Analytic and Algebraic Evaluation of Franck−Condon Overlap Integrals

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An analytic and algebraic evaluation of Franck−Condon overlap integrals for harmonic oscillators displaced by an amount Δ and of different frequencies (ω, ω') is presented. The results are extended to Morse oscillators to first order in effective anharmonicities.

1. Introduction

The problem of calculating Franck−Condon intensities in polyatomic molecules remains of great interest. This calculation requires the knowledge of the wave functions of the initial and final states and the successive evaluation of the overlap integrals. It has been suggested that algebraic methods provide a way to obtain wave functions of polyatomic molecules.[1−5] In the simplest version of this approach, wave functions are expanded into a set of one-dimensional Morse (for stretching) and Pöschl−Teller (for bending) functions, both of which are related to representations of the Lie algebra $u(2)$. To calculate Franck−Condon intensities, one needs to evaluate the overlap integrals between different Morse (or Pöschl−Teller) functions. Although this evaluation can be done numerically, quite often one does not know the potential, and/or the molecule may have many degrees of freedom and consequently many Morse or Pöschl−Teller basis functions. Thus, it may be convenient to develop explicit formulas for the overlap integrals which allow a straightforward and less computer-intensive calculation. The purpose of this note, dedicated to Raphy Levine on the occasion of his 60th birthday, is to provide some explicit formulas for the overlap integrals to be used in conjunction with the algebraic method for the evaluation of Franck−Condon intensities.

2. Harmonic Oscillator, Analytic Methods

Overlap integrals of harmonic oscillator wave functions centered about different equilibrium positions and whose frequencies are also different have been evaluated by several authors.[6−8] The result is typically given in the form of a recurrence relation. In this section, we derive an explicit expression using analytic methods. The integrals we wish to evaluate are

$$I_{n,n'}(\Delta; \alpha, \alpha') = \int_{-\infty}^{\infty} \psi_n(\alpha; x)\psi_{n'}(\alpha'; x - \Delta)\, \mathrm{d}x \tag{2.1}$$

For harmonic oscillators

$$\psi_n(\alpha; x) = \left(\frac{\alpha}{\pi^{1/2}2^n n!}\right)^{1/2} \mathrm{e}^{-(1/2)\alpha^2x^2} H_n(\alpha x) \tag{2.2}$$

where $H_n(x)$ is a Hermite polynomial and α is related to the frequency ω by $\alpha = (\mu\omega/\hbar)^{1/2}$.

The integrals (2.1) can be evaluated by making use of the following formulas. First, using the integral[9]

$$\int_{-\infty}^{\infty} \mathrm{e}^{-x^2} H_n(x)H_{n+2m}(\alpha x)\, \mathrm{d}x = 2^n\sqrt{\pi}\frac{(n + 2m)!}{m!}\alpha^n(\alpha^2 - 1)^m \tag{2.3}$$

with the orthogonality property of the Hermite polynomials

$$\int_{-\infty}^{\infty} \mathrm{e}^{-x^2} H_m(x)H_n(x)\, \mathrm{d}x = \delta_{m,n}2^n n!\sqrt{\pi} \tag{2.4}$$

(for the remainder of the paper all integrals will have limits of $-\infty$ to ∞) one obtains an expansion of the dilatated Hermite polynomials in terms of $H_n(x)$

$$H_s(\alpha x) = \sum_{\substack{n=s\,\mathrm{mod}2\\0\le n\le s}} \frac{s!}{n!\left(\frac{s-n}{2}\right)!}\alpha^n(\alpha^2 - 1)^{(s-n)/2}H_n(x) \tag{2.5}$$

Next, using a translation operator

$$H_n(x - \Delta) = \exp\left(-\Delta\frac{\mathrm{d}}{\mathrm{d}x}\right)H_n(x) \tag{2.6}$$

expanding the exponential and using the identity

$$\frac{\mathrm{d}}{\mathrm{d}x}H_n(x) = 2nH_{n-1}(x) \tag{2.7}$$

one obtains

$$H_n(x - \Delta) = \sum_{k=0}^{n}(-2\Delta)^k\frac{n!}{(n-k)!k!}H_{n-k}(x) \tag{2.8}$$

