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Exact evaluation and recursion relations of two-center harmonic oscillator matrix elements

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Using vibrational wave functions of two relatively displaced harmonic oscillators of arbitrary frequencies, Franck–Condon overlap integrals and matrix elements of x^l, $\exp(-2cx)$, and $\exp(-cx^2)$ (x is the internuclear separation) are obtained. Useful three-term, four-term, and five-term recursion relations among these matrix elements are derived. It is shown that all of the relevant matrix elements can be obtained from a mere knowledge of the lowest two Franck–Condon overlap integrals. Results are illustrated by computation of Franck–Condon factors for the $A\,^1\Sigma_u^+ - X\,^1\Sigma_g^+$ and the $B\,^1\Pi_u - X\,^1\Sigma_g^+$ systems of $^7Li_2$.

I. INTRODUCTION

A quantitative description of transition probabilities for various vibrational levels (that is, vibrational excitation) as well as of intensities of various lines in the spectra of diatomic and polyatomic molecules requires matrix elements of various powers of the internuclear separation x between vibrational levels belonging to two different electronic states of the molecule.[1] A Franck–Condon overlap integral is a special example of such a matrix element. For low-lying vibrational levels, the potential curves of the molecular electronic states can be represented with reasonable accuracy by those of linear harmonic oscillators. For higher vibrational levels, where anharmonicity becomes important, the potential of a Morse oscillator is a better representation of the true potential curve. Even in such a case as the Morse oscillator, if one were to use first-order perturbation theory with the linear harmonic oscillator as the zero-order approximation, the matrix elements of powers of x would appear in the correction factors. With this spirit in mind, an attempt is made in this paper to obtain general analytic expressions and simple recursion relations for two-center harmonic oscillator matrix elements of various functions (powers, exponential, and Gaussian) of x. In fact, a general five-term recursion relation to be derived below [Eq. (32)], is valid for *any* analytical function of x that could be expanded as a power series in x.

The evaluation of Franck–Condon factors, which essentially involves an overlap integral between wave functions of vibrational levels belonging to two different electronic states of a molecule, using linear harmonic oscillator wave functions has been carried out in a number of investigations, and proper kudos have been distributed by Waldenstrøm and Razi Naqvi.[2] Various theoretical methods for obtaining the Franck–Condon factors have been reviewed more recently by Kuz'menko *et al.*[3] Overlap matrix elements of various functions of x using, once again, vibrational wave functions of two different harmonic oscillators, have been analytically obtained in some recent papers.[4,5] In Sec. IV of the present paper we will obtain some general recursion relations among these matrix elements. A single and double ket notation (for example, $|m\rangle$ and $|n\rangle\rangle$) will be used to distinguish between the vibrational eigenfunctions belonging to two different electronic states.

II. THE FRANCK–CONDON OVERLAP INTEGRAL

The relevant potential energy curves are replaced by those of one-dimensional harmonic oscillators of frequency ω_1 and ω_2, with a relative separation of r. For convenience, define $\omega_0 = \hbar\ (\mu r^2)$, where μ is the reduced mass of the nuclei. The two-center Franck–Condon overlap integral is then defined as $\langle m|n\rangle\rangle$, where

$$\langle x|m\rangle = (2^m m!)^{-1/2}[\omega_1/(\pi\omega_0 r^2)]^{1/4} \times\exp[-\omega_1 x^2/(2\omega_0 r^2)]H_m[(\omega_1/\omega_0)^{1/2}x/r] \quad (1)$$

is the wave function of the mth level of the harmonic oscillator associated with the potential $V_1 = \frac{1}{2}\mu\omega_1^2 x^2$, and

$$\langle\langle x|n\rangle\rangle = (2^n n!)^{-1/2}[\omega_2/(\pi\omega_0 r^2)]^{1/4} \times\exp[-\omega_2(x-r)^2/(2\omega_0 r^2)] \times H_n[(\omega_2/\omega_0)^{1/2}(x-r)/r] \quad (2)$$

is the wave function of the nth level of the harmonic oscillator associated with the potential $V_2 = \frac{1}{2}\mu\omega_2^2(x-r)^2$. Thus,

$$\langle m|n\rangle\rangle = \frac{(\omega_1\omega_2)^{1/4}}{[\pi\omega_0 r^2(2^{m+n}m!n!)]^{1/2}}\exp\left[\frac{-\omega_1\omega_2}{2\omega_0(\omega_1+\omega_2)}\right] \times\int_{-\infty}^{\infty}\exp\left\{-\left[\left(\frac{\omega_1+\omega_2}{2\omega_0 r^2}\right)^{1/2}x - \frac{\omega_2}{[2\omega_0(\omega_1+\omega_2)]^{1/2}}\right]^2\right\}H_m[(\omega_1/\omega_0)^{1/2}x/r] \times H_n[(\omega_2/\omega_0)^{1/2}(x-r)/r]dx. \quad (3)$$

