_p)$$

$$= \left(\prod_{i=1}^{p} A_i\right)^n \left(\sum_{i=1}^{p} \prod_{k=1}^{i} A_k\right)^{m-n} \exp\left[-\sum_{l=1}^{p-1} \frac{\alpha_l \beta_l}{\prod_{j=1}^{l} A_j} \sum_{i=l+1}^{p} \prod_{k=1}^{i} A_k\right]$$

$$\times L_n^{m-n}\left[\sum_{j=1}^{p} \alpha_j \beta_j + \sum_{l=1}^{p-1} \frac{\alpha_{l+1}\beta_{l+1}}{\prod_{j=1}^{l+1} A_j} \sum_{i=1}^{l} \prod_{k=1}^{i} A_k + \sum_{l=1}^{p-1} \frac{\alpha_l \beta_l}{\prod_{j=1}^{l} A_j} \sum_{i=l+1}^{p} \prod_{k=1}^{i} A_k\right]. \tag{18}$$

Using the transformation in equation (15) one can write the following equivalent relation:

$$\sum_{k_1=0}^{\infty} \cdots \sum_{k_2=0}^{\infty} \sum_{k_{p-1}=0}^{\infty} A_2^{k_1} A_3^{k_2} \ldots A_p^{k_{p-1}} L_{k_1}^{m-k_1}(\chi_1) L_{k_2}^{k_1-k_2}(\chi_2) \ldots L_{k_{p-1}}^{k_{p-2}-k_{p-1}}(\chi_{p-1}) L_n^{k_{p-1}-n}(\chi_p)$$

$$= \frac{\mathcal{A}_p^n}{\mathcal{A}_1^m} \left(\sum_{i=1}^{p} \mathcal{A}_i\right)^{m-n} \exp\left[-\sum_{l=1}^{p-1} \frac{\chi_l}{\mathcal{A}_l} \sum_{i=l+1}^{p} \mathcal{A}_i\right]$$

$$\times L_n^{m-n}\left[\sum_{j=1}^{p} \chi_j + \sum_{l=1}^{p-1} \frac{\chi_{l+1}}{\mathcal{A}_{l+1}} \sum_{i=1}^{l} \mathcal{A}_i + \sum_{l=1}^{p-1} \frac{\chi_l}{\mathcal{A}_l} \sum_{i=l+1}^{p} \mathcal{A}_i\right] \tag{19}$$

where $\mathcal{A}_j = \prod_{i=1}^{j} A_i$ and χ_i are symbolized for $\alpha_i \beta_i$. In the last relation $\mathcal{A}_i$ and χ_i are independent and, in general, complex. Some special cases are worthy of presentation:

(i) for $p = 2$,

$$\sum_{k_1=0}^{\infty} A_2^{k_1} L_{k_1}^{m-k_1}(\chi_1) L_n^{k_1-n}(\chi_2) = A_2^m \left(\frac{1+A_2}{A_2}\right)^{m-n} e^{-\chi_1 A_2} L_n^{m-n}\left[\chi_1 + \chi_2 + \chi_1 A_2 + \frac{\chi_2}{A_2}\right]$$

(20a)

(ii) for $p = 3$,

$$\sum_{k_1=0}^{\infty}\sum_{k_2=0}^{\infty} A_2^{k_1} A_3^{k_2} L_{k_1}^{m-k_1}(\chi_1) L_{k_2}^{k_1-k_2}(\chi_2) L_n^{k_2-n}(\chi_3)$$

$$= (A_2 A_3)^m \left(\frac{1+A_2+A_2 A_3}{A_2 A_3}\right)^{m-n} e^{-(\chi_1(A_2+A_2 A_3)+\chi_2 A_3)}$$

$$\times L_n^{m-n}\left[(\chi_1 + \chi_2 + \chi_3) + \chi_1(A_2 + A_2 A_3) + \chi_2 A_3 + \left(\frac{\chi_2}{A_2} + \chi_3 \frac{1+A_2}{A_2 A_3}\right)\right].$$

(20b)

Another class of identities is obtained if we take the trace of equation (14). In this case, by using the following standard relation of the generating function of Laguerre polynomials [7]:

$$\sum_{n=0}^{\infty} z^n L_n(x) = \frac{1}{1-z} \exp\left[-\frac{xz}{1-z}\right]$$

