Franck-Condon Factors for Harmonic Oscillators –
An Operator Approach

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We give an explicit derivation of the Franck-Condon factors for harmonic oscillators in the general case where both the origin and the frequencies are changed for one and two dimensions, using operator manipulations in our two-step method. We also discuss the case with rotated coordinates in the excited states of two dimensional transitions. The method is straightforward and can be easily generalized to higher dimensions.

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I. INTRODUCTION

The calculations of Franck-Condon factors have been important in the analysis of electronic transition amplitudes of different molecules [1]. The problem is complicated by the fact that both the equilibrium internuclear distances and the harmonic vibration frequencies in the two electronic states between which the transitions occur are commonly different. Further complications arise from the anharmonic terms of the potential functions and from the distortion of the molecules in the excited states. All these complications make systematic and reliable analysis of the experimental results rather difficult.

Recently we have proposed a two-step method to solve the anharmonic oscillators [2,3]. The method is heavily influenced by the coupled-cluster method (CCM) of many-body problems [4]. In the first step a generalized coherent states ansatz of SUB-2 approximation in the language of CCM is introduced. The variational principle is then applied and the problem is solved via a Bogoliubov transformation. In the present case this is shown to be equivalent to an optimized Gaussian with shifted origin and modified frequency. Correlation corrections are then added in the second step by standard perturbations or by directly diagonalizing the transformed Hamiltonian. The method is simple, straightforward,
and has a clear physical picture. It has been successfully applied to the $\phi^4$ quantum field theory [5], coupled oscillators [6] and the calculation of Franck-Condon factors for the Morse potentials [7].

As a first step in the systematic approach to calculate the Franck-Condon factors, we apply in this paper the two-step method to derive the expressions of the Franck-Condon factors for harmonic oscillators in the general case of shifted origins and frequencies using operator manipulations. In Sec. II we review the geometric meaning of the SUB-1 and SUB-2 approximation in the CCM language for harmonic oscillators. In Sec. III we give the derivation of the Franck-Condon factors in the one-dimensional case for harmonic oscillators with shifted origin and frequency. In Sec. IV we generalize the results to two dimensions. Further generalization to the case with rotated coordinates is also included in this section. The conclusion and discussion are given in the final section.

II. GEOMETRIC MEANING OF THE SUB-1 AND SUB-2 APPROXIMATIONS

We start with the Hamiltonian for the one dimensional harmonic oscillator.

$$H = \frac{1}{2} p^2 + \frac{1}{2} q^2.$$  \hspace{1cm} (2.1)

To simplify the notation, we adopt the unit such that $\hbar = m = \omega = 1$, where $m$ and $\omega$ are the mass and the frequency respectively. The Hamiltonian (2.1) can be solved easily by introducing the creation and the annihilation operators:

$$q = \frac{1}{\sqrt{2}} (a + a^+)$$ \hspace{1cm} (2.2a)

$$p = \frac{1}{i} \frac{\partial}{\partial q} = \frac{i}{\sqrt{2}} (a^+ - a).$$ \hspace{1cm} (2.2b)

The creation and the annihilation operators $a^+$ and $a$ satisfy the commutation relation

$$[a, a^+] = 1.$$ \hspace{1cm} (2.3)

The Hamiltonian (2.1) may be written in the second-quantized form as

$$H = a^+ a + \frac{1}{2}.$$ \hspace{1cm} (2.4)

The ground state $|0\rangle$ of the Hamiltonian (2.4) satisfies the relation

$$a |0\rangle = 0.$$ \hspace{1cm} (2.5)

The general eigenvectors of the Hamiltonian (2.4) are given by
\[ |n \rangle = \frac{(a^+)^n}{\sqrt{n!}} |0 \rangle \]  

with corresponding eigenvalues
\[ E_n = n + \frac{1}{2}. \]  

We may also approach the problem in the following way. We first solve for the creation and the annihilation operator \( a \) and \( a^+ \) from (2.2)
\[ a = \frac{1}{\sqrt{2}} (q + ip) = \frac{1}{\sqrt{2}} \left( q \frac{\partial}{\partial q} \right) \]  
\[ a^+ = \frac{1}{\sqrt{2}} (q - ip) = \frac{1}{\sqrt{2}} \left( q \frac{\partial}{\partial q} \right). \]  