Now, on changing the integration variable from x to $t = x[(\omega_1+\omega_2)/(2\omega_0 r^2)]^{1/2}$,

$$\langle m|n\rangle\rangle = N_{mn}\pi^{-1/2}\int_{-\infty}^{\infty}\exp[-(t-y)^2] \times H_m\left[\left(\frac{2\omega_1}{\omega_1+\omega_2}\right)^{1/2}t\right] \times H_n\left[\left(\frac{2\omega_2}{\omega_1+\omega_2}\right)^{1/2}t - \left(\frac{\omega_2}{\omega_0}\right)^{1/2}\right]dt, \quad (4)$$

where

$$N_{mn} = (\omega_1\omega_2)^{1/4}[(\omega_1+\omega_2)2^{m+n-1}m!n!]^{-1/2} \times\exp(-y^2\omega_1/\omega_2)$$

and

$$y=\omega_2/[2\omega_0(\omega_1+\omega_2)]^{1/2}. \quad (5)$$

The integral in Eq. (4) is of the same form as the integral defined in the Appendix. A direct use of Eq. (A8) yields a closed-form expression for the Franck–Condon integral:

$$\langle m|n\rangle\rangle = N_{mn}\sum_{k=0}^{[m,n]}\binom{m}{k}\binom{n}{k}\left(\frac{\omega_1-\omega_2}{\omega_1+\omega_2}\right)^{(n-k)/2} \times\left(\frac{\omega_2-\omega_1}{\omega_1+\omega_2}\right)^{(m-k)/2}\left[\frac{4(\omega_1\omega_2)^{1/2}}{\omega_1+\omega_2}\right]^k! \times H_{m-k}\left[\left(\frac{\omega_1\omega_2^2}{\omega_0(\omega_2^2-\omega_1^2)}\right)^{1/2}\right] \times H_{n-k}\left[-\left(\frac{\omega_1^2\omega_2}{\omega_0(\omega_1^2-\omega_2^2)}\right)^{1/2}\right]. \quad (6)$$

This expression has been obtained, using various procedures, by a number of investigators.[6–8] It is interesting to note that for the two special cases, $m=0$ or $n=0$, the above sum reduces to a single term containing only one Hermite polynomial. [We note parenthetically that the above sum (6) also reduces to a single term for the case of equal frequency oscillators.] From the recursion relation for Hermite polynomials (A3), it follows:

$$\langle 0|n+2\rangle\rangle = \frac{-\omega_1}{\omega_1+\omega_2}\left[\frac{2\omega_2}{\omega_0(n+2)}\right]^{1/2}\langle 0|n+1\rangle\rangle - \left(\frac{\omega_1-\omega_2}{\omega_1+\omega_2}\right)\left(\frac{n+1}{n+2}\right)^{1/2}\langle 0|n\rangle\rangle, \quad (7)$$

$$\langle m+2|0\rangle\rangle = \frac{\omega_2}{\omega_1+\omega_2}\left[\frac{2\omega_1}{\omega_0(m+2)}\right]^{1/2}\langle m+1|0\rangle\rangle + \left(\frac{\omega_1-\omega_2}{\omega_1+\omega_2}\right)\left(\frac{m+1}{m+2}\right)^{1/2}\langle m|0\rangle\rangle. \quad (8)$$

In fact, on using the one-term expressions for $\langle 0|n\rangle\rangle$ and $\langle m|0\rangle\rangle$, Eq. (6) can be rewritten as

$$\langle m|n\rangle\rangle = \sum_{k=0}^{[m,n]}\left[\frac{2(\omega_1\omega_2)^{1/2}}{\omega_1+\omega_2}\right]^k\binom{m}{k}^{1/2}\binom{n}{k}^{1/2} \times\frac{\langle m-k|0\rangle\rangle\langle 0|n-k\rangle\rangle}{\langle 0|0\rangle\rangle}. \quad (9)$$

Equivalent expressions have been obtained previously by Manneback[6] and Smith.[9] It is remarkable—and this fact has apparently not been appreciated earlier in the literature—that the complete Franck–Condon matrix $\langle m|n\rangle\rangle$ can be determined using Eqs. (7), (8), and (9) from the mere knowledge of either $\langle 0|0\rangle\rangle$ and $\langle 0|1\rangle\rangle$, or $\langle 0|0\rangle\rangle$ and $\langle 1|0\rangle\rangle$.