Using (2.5) and (2.8), making appropriate changes of integration variables, and simplifying, one arrives at the final result

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$$\int \psi_n(\alpha; x)\psi_{n'}(\alpha'; x - \Delta)\, dx = \exp\left[-\frac{(\alpha\alpha'\Delta)^2}{2(\alpha_+^{\ 2})}\right]\left(\frac{\alpha\alpha' n! n'!}{2^{n+n'}}\frac{2}{\alpha_+^{\ 2}}\right)^{1/2}\left(\frac{1}{\alpha_+^{\ 2}}\right)^{(n+n')/2} \times \sum_{l=0}^{\min[n,n']}\frac{1}{l!}\left(\frac{-\alpha_+^{\ 2}}{(\alpha'\alpha\Delta)^2}\right)^{l} \times \sum_{\substack{j=n\bmod 2\\ n\geq j\geq l}}\ \sum_{\substack{j'=n'\bmod 2\\ n'\geq j'\geq l}}\left[\frac{(\alpha_-^{\ 2})^{(n-j)/2}(-\alpha_-^{\ 2})^{(n'-j')/2}}{(\alpha_+^{\ 2})^{(j+j')/2}} \times \frac{\alpha^j\alpha'^{j'}(\alpha'^2)^j(-\alpha^2)^{j'}(2\Delta)^{j+j'}}{\left(\frac{n-j}{2}\right)!\left(\frac{n'-j'}{2}\right)!(j-l)!(j'-l)!}\right] \quad (2.9)$$

where $\alpha_+^{\ 2} = \alpha^2 + \alpha'^2$ and $\alpha_-^{\ 2} = \alpha^2 - \alpha'^2$.

This is a finite sum that can be computed easily. The behavior of the square of the overlap integrals, $|I_{n\to n'}|^2$, is shown in Figure 1 for some typical values of α, α', and Δ. It is easy to see that the summation is even or odd in Δ depending on the parity of $n + n'$. Thus, by examining the limits of the summation, one finds the leading term of $I_{n\to n'}$ for small Δ goes like $\Delta^{(n+n')\bmod 2}$.

The intensities of the Franck−Condon transitions are obtained by multiplying the square of the overlap integrals by appropriate phase-space factors,[10]

$$R_{n,n'} \propto \nu_{n,n'}|I_{n\to n'}|^2 \quad \text{(absorption)}$$

$$R_{n,n'} \propto \nu_{n,n'}^{\ 4}|I_{n\to n'}|^2 \quad \text{(emission)} \qquad (2.10)$$

3. Harmonic Oscillator, Algebraic Methods

An alternative derivation of (2.9) can be obtained by making use of algebraic methods. This derivation is of interest in its own sake, and in addition, it provides hints on how to extend the results to anharmonic Pöshl−Teller (or Morse) oscillators. The harmonic oscillator (Weyl−Heisenberg) algebra, $H(2)$, used in this section can in fact be viewed as a contraction of the algebra, $u(2)$, which describes Pöschl−Teller (or Morse) oscillators.[11−13] The inverse procedure of contraction (expansion) can be used to go from harmonic to anharmonic oscillators.

By introduction of the standard creation and annihilation operators

$$a^\dagger = (1/\sqrt{2})\left(x - \frac{d}{dx}\right)$$

$$a = (1/\sqrt{2})\left(x + \frac{d}{dx}\right) \qquad (3.1)$$

with the commutation relation $[a, a^\dagger] = 1$, one can recast the integrals in algebraic form. The algebraic form of the wave functions of the harmonic oscillator is

$$|n\rangle = (1/\sqrt{n!})(a^\dagger)^n|0\rangle \qquad (3.2)$$

In the algebraic derivation, the overlap integrals are calculated as the matrix elements of some operators, in particular the translation and dilatation operators.