The equation for the ground state \( |0\rangle \), Eq. (2.5), may be written as
\[ \left( q + \frac{\partial}{\partial q} \right) |0\rangle = 0. \]  
The normalized solution of the differential equation (2.9) is given by
\[ |0\rangle = \frac{1}{(\pi)^{1/4}} e^{-\frac{1}{2} q^2}, \]  
and the eigenvectors \( |n\rangle \) for the excited states are given by
\[ |n\rangle = \frac{(a^+)^n}{\sqrt{n!}} |0\rangle, \]  
which may also be put in the form
\[ |n\rangle = \frac{1}{(\pi)^{1/4}} \frac{1}{\sqrt{n!}} \left( \frac{1}{\sqrt{2}} \right)^n \left( q - \frac{\partial}{\partial q} \right)^n e^{-\frac{1}{2} q^2} = \frac{1}{(\pi)^{1/4}} \frac{1}{\sqrt{n!}} \left( \frac{1}{\sqrt{2}} \right)^n H_n(q) e^{-\frac{1}{2} q^2}, \]  
where \( H_n(q) \) is the Hermite polynomial of degree \( n \).
To improve the wave function, it is possible to expressed a modified wave function in the form
\[ e^{\sum_n \alpha_n (a^+)^n} |0\rangle. \]  
In the SUB-1 approximation we truncate the above sum with only \( n = 1 \) and study the coherent-state wave function of the form
\[ |0\rangle, = N e^{(a^+)} |0\rangle, \]
where
\[ N = e^{-\frac{t^2}{2}}, \]  
(2.13)
is the normalization factor. Using the operator identity
\[ e^{(A+B)} = e^A e^B e^{-\frac{1}{2} [A, B]}, \]
which holds when the commutator \([A, B]\) commutes with both operators \(A\) and \(B\), we rewrite the coherent state (2.12) in the following form:
\[ |0\rangle_t = N e^{(t*^+)} e^{-t^*} |0\rangle = e^{t^* - t} |0\rangle \]
(2.14)
An expansion of (2.14) in powers of \(t\) shows that the coherent state \(|0\rangle_t\) is equivalent to a Taylor series expansion of a ground state of the form (2.10) with shifted origin:
\[ |0\rangle_t = \sum_n \frac{(-\sqrt{2} t)^n}{n!} \left( \frac{\partial}{\partial \varphi} \right)^n \frac{1}{(\pi)^{\frac{1}{2}}} e^{-\frac{\varphi^2}{2}} \]
(2.15)
This result is also obtained from a different point of view. From (2.12), it is readily shown that the coherent state \(|0\rangle_t\) is an eigenfunction of the annihilation operator:
\[ \hat{a}|0\rangle_t = t|0\rangle_t. \]
(2.16)
In other words, it is annihilated by a new operator \(\hat{a}\)
\[ \hat{a}|0\rangle_t = 0, \]
(2.17)
where the operator \(\hat{a}\) is defined by
\[ \hat{a} = a - t. \]
(2.18)
We now introduce the corresponding new creation operator \(\hat{a}^+\) by:
\[ \hat{a}^+ = a^+ + t. \]
(2.19)
It is obvious that the pair of operators \((\hat{a}, \hat{a}^+)\) satisfies the same commutator relation as that of the standard creation and annihilation operators:
\[ [\hat{a}, \hat{a}^+] = 1. \]
(2.20)
A whole series of eigenfunctions may be similarly generated by:
Together they form a complete orthonormal basis set in the Hilbert space. Using Eqs. (2.2a) and (2.2b), we note that

\[
q = \frac{1}{\sqrt{2}} (\hat{a} + \hat{a}^+ + \sqrt{2} t)
\]

(2.22a)

\[
p = \frac{1}{\sqrt{2}} (\hat{a}^+ - \hat{a})
\]

(2.22b)

Equations (2.22) demonstrate again that the SUB-1 approximation \( |0\rangle_i = e^{(\hat{a}^+)^{2}} |0\rangle \) is equivalent to a shift of the origin of the ground state.