III. MATRIX ELEMENTS OF SOME FUNCTIONS

Now let us consider the two-center matrix elements of x^l, $\exp(-2cx)$, and $\exp(-cx^2)$ in the harmonic oscillator basis. Various matrix elements can be written in terms of integrals of the form

$$I[f(t);m,n;a,b,y,z] = \int_{-\infty}^{\infty} f(t)\exp[-(t-y)^2]H_m(at)H_n(bt-z)dt, \quad (10)$$

which is derived in detail for the case $f(t)=1$ in the Appendix [see, for example, Eq. (A8)].

A. Powers of the coordinate *x*

The required matrix elements can be written as

$$\langle m|x^l|n\rangle\rangle = \frac{N_{mn}}{\pi^{1/2}}\left(\frac{2\omega_0 r^2}{\omega_1+\omega_2}\right)^{l/2} \times\int_{-\infty}^{\infty} t^l\exp[-(t-y)^2] \times H_m(at)H_n(bt-z)dt, \quad (11)$$

where

$$a=[2\omega_1/(\omega_1+\omega_2)]^{1/2},\quad b=[2\omega_2/(\omega_1+\omega_2)]^{1/2},\quad \text{and } z=(\omega_2/\omega_0)^{1/2}. \quad (12)$$

N_{mn} and y are defined in Eq. (5). Using Eq. (A13), the matrix elements of x^l can be written as a sum of Franck–Condon integrals,

$$\langle m|x^l|n\rangle\rangle = \left[\frac{\omega_0 r^2}{2(\omega_1+\omega_2)}\right]^{l/2} l! \times\sum_{p=0}^{[m,l]}\sum_{q=0}^{[n,l-p]}\left[\frac{m!n!}{(m-p)!(n-q)!}\right]^{1/2} \times\frac{(4\omega_1)^{p/2}(4\omega_2)^{q/2}}{(\omega_1+\omega_2)^{(p+q)/2}p!q!} \times\frac{(-i)^{l-p-q}}{(l-p-q)!}H_{l-p-q}(iy) \times\langle m-p|n-q\rangle\rangle. \quad (13)$$

This expression was obtained earlier by Morales *et al.*,[5] though there appears to be an error in the constants of their expression.

B. Exponential function exp(−2*cx*)

Here, in obtaining the relevant integral, we follow exactly the same steps as in the Appendix, Eqs. (A4)–(A6), except there now is an extra factor of $\exp(-2ct)$ in the integrand. It leads to the following result for the integral:

$$I[\exp(-2ct);m,n;a,b,y,z] = \pi^{1/2}\exp(c^2-2cy)\left(\frac{\partial}{\partial t_2}\right)^n_{t_2=0}\left(\frac{\partial}{\partial t_1}\right)^m_{t_1=0} \times\exp\{-(1-a^2)t_1^2-(1-b^2)t_2^2 + 2a(y-c)t_1+2[b(y-c)-z]t_2+2abt_1t_2\}. \quad (14)$$

Except for the constant $\exp(c^2-2cy)$, Eq. (14) looks just like Eq. (A6), and we can immediately write down the final result:

$$I[\exp(-2ct);m,n;a,b,y,z] = \exp(c^2-2cy)I[1;m,n;a,b,y-c,z]. \quad (15)$$

The matrix element $\langle m|\exp(-2cx)|n\rangle\rangle$ is related to $I[\exp(-2ct);m,n;a,b,y,z]$ and by using Eq. (15) one can write

$$\langle m|\exp(-2cx)|n\rangle\rangle = N_{mn}\exp(\alpha^2 - 2\alpha y) \times I[1;m,n;a,b,y-\alpha,z]/\pi^{1/2}, \quad (16)$$

where $\alpha = c[(2\omega_0 r^2)/(\omega_1+\omega_2)]^{1/2}$ is introduced by a change of the integration variable from x to the dimensionless $t = x(\omega_1+\omega_2)^{1/2}/(2\omega_0 r^2)^{1/2}$.