The translation operator in coordinate space is

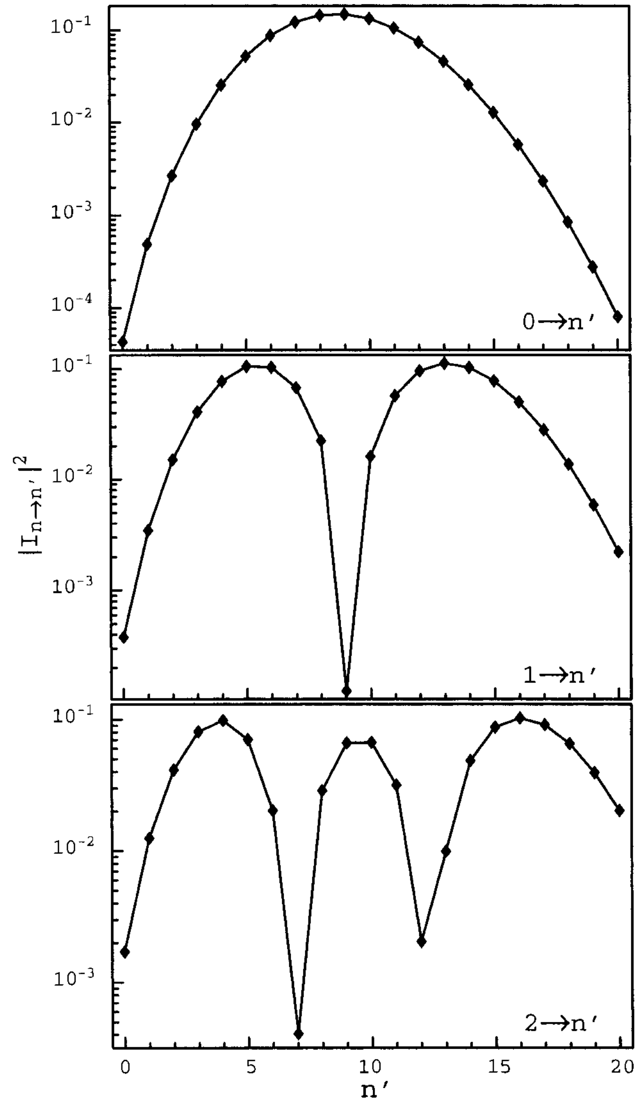

Figure 1. Square of the overlap integrals, $|I_{n\to n'}|^2$, vs n' for $n = 0$, 1, 2. The values of α, α', and Δ are determined by the harmonic approximation to the Morse oscillators fitting the S−S stretch progression of S_2O. They may be obtained from Table 1 via eq 4.10. A logarithmic scale is used to emphasize the fact that the overlap integrals vary over many orders of magnitude.

$$T(\Delta) = e^{\Delta(d/dx)}$$

$$\psi(x - \Delta) = T(-\Delta)\psi(x) \qquad (3.3)$$

Using (3.1), one can write down the algebraic form of $T(\Delta)$

$$T(\Delta) = \exp[(\Delta/\sqrt{2})(a - a^\dagger)] \qquad (3.4)$$

Evaluation of the matrix elements of $T(-\Delta)$ is an elementary quantum mechanical problem. The operators a, $a^\dagger$, $a^\dagger a$, and 1 form the well-known Weyl−Heisenberg algebra, $H(2)$,

$$[a, a^\dagger] = 1, \quad [a, a^\dagger a] = a, \quad [a^\dagger, a^\dagger a] = -a^\dagger \qquad (3.5)$$

To calculate

$$\frac{1}{\sqrt{n!n'!}}\langle 0|a^n \exp[-(\Delta/\sqrt{2})(a - a^\dagger)](a^\dagger)^{n'}|0\rangle \qquad (3.6)$$

one uses a special case of the Baker−Campbell−Hausdorff (BCH) formula:

$$e^{A}e^{B} = \exp(A + B + (1/2)[A, B]) \quad (3.7)$$

for any two operators A and B which commute with the commutator of A and B. When applied to (3.6), the BCH formula yields

$$\frac{e^{-\Delta^2/4}}{\sqrt{n!n'!}}\langle 0|a^n e^{(\Delta/\sqrt{2})a^\dagger} e^{-(\Delta/\sqrt{2})a}(a^\dagger)^{n'}|0\rangle \quad (3.8)$$