We now discuss the SUB-2 approximation in the CCM language where we include only the term \( n = 2 \). We consider a generalized coherent state of the form

\[
|0_k\rangle = B e^{\frac{(\hat{a}^+)^{2}}{2}} |0\rangle,
\]

(2.23)

where \( B \) is a normalization constant. Expanding (2.23) in a power series of \( s \) yields for the normalization condition the relation

\[
1 = B^2 \sum_{n=0}^{\infty} \frac{(2n)!}{(n!)^2} \left( \frac{s}{2} \right)^{2n} \frac{B^2}{\sqrt{1 - s^2}},
\]

(2.24)

or

\[
B = (1 - s^2)^{1/4}.
\]

(2.25)

A simple calculation shows that the generalized coherent state \( |0_k\rangle \) in (2.23) satisfies the following relation

\[
a |0_k\rangle = s a^+ |0_k\rangle.
\]

(2.26)

Following Ref. [2], we introduce a pair of new operators \( b \) and \( b^+ \) by a Bogoliubov transformation

\[
b = \frac{a - sa^+}{\sqrt{1 - s^2}},
\]

(2.27a)

\[
b^+ = \frac{a^+ - sa}{\sqrt{1 - s^2}}.
\]

(2.27b)

From (2.26), we see that the generalized coherent state \( |0_k\rangle \) is annihilated by the operator \( b \),

\[
b |0_k\rangle = 0.
\]

(2.28)
Furthermore, it is easy to show that the pair of operators $b^+$ and $b$ satisfy the same commutator relation for the original creation and the annihilation operators:

$$[b, b^+] = 1. \quad (2.29)$$

Thus the pair of operators $b^+$ and $b$ may be considered as a new set of creation and annihilation operators with the ground state given by the generalized coherent state $|0_s\rangle$.

This fact may be further understood from the following consideration. Inserting (2.8) into (2.27a) we have

$$b = \frac{1}{\sqrt{1 - s^2}} \left\{ \frac{1}{\sqrt{2}} \left( q + \frac{\partial}{\partial q} \right) - s \frac{\sqrt{2}}{2} \left( q - \frac{\partial}{\partial q} \right) \right\}$$

$$= \frac{(1 + s)}{\sqrt{2(1 - s^2)}} \left( \frac{\partial}{\partial q} + \frac{1 - s}{1 + s} q \right). \quad (2.30)$$

Introducing the variable

$$\omega = \frac{1 - S}{1 + S}, \quad (2.31)$$

we may rewrite (2.28) as

$$\left( \frac{\partial}{\partial q} + \omega q \right) |0_s\rangle = 0. \quad (2.32)$$

The differential Eq. (2.32) yields the solution

$$|0_s\rangle = N e^{-\omega q^2/2}, \quad (2.33)$$

with the normalization constant

$$N = \left( \frac{\omega}{\pi} \right)^{1/4}. \quad (2.34)$$

Eqs. (2.33) and (2.28) together show that the generalized coherent state $|0_s\rangle$ of (2.23) is the ground eigenstate of the harmonic oscillator with a modified frequency $\omega$. The corresponding excited states are

$$|n_s\rangle = \frac{b^{+n}}{\sqrt{n!}} |0_s\rangle = \frac{1}{\sqrt{\sqrt{\pi} / \omega \ 2^n n!}} H_n(\sqrt{\omega} q) e^{-\frac{1}{2} \omega q^2}. \quad (2.35)$$

Together they form a complete set of the eigenfunctions for the Hamiltonian $\hat{H}$ of harmonic oscillators with a modified frequency $\omega$:

$$\hat{H} = \frac{1}{2} \dot{q}^2 + \frac{1}{2} \omega^2 q^2. \quad (2.36)$$

The inverse Bogoliubov transformation may be obtained by solving (2.27a) and (2.27b). We have
Inserting (2.37a) and (2.37b) into (2.2a), we have

\[ a = b + sb^+ \]

\[ a^+ = \frac{b^+ + sb}{\sqrt{1 - s^2}}. \]  