(21)

the trace of the right-hand side (rhs) of equation (14) becomes

$$\text{rhs} = e^{-\frac{(\mathcal{X}\mathcal{Y}-\mathcal{Z})}{2}} \frac{1}{1-\prod_{i=1}^{p} A_i} \exp\left[-\frac{\prod_{i=1}^{p} A_i \mathcal{X}\mathcal{Y}}{1-\prod_{i=1}^{p} A_i}\right].$$

(22)

Thus, we arrive at

$$\sum_{m=0}^{\infty}\sum_{k_1=0}^{\infty}\cdots\sum_{k_{p-1}=0}^{\infty} A_1^m A_2^{k_1} \ldots A_{p-1}^{k_{p-2}} A_p^{k_{p-1}} L_{k_1}^{m-k_1}(\chi_1) L_{k_2}^{k_1-k_2}(\chi_2) \ldots L_{k_{p-1}}^{k_{p-2}-k_{p-1}}(\chi_{p-1}) L_m^{k_{p-1}-m}(\chi_p)$$

$$= \frac{1}{1-\mathcal{A}_p} \exp\left[-\frac{\mathcal{A}_p}{1-\mathcal{A}_p}\left\{\sum_{i=1}^{p}\chi_i + \sum_{l=1}^{p-1}\frac{\chi_{l+1}}{\mathcal{A}_{l+1}}\sum_{i=1}^{l}\mathcal{A}_i + \frac{1}{\mathcal{A}_p}\sum_{l=1}^{p-1}\frac{\chi_l}{\mathcal{A}_l}\sum_{i=l+1}^{p}\mathcal{A}_i\right\}\right].$$

(23)

Here A_i and χ_i are independent complex numbers. The convergence can be shown to be guaranteed if $|A_i| < 1$ for all i. Some special cases are given by:

(i) for $p = 2$,

$$\sum_{m=0}^{\infty}\sum_{k_1=0}^{\infty} A_1^m A_2^{k_1} L_{k_1}^{m-k_1}(\chi_1) L_m^{k_1-m}(\chi_2)$$

$$= \frac{1}{1-A_1 A_2} \exp\left[-\frac{(\chi_1+\chi_2)A_1 A_2 + \chi_2 A_1 + \chi_1 A_2}{1-A_1 A_2}\right]$$

(24a)

(ii) for $p = 3$,

$$\sum_{m=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{k_2=0}^{\infty} A_1^m A_2^{k_1} A_3^{k_2} L_{k_1}^{m-k_1}(\chi_1) L_{k_2}^{k_1-k_2}(\chi_2) L_m^{k_2-m}(\chi_3)$$

$$= \frac{1}{1-A_1 A_2 A_3} \exp\{-[(\chi_1 + \chi_2 + \chi_3)A_1 A_2 A_3$$

$$+(\chi_1 A_2 A_3 + \chi_2 A_3 A_1 + \chi_3 A_1 A_2) + (\chi_1 A_2 + \chi_2 A_3 + \chi_3 A_1)]$$

$$\times[1 - A_1 A_2 A_3]^{-1}\}.$$

(24b)

Thus, equations (19) and (23) are the central result of this part of the work. The result reported in (9) can be shown as the special cases of equations (24a) and (24b) where χ_i is real and $\chi_i = \chi_j$ for all i and j. When χ_i is, in general, complex it can be shown to be useful in the construction of the quantum theory of dissipation which will be shown elsewhere.

Next we calculate the thermal average bandshape function for the ultrashort laser absorption of a molecule. For femtosecond time-resolved absortion spectroscopy [3], we consider the Born–Oppenheimer adiabatic approximation. The wavefunction of the molecule Ψ_{av} can be written as a product of the electronic wavefunction ϕ_a and the nuclear wavefunction θ_{av}, i.e.,

$$\Psi_{av} = \phi_a \theta_{av}. \tag{25}$$

In a pump–probe absorption measurement, we assume the pump laser excites the system to the vibronic manifold av and the probing laser excites the system from the vibronic manifold $\{av\}$ to the $\{bu\}$ vibronic manifold.