C. Gaussian function $\exp(-cx^2)$

The case $f(t) = \exp(-ct^2)$ can be worked out in a fashion very similar to the case of the exponential above. Following the same steps as Eqs. (A4) and (A5), we obtain

$$I[\exp(-ct^2);m,n;a,b,y,z] = \beta\exp(-c\beta^2 y^2)\left(\frac{\partial}{\partial t_2}\right)^n_{t_2=0}\left(\frac{\partial}{\partial t_1}\right)^m_{t_1=0} \times \exp(-t_1^2 - t_2^2 - 2zt_2 - \beta^2 y^2) \times \int_{-\infty}^{\infty}\exp[-t^2 - 2(a\beta t_1 + b\beta t_2 + \beta y)t]dt, \quad (17)$$

where $\beta = (1+c)^{-1/2}$.

The expression in Eq. (17) has essentially the same form as Eq. (A5), and we can immediately write down the result by inspection,

$$I[\exp(-ct^2);m,n;a,b,y,z] = \beta\exp(-c\beta^2 y^2)I[1;m,n;a\beta,b\beta,y\beta,z]. \quad (18)$$

The matrix elements $\langle m|\exp(-cx^2)|n\rangle\rangle$ are related to the above integral by

$$\langle m|\exp(-cx^2)|n\rangle\rangle = N_{mn}\gamma\exp[-(1-\gamma^2)y^2] \times I[1;m,n;\gamma a,\gamma b,\gamma y,z]/\pi^{1/2}, \quad (19)$$

where $\gamma = [1 + 2c\omega_0 r^2/(\omega_1+\omega_2)]^{-1/2}$ is once again introduced by the change of integration variable.

Summarizing this section, the integral for $f(t) = t^l$ can be written as a finite sum of integrals for $f(t) = 1$. The integrals for the exponential and Gaussian functions can each be obtained by a simple scaling of an $f(t) = 1$ integral.

IV. RECURSION RELATIONS

Four-term recursion relations among Franck–Condon overlap integrals were derived by Ansbacher[7] and, in equivalent form, by Manneback.[6] These recursion relations are special cases of the more general recursion relations, to be obtained below, for the integral $I[t^l;m,n;a,b,y,z]$. In the preceding section it was shown that the integrals for the exponential and Gaussian functions could be written in terms of $I[1;m,n;a,b,y,z]$ so that the recursion relations for the integrals for these functions are also obtained from the recursion relations for $I[t^l;m,n;a,b,y,z]$.

For brevity, define $I_l(m,n) \equiv I[t^l;m,n;a,b,y,z]$ in the following discussion. Thus,

$$I_l(m,n) = \int_{-\infty}^{\infty}\exp[-(t-y)^2]t^l H_m(at)H_n(bt-z)dt \quad (20)$$

$$= 2aI_{l+1}(m-1,n) - 2(m-1)I_l(m-2,n) \quad (21)$$

or equivalently,

$$2aI_{l+1}(m,n) = I_l(m+1,n) + 2mI_l(m-1,n). \quad (22)$$

In going from Eq. (20) to Eq. (21), the recursion relation for Hermite polynomials (A3) was applied to $H_m(at)$. Using the recursion relation for Hermite polynomials on the $H_n(bt-z)$ term in Eq. (20), on the other hand, gives

$$2bI_{l+1}(m,n) = I_l(m,n+1) + 2zI_l(m,n) + 2nI_l(m,n-1). \quad (23)$$

It is important to note that from Eq. (22) or (23), the complete matrix of any power of t (for example, t^l) can be obtained from the knowledge of the matrix of the next lower power (namely, t^{l-1}). We reemphasize that the matrix of Franck–Condon overlap integrals can be completely determined from a mere knowledge of only two matrix elements, $\langle 0|0\rangle\rangle$ and $\langle 0|1\rangle\rangle$ (or $\langle 0|0\rangle\rangle$ and $\langle 1|0\rangle\rangle$), so, in principle, the complete matrix of any power of x can be built up from only two overlap matrix elements.