(2.37a)  

(2.37b)

Similarly, we obtain

\[ q = \frac{1}{\sqrt{2}} \sqrt{1 + s} \frac{b + b^+}{1 - s}, \]

(2.38a)

\[ p = i \sqrt{\frac{\omega}{2}} (b^+ - b). \]  

(2.38b)

Eqs. (2.38a) and (2.38b) are precisely what we would have obtained by expanding in the second-quantized form of the Hamiltonian \( \hat{H} \) in (2.36) with frequency \( \omega \). Hence we have shown that the generalized coherent state (2.23) is a ground state of the harmonic oscillator with a modified frequency. To conclude this section we noted that a similar attempt for a SUB-3 coherent state of the form \( \exp(\sqrt{s^2})|0\rangle \) will no work because the norm will not be bounded. In this case one probably has to resort to the standard CCM method directly.

### III. DERIVATION OF THE FRANCK-CONDON FACTORS FOR THE HARMONIC OSCILLATORS IN THE ONE-DIMENSIONAL CASE

From the discussion in Sec. II, the overlap integral between the ground states of harmonic oscillators with shifted origin and modified frequency may be expressed as the scalar product between \( |0\rangle \) and \( |0\rangle \), where

\[ |0\rangle = (1 - s^2)^{1/4} e^{(1/2)ns^2 t^2} |0\rangle \]

is the ground state with a modified frequency \( \omega \) and

\[ |0\rangle = e^{1/2 s^2} e^{ns^2} |0\rangle \]

(3.1)

(3.2)

is the one with shifted origin. The value \( t \) is related to the difference of the origin \( \delta \) by the relation

\[ t = -\frac{\delta}{\sqrt{2} \omega} \]

(3.3)

and the ratio of the two frequencies is given by
Here $\omega, \bar{\omega}$ are the vibrational frequencies of the different electronic states of a molecule. The general overlap integrals $\int \langle n|\tilde{n}\rangle$ for the different vibrational states between the initial and the final electronic state of the transition is given by

$$\int \langle n|\tilde{n}\rangle = \int \langle 0| \frac{\tilde{a}^n}{\sqrt{n!}} |0\rangle,$$

(3.5)

where $\tilde{a} = a - t$ and $b^*$ is given by Eq. (2.27b). The calculation of (3.5) is best handled through the introduction of the generating function

$$F(x_1, x_2) = \int \langle 0| e^{x_1 \tilde{a}} e^{x_2 b^*} |0\rangle.$$

(3.6)

Expanding the above matrix element in powers of $x_1$ and $x_2$, we have

$$F(x_1, x_2) = \sum_n \sum_{\tilde{n}} \frac{x_1^n}{\sqrt{n!}} \frac{x_2^{\tilde{n}}}{\sqrt{\tilde{n}!}} \int \langle n|\tilde{n}\rangle.$$

(3.7)

The evaluation of (3.6) may be carried out in the following way. Substituting (3.1) and (3.2) in Eq. (3.6) we have

$$F(x_1, x_2) = e^{-\frac{t^2}{2}} e^{-\frac{s^2}{2}} \int \langle 0| e^{x_1 a + s} e^{x_2 b^*} e^{s a + 210} |0\rangle.$$

(3.8)

From (2.14) and (2.27b) we have

$$e^{x_2 b^*} = e^{-x_2} e^{x_2 s}.$$

(3.9)

Using (2.16), we obtain for the matrix element in (3.6) the following expression

$$\langle 0| e^{(t+s)x_1} e^{x_2 b^*} e^{s a + 210} |0\rangle.$$

(3.10)

Employing the same device again we finally arrive at the following result for the generating function

$$F(x_1, x_2) = (1 - s^2)^{\frac{1}{2}} e \left\{ \frac{1}{2} t^2 (1 - s) - \frac{1}{2} s x_2^2 + x_2 t \sqrt{1 - s^2} + \frac{1}{2} s x_1^2 + x_1 t (s - 1) + x_1 x_2 \sqrt{1 - s^2} \right\}.$$