For a randomly oriented system the absorption part of the susceptibility, using linear response theory, can be expressed as

$$Q = \frac{2\pi}{3\hbar} \omega |E(\omega)|^2 |\mu_{ab}|^2 \sum_{v=0}^{\infty} (\hat{\rho}_e)_{av,av} \alpha_{av,av}(\omega) \tag{26}$$

where $(\hat{\rho}_e)$ represents the Boltzmann distribution. $E(\omega)$ is the applied laser field, μ_{ab} is the electronic-transition dipole moment and

$$\alpha_{av,av} = \frac{1}{2\pi} \sum_u |\langle\theta_{av}|\theta_{bu}\rangle|^2 [J(\omega + \omega'_{av,bu}) + J(-\omega + \omega'_{av,bu})]. \tag{27}$$

Here $J(\omega)$ corresponds to the Lorentzian lineshapes for the transition from one vibrational state to another. If the broadening from sources other than the probing laser pulse width (T_l) is dominant, which is also true for a very short pulse laser, then

$$\alpha_{av,av} = \frac{1}{\pi} \sum_u |\langle\theta_{av}|\theta_{bu}\rangle|^2 \frac{\frac{2}{T_l}}{(\frac{2}{T_l})^2 + (\omega - \omega_{bu,av})^2} \tag{28}$$

where $|\langle\theta_{av}|\theta_{bu}\rangle|^2$ represents the Franck–Condon factor and the lineshape function takes the Lorentzian form.

However, the above situation is not valid when the lower electronic state is not in thermal equilibrium and in that case conventional linear response theory is not applicable. But this is the simplest possible situation where one can find a tangible analytical result.

Now, the quantity of interest is the thermal average bandshape function $\alpha_{a\to b}(\omega)$:

$$\alpha_{a\to b}(\omega) = \sum_{v=0}^{\infty} P_{av} \alpha_{av,av} \tag{29}$$

where

$$P_{av} = \frac{e^{-\frac{v\hbar\omega_0}{kT}}}{1 - e^{\frac{\hbar\omega_0}{kT}}} \tag{30}$$

with the adiabatic potential surface of the electronic state a is harmonic. Thus $\alpha_{a\to b}(\omega)$ can be written as

$$\alpha_{a\to b}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \sum_u \sum_v e^{it(\omega - \omega_{bu,av})} e^{-\frac{2}{T_l}|t|} P_{av} \langle\theta_{av}|\theta_{bu}\rangle \langle\theta_{bu}|\theta_{av}\rangle. \tag{31}$$

For a single-mode displaced-oscillator model the Hamiltonians for the electronic states a and b are given as

$$H_a = \frac{P^2}{2M} + \frac{1}{2}M\omega_0^2 R^2 \tag{32a}$$

$$H_b = (E_b - E_a) + \frac{P^2}{2M} + \frac{1}{2}M\omega_0^2(R - R_0)^2. \tag{32b}$$

Here R_0 is the displacement of state b from a.

One can show that

$$D(R_0)RD^\dagger(R_0) = R - R_0 \tag{33}$$

where

$$D(R_0) = e^{-\frac{i}{\hbar}R_0 P}. \tag{34}$$

Therefore, it is easy to convince oneself that

$$|\theta_{bv}\rangle = D(R_0)|\theta_{av}\rangle \tag{35}$$

and

$$\langle \theta_{bu}|\theta_{av}\rangle = \langle \theta_{au}|D^\dagger(R_0)|\theta_{av}\rangle = e^{-\frac{x^2}{2}}\left(\frac{v!}{u!}\right)^{\frac{1}{2}} x^{u-v}L_v^{u-v}(x^2) \tag{36}$$

where

$$x = \sqrt{\left(\frac{M\omega_0}{2\hbar}\right)}R_0. \tag{37}$$

Thus, one arrives at

$$\alpha_{a\to b}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{it(\omega - \frac{E_b - E_a}{\hbar})}e^{-\frac{2}{T_l}|t|}$$
$$\times e^{-x^2}\sum_{u=0}^{\infty}\sum_{v=0}^{\infty}(-1)^{v-u}e^{(v-u)it\omega_0}\frac{e^{-\frac{v\hbar\omega_0}{kT}}}{(1 - e^{-\frac{\hbar\omega_0}{kT}})^{-1}}L_v^{u-v}(x^2)L_u^{v-u}(x^2). \tag{38}$$

Using equation (24a) this can be rewritten as

$$\alpha_{a\to b}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{it(\omega - \omega_e) - \frac{2}{T_l}|t|}\exp\left[-x^2\frac{1 + e^{-\frac{\hbar\omega_0}{kT}} - (e^{it\omega_0 - \frac{\hbar\omega_0}{kT}} + e^{-it\omega_0})}{(1 - e^{-\frac{\hbar\omega_0}{kT}})}\right] \tag{39}$$

where $\omega_c = (E_b - E_a)/\hbar$.