Using, in the integrands of the terms on the left-hand sides of Eqs. (22) and (23),

$$t\exp[-(t-y)^2] = -\tfrac{1}{2}\left(\frac{d}{dt}\right)\exp[-(t-y)^2] + y\exp[-(t-y)^2],$$

then performing integration by parts and the necessary derivatives we obtain

$$alI_{l-1}(m,n) = I_l(m+1,n) - 2nabI_l(m,n-1) + 2m(1-a^2)I_l(m-1,n) - 2ayI_l(m,n) \quad (24)$$

and

$$blI_{l-1}(m,n) = I_l(m,n+1) - 2mabI_l(m-1,n) + 2n(1-b^2)I_l(m,n-1) - 2(by-z)I_l(m,n). \quad (25)$$

The recursion relations for these integrals can easily be adapted to the matrix elements $\langle m|x^l|n\rangle\rangle$, using Eq. (11):

$$2lr(\omega_1\omega_0)^{1/2}\langle m|x^{l-1}|n\rangle\rangle = [2(m+1)]^{1/2}(\omega_1+\omega_2)\langle m+1|x^l|n\rangle\rangle - (8n\omega_1\omega_2)^{1/2}\langle m|x^l|n-1\rangle\rangle + (2m)^{1/2}(\omega_2-\omega_1)\langle m-1|x^l|n\rangle\rangle - (\omega_1/\omega_0)^{1/2}2\omega_2\langle m|x^l|n\rangle\rangle, \quad (26)$$

$$2lr(\omega_2\omega_0)^{1/2}\langle m|x^{l-1}|n\rangle\rangle = [2(n+1)]^{1/2}(\omega_1+\omega_2)\langle m|x^l|n+1\rangle\rangle - (8m\omega_1\omega_2)^{1/2}\langle m-1|x^l|n\rangle\rangle + (2n)^{1/2}(\omega_1-\omega_2)\langle m|x^l|n-1\rangle\rangle + (\omega_2/\omega_0)^{1/2}2\omega_1\langle m|x^l|n\rangle\rangle. \quad (27)$$

Equations (26) and (27) are generalized forms of Ansbacher's[7] recursion relations for Franck–Condon overlap integrals which are obtained by letting $l = 0$.

Equations (22) and (23) can be adapted to the integrals for the exponential and Gaussian functions by multiplying the equations by $(-2c)^l/l!$ or $(-ct)^l/l!$, respectively, and then summing over l. This yields, for the exponential case (suppressing the constants a, b, y, and z):

$$2aI[t\exp(-2ct);m,n] = I[\exp(-2ct);m+1,n] + 2mI[\exp(-2ct);m-1,n], \quad (28)$$

$$2bI[t\exp(-2ct);m,n] = I[\exp(-2ct);m,n+1] + 2zI[\exp(-2ct);m,n] + 2nI[\exp(-2ct);m,n-1]. \quad (29)$$

Note that these equations relate the $f(t)=\exp(-2ct)$ integral to the $f(t)=t\exp(-2ct)$ integral. Analogous relations for the Gaussian case can be obtained in a similar manner.

Equations (24) and (25) [or Eqs. (26) and (27)] can be similarly adapted for integrals for the exponential and Gaussian functions. For the exponential case, Eqs. (24) and (25) are transformed into

$$2a(y-c)I[\exp(-2ct);m,n] = I[\exp(-2ct);m+1,n] - 2nabI[\exp(-2ct);m,n-1] + 2m(1-a^2)I[\exp(-2ct);m-1,n], \quad (30)$$

$$2[b(y-c)-z]I[\exp(-2ct);m,n] = I[\exp(-2ct);m,n+1] - 2mabI[\exp(-2ct);m-1,n] + 2n(1-b^2)I[\exp(-2ct);m,n-1]. \quad (31)$$

Equations (30) and (31) could have been obtained by an alternative method using the results of Sec. III B, in which it was shown that the integrals for the exponential and Gaussian functions were related by simple scaling to the $f(t)=1$ integral. Thus setting $l=0$ in Eqs. (24) and (25) or in Eqs. (26) and (27), and using Eq. (15) for the scaling property of the exponential case, the recursion relations (30) and (31) are immediately obtained. This alternative procedure provides a self-consistent check on the present results. A similar check can be easily verified for the Gaussian case using the scaling property (18).