(3.11)
Expanding (3.11) in power series of \( x_1^2 \) and \( x_2^2 \), we immediately obtain all the Franck-Condon factors through the expansion (3.7). This expansion may be easily handled by using algebraic manipulation with computers [8]. We point out here the connection of the generating function (3.11) to the usual formula used in the literature [9] which employs the Hermite polynomials. From the generating function of the Hermite polynomials:

\[
e^{2x^2} = \sum \frac{1}{n!} H_n(x)x^n,
\]

we have

\[
e^{-\frac{1}{2}x_1^2 + x_2^2 + \sqrt{x_1^2 - x_2^2}} = \sum \frac{1}{n!} H_n \left( \sqrt{\frac{1 - \sigma^2}{2\sigma}} \right) \left( \sqrt{\frac{\sigma}{2}} x_1^2 \right)^n,
\]

and

\[
e^{\frac{1}{2}x_1^2 + x_2^2 + \sqrt{x_1^2 - x_2^2}} = \sum \frac{1}{n!} H_n \left( \frac{\sigma - 1}{\sqrt{2\sigma}} \right) \left( \sqrt{\frac{\sigma}{2}} x_1^2 \right)^n.
\]

Inserting (3.3), (3.4), (3.13a), and (3.13b) into (3.11), we finally obtain

\[
F(x_1, x_2) = \frac{4f}{(1 + f)^2} e^{-\frac{f}{2(1 + f)}} \sum \frac{1}{n!} H_n \left( \frac{\sqrt{f}}{\sqrt{1 - f^2\delta}} \right) x_1^2 \left( \frac{1 - f}{2(1 + f)} \right)^{\frac{1}{2}}
\cdot \sum \frac{1}{k!} H_k \left( -\frac{f\delta}{\sqrt{1 - f^2}} \right) \left( \frac{f - 1}{2(1 + f)} \right)^{\frac{3}{2}} x_1^k
\cdot \sum \frac{1}{n!} \left( \frac{4f}{(1 + f)^2} \right)^{\frac{3}{2}} x_1^n x_2^n,
\]

where for simplicity, we have chosen the units such that \( w = 1 \) in Eq. (3.14) and \( f \) is the ratio of the frequencies in Eq. (3.4). Formula (3.14) is identical with Eq. (9) of [9].

**IV. GENERALIZATION TO THE TWO-DIMENSIONAL CASE**

If there is more than one dimension, further complications arise because the coordinates may rotate with respect to each other. We start by considering two harmonic oscillators with the same origins in two dimensional space. The Hamiltonians are

\[
H_1 = \frac{1}{2m} (p_{1x}^2 + p_{1y}^2) + \frac{1}{2} k_1 x^2 + \frac{1}{2} k_2 y^2,
\]

and

\[
H_2 = \frac{1}{2m} (p_{2x}^2 + p_{2y}^2) + \frac{1}{2} k_1 \tilde{x}^2 + \frac{1}{2} k_2 \tilde{y}^2,
\]

where

\[
\tilde{x} = x \cos \theta + y \sin \theta
\]
and
\[ \tilde{y} = y \cos \theta - x \sin \theta \]
\[ (4.4) \]
are the rotated coordinates. We express the Hamiltonians (4.1) and (4.2) in second-quantized form by introducing
\[ x = \frac{1}{\sqrt{2\omega_1}} (a_x + a_x^+), \quad p_{1x} = i\sqrt{\frac{\omega_1}{2}} (a_x - a_x^+), \]
\[ y = \frac{1}{\sqrt{2\omega_1}} (a_y + a_y^+), \quad p_{1y} = i\sqrt{\frac{\omega_1}{2}} (a_y - a_y^+), \]
\[ \tilde{x} = \frac{1}{\sqrt{2\omega_1}} (\tilde{a}_x + \tilde{a}_x^+), \quad \tilde{p}_{1x} = i\sqrt{\frac{\omega_1}{2}} (\tilde{a}_x - \tilde{a}_x^+), \]
\[ \tilde{y} = \frac{1}{\sqrt{2\omega_1}} (\tilde{a}_y + \tilde{a}_y^+), \quad \tilde{p}_{1y} = i\sqrt{\frac{\omega_1}{2}} (\tilde{a}_y - \tilde{a}_y^+), \]
\[ (4.5) \]
where the pairs of the creation operators \( a_x^+, a_y^+, \tilde{a}_x^+, \tilde{a}_y^+ \) and the corresponding annihilation operators \( a_x, a_y, \tilde{a}_x, \tilde{a}_y \) satisfy the same transformation formula as in Eqs. (3.3) and (3.4).