Finally, one obtains

$$\alpha_{a\to b}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{it(\omega - \omega_e) - \frac{2}{T_l}|t|}e^{-ix^2\sin(t\omega_0)}\exp\left[-2x^2\sin^2\left(\frac{t\omega_0}{2}\right)\coth\left(\frac{\hbar\omega_0}{2kT}\right)\right]. \tag{40}$$

Thus, when the excited electronic state b is coupled with the state a which is in thermal equilibrium, an additional time-dependent damping term appears along with a time-dependent frequency shift term. The frequency shift term is temperature independent. From the above expression one should be able to derive the temperature-dependent bandshape function.

For a dense medium the effect of laser linewidth is very small compared with the above damping effect. If we neglect this term and calculate the integral with the steepest descent method we will be able to obtain an expression of the bandshape function which is amenable to classical interpretation.

To calculate the time integral we assume the short-time approximation

$$\sin(t\omega_0) = t\omega_0. \tag{41}$$

If

$$f_{ab}(t) = \mathrm{i}t\,(\omega - \omega_e) - \mathrm{i}x^2\omega_0 t - x^2\omega_0^2\frac{t^2}{2}C \tag{42}$$

where

$$C = \coth\left(\frac{\hbar\omega_0}{2kT}\right) \tag{43}$$

therefore,

$$f'_{ab}(t) = \mathrm{i}(\omega - \omega_e) - \mathrm{i}x^2\omega_0 - x^2\omega_0^2 tC \tag{44}$$

and

$$f''_{ab}(t) = -x^2\omega_0^2 C. \tag{45}$$

Now, for $f'_{ab}(t^*) = 0$ one obtains

$$t^* = \frac{\mathrm{i}(\omega - \omega_e) - \mathrm{i}x^2\omega_0}{x^2\omega_0^2 C} \tag{46}$$

and writing

$$f_{ab}(t) = f_{ab}(t^*) + \tfrac{1}{2}f''_{ab}(t^*)(t - t^*)^2 \tag{47}$$

one obtains

$$f_{ab}(t^*) = \frac{\{\mathrm{i}(\omega - \omega_e) - \mathrm{i}x^2\omega_0\}^2}{2x^2\omega_0^2 C}. \tag{48}$$

Thus, the bandshape can be written as

$$\alpha_{a\to b} = \frac{\exp[f_{ab}(t^*)]}{[-2\pi f''_{ab}(t^*)]^{\frac{1}{2}}}. \tag{49}$$

Inserting the values of x and C the final expression can be obtained as

$$\alpha_{a\to b} = \frac{1}{[\pi\frac{M\omega_0^3}{\hbar}R_0^2\coth(\frac{\hbar\omega_0}{2kT})]^{\frac{1}{2}}}\exp\left[-\frac{[(\omega - \omega_e) - \frac{M\omega_0^2}{2\hbar}R_0^2]^2}{\frac{M\omega_0^3}{\hbar}R_0^2\coth(\frac{\hbar\omega_0}{2kT})}\right] \tag{50}$$

which means that in this case the bandshape is Gaussian. The finite-temperature effect can be easily obtained from the above expression. The dependence of the displacement of the excited potential surface from the ground state simply comes as displaced wavefunction like. The displacement not only shifts the absorption band but also affects the width and intensity of the bandshape function.

The generating functions developed in this work are shown to be useful in physical and chemical problems involving displaced oscillators. Through the process we have introduced some interesting relations of the nonunitary generalized displacement operators which can be used to describe equilibrium and nonequilibrium quantum open systems. Here a thermal equilibrium property of a quantum system, namely a model molecular system, is investigated. An exact quantum dissipation theory can be constructed by using these generating functions which will be reported elsewhere.

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