Equations (22) and (23) or Eqs. (24) and (25) can be combined to eliminate the integral on the left side in each case, and obtain a five-term recursion relation valid for the matrix elements of powers of x. It turns out that the recursion relation thus obtained is very general; since it is good for any power of x, it will be valid for any analytic function of x which can be expanded in a power series. Thus,

$$\langle m|f(x)|n\rangle\rangle = \left(\frac{\omega_0}{2\omega_1}\right)^{1/2}\{(m+1)^{1/2}\langle m+1|f(x)|n\rangle\rangle + m^{1/2}\langle m-1|f(x)|n\rangle\rangle\} - \left(\frac{\omega_0}{2\omega_2}\right)^{1/2} \times\{(n+1)^{1/2}\langle m|f(x)|n+1\rangle\rangle + n^{1/2}\langle m|f(x)|n-1\rangle\rangle\}, \quad (32)$$

where $f(x)$ can be a power, exponential, Gaussian, trigonometric function, etc.

V. DISCUSSION AND CONCLUSIONS

For the special case of equal frequency oscillators ($\omega_1=\omega_2$), expression (6) for the Franck–Condon overlap integral reduces to a series which can be identified as a representation of an associated Laguerre polynomial.[10] Explicitly, for $\omega_1=\omega_2=\omega$,

$$\langle m|n\rangle\rangle = (-1)^{n-m}\left[\frac{m!}{n!}\left(\frac{\omega}{2\omega_0}\right)^{n-m} \times\exp\left(-\frac{\omega}{2\omega_0}\right)\right]^{1/2} L_m^{n-m}\left(\frac{\omega}{2\omega_0}\right). \quad (33)$$

During their numerical evaluation of integrals of the form $\langle m|x^l|n\rangle\rangle$ for the first positive system of N_2, Fraser[11] and Nicholls and Jarmain[12] observed that under certain conditions the following equality nearly holds:

$$\frac{\langle m|x^2|n\rangle\rangle}{\langle m|x|n\rangle\rangle} \approx \frac{\langle m|x|n\rangle\rangle}{\langle m|x^0|n\rangle\rangle}. \quad (34)$$

That this should be true is easily seen by using the recursion relation (22). For the case $\omega \gg \omega_0$ and $(\omega/\omega_0) \gg m,n$ [which are equivalent[11,12] to the conditions necessary for equality (34) to hold], it is readily seen that the ratios in Eq. (34) are approximately equal to $\frac{1}{2}r$, independent of m or n.

In order to illustrate the results of the recursion relations derived above, we have numerically evaluated the Franck–Condon factors for the $A\,{}^1\Sigma_u^+$–$X\,{}^1\Sigma_g^+$ and the $B\,{}^1\Pi_u$–$X\,{}^1\Sigma_g^+$ systems of ${}^7Li_2$ using Eqs. (7), (8), and (9). The harmonic oscillators representing the potential curves of the X, A, and B electronic states have frequencies 351.43, 255.45, and 269.69 cm^{-1}, respectively, and potential minimum at 2.672, 3.107, and 2.936 Å, respectively. It is easy to verify that the first five vibrational levels of the above three simple harmonic oscillators have the same energy levels, within 5%, as the actual vibrational energy levels of the three electronic states, indicating that the harmonic oscillator approximation is reasonable for these levels. The computed numbers for Franck–Condon factors are compared, in Table I, with the experimentally obtained values of these factors for the above transitions in Li_2 by Hessel and coworkers.[14,15] To make comparison easy, we use a double ket notation, $|m\rangle\rangle$, to indicate the mth vibrational level of the ground state (analogous to the double prime, v'', notation of Hessel) and a single ket notation, $|n\rangle$, to indicate the nth vibrational level of the excited A or B states (analogous to the single prime, v', notation of Hessel). The results shown in Table I indicate that the agreement between computed factors, $|\langle m|n\rangle\rangle|^2$, and experimental values is not encouraging even for the low vibrational levels where the harmonic oscillator is supposed to be a good approximation. However, we note that the agreement becomes reasonable when the designation of the vibrational quantum numbers of two relevant levels are interchanged, that is, when the experimental $|\langle m|n\rangle\rangle|^2$ is compared with $|\langle\langle m|n\rangle|^2$. For ease of comparison, we have displayed $|\langle m|n\rangle\rangle|^2$ and $|\langle\langle m|n\rangle|^2$ side-by-side in Table I. We do not yet understand the reason for this puzzling observation.