The frequency \( \omega_1 \) is given by \( \sqrt{\hbar/\kappa} \). Thus for example, we have
\[ \tilde{a}_x^+ = a_x^+ \cos \theta + a_x^+ \sin \theta \]
\[ \tilde{a}_y^+ = -a_y^+ \sin \theta + a_y^+ \cos \theta \]
\[ (4.6) \]
and the accompanying formula for the annihilation operators. After this rotation with the same frequency \( \omega_1 \), we then use freely the techniques described in Sec. II to translate the origins of the potential well and also to change the frequencies in each direction. Notice that all the annihilation operators \( a_x, a_y, \tilde{a}_x, \tilde{a}_y \) annihilate the same state \( |0, 0\rangle \), which is really the tensor product of one dimensional ground states of the form (2.33):
\[ |0\omega_1, 0\omega_2\rangle = \sqrt{\omega_1/\pi} e^{-\frac{1}{2} \omega_1 x^2 - \frac{1}{2} \omega_2 y^2} = \sqrt{\omega_1/\pi} e^{-\frac{1}{2} \omega_1 \tilde{x}^2 - \frac{1}{2} \omega_2 \tilde{y}^2} \]
\[ (4.7) \]
\[ \quad = |0(x)\omega_1 \rangle \otimes |0(y)\omega_2 \rangle = |0(\tilde{x})\omega_1 \rangle \otimes |0(\tilde{y})\omega_2 \rangle \]
The ground state wave function of the Hamiltonian (4.1) is given by
\[ |0\omega_1, 0\omega_2\rangle = (1 - \kappa^2) \frac{1}{e^{\frac{1}{2} \omega_2 \kappa^2}} |0\omega_1, 0\omega_2\rangle, \]
\[ (4.8) \]
where \( \kappa \) is given by the relation
\[ \frac{\omega_2}{\omega_1} = \frac{1 - \kappa^2}{1 + \kappa^2} \]
\[ (4.9) \]
Notice that by definition, we do not change the frequency of the x variable for the Hamiltonian (4.1a). Similarly the ground state wave function for the Hamiltonian (4.2) is given by
Furthermore we shift the origin of the potential well. If the Hamiltonian in (4.1a) is given instead by

$$\tilde{H}_1 = \frac{1}{2m} (p_x^2 + p_y^2) + \frac{1}{2} k_1 (x - \delta_x)^2 + \frac{1}{2} k_2 (y - \delta_y)^2.$$  \hfill (4.1b)

The corresponding ground state is given by

$$|0_{\omega_1}, 0_{\omega_2}\rangle_{s_x, s_y} = (1 - s_x^2)^{\frac{1}{4}} e^{-\frac{1}{4} s_x^2} e^{\frac{1}{2} s_x^2} e^{-\frac{1}{2} s_y^2} e^{\frac{1}{2} s_y^2} e^{-\frac{1}{2} (s_x^2 + s_y^2)^2} |0_{\omega_1}, 0_{\omega_2}\rangle,$$  \hfill (4.11)

where \( s_x, s_y \) are given by

$$s_x = - \frac{\delta_x}{\sqrt{2\omega_1}},$$  \hfill (4.12a)

and

$$s_y = - \frac{\delta_y}{\sqrt{2\omega_2}},$$  \hfill (4.12b)

respectively. The corresponding creation operators for the new ground state of (4.10) and (4.11) are given by

$$\tilde{a}_x^+ = a_x^+ - s_x,$$

$$\tilde{a}_y^+ = a_y^+ - s_y,$$  \hfill (4.13)