TABLE I. A comparison of the Franck–Condon factors for the $A\,^1\Sigma_u^+ - X\,^1\Sigma_g^+$ system (multiplied by 10^3) and the $B\,^1\Pi_u - X\,^1\Sigma_g^+$ system (multiplied by 10^4) of $^7Li_2$. A double ($|\rangle\rangle$) and a single ($|\rangle$) ket notation refers to the vibrational levels of the ground and the excited electronic state, respectively.

Vibrational quantum number	$A\,^1\Sigma_u^+ - X\,^1\Sigma_g^+$			$B\,^1\Pi_u - X\,^1\Sigma_g^+$		
	experiment (Ref. 14)			experiment (Ref. 15)		
m , n	$\|\langle m\|n\rangle\rangle\|^2$	$\|\langle m\|n\rangle\rangle\|^2$	$\|\langle\langle m\|n\rangle\|^2$	$\|\langle m\|n\rangle\rangle\|^2$	$\|\langle m\|n\rangle\rangle\|^2$	$\|\langle\langle m\|n\rangle\|^2$
0 , 0	53	52	53	3267	3188	3267
0 , 1	131	176	180	3149	3827	4104
0 , 2	182	270	278	1961	2103	2065
0 , 3	187	250	254	969	698	507
0 , 4	158	156	153	413	156	55
1 , 0	180	134	131	4104	3340	3149
1 , 1	191	197	191	39	77	39
1 , 2	78	58	54	844	1511	2042
1 , 3	4	9	12	1692	2711	3127
1 , 4	15	134	145	1516	1657	1395
2 , 0	277	187	182	2065	2008	1961
2 , 1	54	79	78	2042	942	844
2 , 2	13	15	13	1110	1345	1110
2 , 3	9	127	120	0.5	63	329
2 , 4	88	56	51	622	1834	2826
3 , 0	254	190	188	507	918	969
3 , 1	12	3	4	3127	1884	1692
3 , 2	120	98	90	329	1	0.5
3 , 3	46	45	46	1391	1508	1391
3 , 4	2	25	20	423	303	28
4 , 0	153	157	158	55	358	413
4 , 1	145	18	15	1395	1585	1516
4 , 2	51	90	89	2826	711	622
4 , 3	20	4	2	28	550	423
4 , 4	84	92	84	800	661	800

To summarize, we have obtained explicit expressions for the matrix elements of x^l, $\exp(-2cx)$, and $\exp(-cx^2)$, x being the internuclear separation, in the two-center simple harmonic basis. It is shown that in principle, the complete matrices of combinations of these functions could be determined in terms of only the lowest two Franck–Condon overlap matrix elements. Furthermore, a very general five-term recursion relation (32) is obtained which is valid for the matrix elements of *any* analytic function of x.

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APPENDIX

The integral

$$I[f(t);m,n;a,b,y,z] = \int_{-\infty}^{\infty} f(t)\exp[-(t-y)^2]H_m(at)H_n(bt-z)dt \tag{A1}$$

with a, b, y, and z constant, is very useful in the evaluation of the Franck–Condon factors, and the matrix elements of powers of the coordinate x. The matrix elements of exponential and Gaussian functions, $\exp(-2cx)$ and $\exp(-cx^2)$, respectively, can also be easily obtained with only slight modifications in the solution of the integral for the case $f(t) = 1$. To this end, a detailed derivation of the integral, $I(1;m,n;a,b,y,z) \equiv I_0$, is given in this Appendix. Some formulas, useful in the evaluation of the integral, and in obtaining recursion relations for it are presented first.

From the generating function of Hermite polynomials,

$$\sum_{n=0}^{\infty} H_n(x)t^n/n! = \exp(-t^2+2xt),$$

the following representation for Hermite polynomials is obtained:

$$H_n(B/A) = A^{-n}\left(\frac{\partial}{\partial t}\right)^n_{t=0} \exp(-A^2t^2+2Bt). \tag{A2}$$