and

$$\tilde{a}_x^+ = a_x^+ - t_x,$$

$$\tilde{a}_y^+ = a_y^+ - t_y,$$  \hfill (4.14)

respectively. Using these pairs of creation and annihilation operators, we may write the generating function for the overlapping integral between the eigenfunctions of the Hamiltonian (4.1b) and (4.2) as

$$F(x_1, y_1, x_2, y_2) = \langle 0_{\omega_1}, 0_{\omega_2} | e^{x_1 \tilde{a}_x^+ + y_1 \tilde{a}_y^+} e^{x_2 \tilde{a}_x^+ + y_2 \tilde{a}_y^+} | 0_{\omega_1}, 0_{\omega_2}\rangle_{s_x, s_y},$$  \hfill (4.15)

$$= \sum_{n_1, n_2, m_1, m_2} \langle n_{1, \omega_1}, m_{1, \omega_1} | \tilde{a}_x^+ \tilde{a}_y^+ | n_{2, \omega_2}, m_{2, \omega_2}\rangle_{s_x, s_y} \frac{z_{1, \omega_1} y_{1, \omega_1} z_{2, \omega_2} y_{2, \omega_2}}{\sqrt{n_{1, \omega_1} m_{1, \omega_1} n_{2, \omega_2} m_{2, \omega_2}}}.$$
The evaluation of (4.15) follows similar procedures adopted in Sec. III. We give here the results for the special case $s_y = 0$. In this case, the generating function of (4.15) has a closed form as

\[
F(x_1, y_1, x_2, y_2) = [(1 - s_x^2)(1 - s_y^2)]^{1/4} \exp \left\{ -\frac{1}{2} (t_x^2 + t_y^2) - x_2 t_x - y_2 t_y \right\} \nonumber
\]

\[
- \frac{s_x - s_y}{2(1 - s_x^2)} - \frac{y_1 s_y}{2(1 - s_y^2)} + \frac{x_1 s_x}{\sqrt{1 - s_x^2}} (\cos \theta (x_2 + t_x) + \sin \theta (y_2 + t_y)) \nonumber
\]

\[
+ \frac{y_1}{\sqrt{1 - s_y^2}} \left( - \sin \theta (x_2 + t_x) + \cos \theta (y_2 + t_y) \right) \nonumber
\]

\[
+ \cos \theta \sin \theta (s_x - s_y) \left( x_2 + t_x + \frac{y_1 s_y}{\sqrt{1 - s_y^2}} \sin \theta - \frac{x_1 s_x}{\sqrt{1 - s_x^2}} \cos \theta \right)^2 \nonumber
\]

\[
- \left( y_2 + t_y + \frac{x_1 s_x}{\sqrt{1 - s_x^2}} \sin \theta - \frac{y_1 s_y}{\sqrt{1 - s_y^2}} \cos \theta \right) \nonumber
\]

\[
+ \frac{1}{2} (s_x \cos^2 \theta + s_y \sin^2 \theta) \left( x_2 + t_x + \frac{y_1 s_y}{\sqrt{1 - s_y^2}} \sin \theta - \frac{x_1 s_x}{\sqrt{1 - s_x^2}} \cos \theta \right)^2 \nonumber
\].

(4.16)

V. COMMENTS AND CONCLUSIONS

In this paper, we have derived the generating functions for the overlap integrals of the eigenfunctions of harmonic oscillators with shifted origins and modified frequencies including rotation of coordinates. The case with rotated coordinates is important for transitions where the excited electronic states of the molecules is distorted in form. For real molecular, anharmonic coupling terms are important, which mix eigenstates of different energies and symmetries. A crucial point in our two step method [2] is that we select the optimized values of the origins and the frequencies by the variational method, using purely algebraic manipulations. For all the cases treated, the transformed Hamiltonians have the useful property that the corresponding perturbation calculations converge rapidly. Our procedure eliminates the necessity of the usual time-consuming method of trial and error of iterative search. The present work lays the foundation for the calculation of the Franck-Condon factors. The generalization to higher dimensionality is straightforward but tedious and need the aid of computer algebraic manipulations. Explicit application to specific molecules will be reported in future publications.
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