The three-term recursion relation for Hermite polynomials is

$$2xH_n(x) = H_{n+1}(x) + 2nH_{n-1}(x). \tag{A3}$$

The integral to be evaluated is

$$I_0 = \int_{-\infty}^{\infty} \exp[-(t-y)^2]H_m(at)H_n(bt-z)dt. \tag{A4}$$

Using Eq. (A2) for the Hermite polynomials in Eq. (A4) we obtain

$$I_0 = \left(\frac{\partial}{\partial t_1}\right)^m_{t_1=0}\left(\frac{\partial}{\partial t_2}\right)^n_{t_2=0} \exp(-t_1^2 - t_2^2 - 2zt_2 - y^2) \times \int_{-\infty}^{\infty} \exp[-t^2 + 2(at_1+bt_2+y)t]dt \tag{A5}$$

$$= \pi^{1/2}\left(\frac{\partial}{\partial t_1}\right)^m_{t_1=0}\left(\frac{\partial}{\partial t_2}\right)^n_{t_2=0} \exp[-(1-a^2)t_1^2 - (1-b^2)t_2^2 + 2abt_1t_2 + 2ayt_1 + 2(by-z)t_2]. \quad \text{(A6)}$$

Carrying out the t_2 derivatives, and using the definition (A2) of the Hermite polynomials leads to

$$I_0 = \pi^{1/2}\sum_{k=0}^{n}\binom{n}{k}(1-b^2)^{(n-k)/2}H_{n-k}\left[\frac{by-z}{(1-b^2)^{1/2}}\right] \times \sum_{j=0}^{m}\binom{m}{j}\left(\frac{\partial}{\partial t_1}\right)^j_{t_1=0}(2abt_1)^k\left(\frac{\partial}{\partial t_1}\right)^{m-j}_{t_1=0} \times \exp[-(1-a^2)t_1^2 + 2ayt_1] \quad \text{(A7)}$$

$$= \pi^{1/2}\sum_{k=0}^{[m,n]}\binom{n}{k}\binom{m}{k}(1-b^2)^{(n-k)/2}(1-a^2)^{(m-k)/2} \times (2ab)^k k!H_{m-k}\left[\frac{ay}{(1-a^2)^{1/2}}\right] \times H_{n-k}\left[\frac{by-z}{(1-b^2)^{1/2}}\right] \quad \text{(A8)}$$

since, on setting $t_1 = 0$, the only nonzero term in the j sum is $j = k$. Thus the k sum runs from zero to the smaller of m or n, indicated by $[m,n]$.

We can evaluate $I[t^l;m,n;a,b,y,z] \equiv I_l$ by following the same procedure as above, through Eq. (A6), and using the standard integral,[13]

$$\int_{-\infty}^{\infty} t^l \exp(-t^2 + 2ut)dt = \pi^{1/2}\exp(u^2)(2i)^{-l}H_l(iu).$$

We obtain

$$I_l = (2i)^{-l}\pi^{1/2}\left(\frac{\partial}{\partial t_2}\right)^n_{t_2=0}\left(\frac{\partial}{\partial t_1}\right)^m_{t_1=0} \times H_l(iu)A(t_1,t_2) \quad \text{(A9)}$$

$$= (2i)^{-l}\pi^{1/2}\sum_{p=0}^{m}\sum_{q=0}^{n}\binom{m}{p}\binom{n}{q} \times\left[\left(\frac{\partial}{\partial t_2}\right)^q_{t_2=0}\left(\frac{\partial}{\partial t_1}\right)^p_{t_1=0}H(iu)\right] \times\left[\left(\frac{\partial}{\partial t_2}\right)^{n-q}_{t_2=0}\left(\frac{\partial}{\partial t_1}\right)^{m-p}_{t_1=0}A(t_1,t_2)\right], \quad \text{(A10)}$$

where

$$A(t_1,t_2) = \exp[-(1-a^2)t_1^2 - (1-b^2)t_2^2 + 2ayt_1 + 2(by-z)t_2 + 2abt_1t_2],$$

$$u = at_1 + bt_2 + y \text{ and } i = (-1)^{1/2}. \quad \text{(A11)}$$

Using Eq. (A6) and

$$\left(\frac{\partial}{\partial t_2}\right)^q_{t_2=0}\left(\frac{\partial}{\partial t_1}\right)^p_{t_1=0}H_l(iu) = \frac{l!a^p b^q (2i)^{p+q}}{(l-p-q)!}H_{l-p-q}(iy); \quad p+q \leqslant l \quad \text{(A12)}$$

we obtain the final result:

$$I[t^l;m,n;a,b,y,z] = \sum_{p=0}^{[m,l]}\sum_{q=0}^{[n,l-p]}\binom{m}{p}\binom{n}{q} \times\frac{l!a^p b^q}{(2i)^{l-p-q}(l-p-q)!}H_{l-p-q}(iy) \times I[1;m-p,n-q;a,b,y,z]. \quad \text{(A13)}$$

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