Expanding the exponentials and noting that the series truncates after a finite number of terms, one finds

$$\frac{e^{-\Delta^2/4}}{\sqrt{n!n'!}}\sum_{j',j=0}^{n',n}\frac{(\Delta/\sqrt{2})^j(-\Delta/\sqrt{2})^{j'}}{j'!j!}\langle 0|a^n(a^\dagger)^j a^{j'}(a^\dagger)^{n'}|0\rangle \quad (3.9)$$

Evaluating the remaining matrix element and simplifying, one obtains the final expression

$$\langle n|T(-\Delta)|n'\rangle = e^{-\Delta^2/4}\sqrt{n!n'!}(-1)^n(\Delta/\sqrt{2})^{n+n'}\sum_{0\le l\le \min(n',n)}\frac{(-\Delta^2/2)^{-l}}{(n'-l)!(n-l)!l!} \quad (3.10)$$

To evaluate Franck−Condon integrals for oscillators of different frequencies (or equivalently different α), one uses a dilatation operator

$$\exp\left(\alpha x\frac{d}{dx}\right)f(x) = f(e^{\alpha}x) \quad (3.11)$$

Hence, for the harmonic oscillator wave functions given by (2.2)

$$\psi_n(\alpha;x) = \sqrt{\alpha}\exp\left((\ln\alpha)\,x\frac{d}{dx}\right)\psi_n(x) \quad (3.12)$$

From (3.1) calculating overlaps for different α (and $\Delta = 0$) is equivalent to finding the matrix elements of the operator

$$D(\alpha) = \sqrt{\alpha}\exp[(\ln\alpha)(a^2 - a^{\dagger 2} - 1)/2] = \exp[(\ln\alpha)(a^2 - a^{\dagger 2})/2] \quad (3.13)$$

To calculate the matrix elements of $D(\alpha)$ one notes that the operators $a^{\dagger 2}$, a^2, and $a^\dagger a$ form the Lie algebra of $su(1,1)$[14]

$$[a^\dagger a, a^{\dagger 2}] = 2a^{\dagger 2}$$
$$[a^\dagger a, a^2] = -2a^2$$
$$[a^2, a^{\dagger 2}] = 2 + 4a^\dagger a \quad (3.14)$$

or, introducing the quasispin operators $J_+ = (1/2)a^{\dagger 2}$, $J_- = (1/2)a^2$, and $J_z = (1/4)(1 + 2a^\dagger a)$

$$[J_+, J_-] = -2J_z$$
$$[J_z, J_\pm] = \pm J_\pm \quad (3.15)$$

The matrix elements of the dilatation operator can thus be simply obtained from the group elements of $SU(1,1)$. Using a BCH factorization formula for $SU(1,1)$, one has

$$e^{\lambda(J_- - J_+)} = e^{-\tanh\lambda J_+}\, e^{-2\{\ln\cosh\lambda\}J_z}\, e^{\tanh\lambda\, J_-} \quad (3.16)$$

and consequently

$$D(\alpha) = e^{(\ln\alpha)(a^2 - a^{\dagger 2})/2} = e^{(-\ln\cosh\beta)/2}e^{-(\tanh\beta)a^{\dagger 2}/2}e^{-(\ln\cosh\beta)a^\dagger a}\, e^{(\tanh\beta)a^2/2} \quad (3.17)$$

where we have let $\beta = \ln\alpha$.

The matrix elements may now be calculated in a manner analogous to the calculations of (3.8)−(3.10). Expansion of the exponentials (except $e^{-(\ln\cosh\beta)a^\dagger a}$, which is diagonal) and simplification gives

$$\int\psi_n(x)\psi_{n'}(\alpha;x)\,dx = \langle n|D(\alpha)|n'\rangle = \sqrt{\frac{\alpha n!n'!}{2^{n+n'}}\frac{2}{1+\alpha^2}}\left(\frac{1}{\alpha^2+1}\right)^{(n+n')/2}\times \sum_{\substack{k=n=n'\mathrm{mod}2\\ \min(n,n')\ge k\ge 0}} 2^{2k}\frac{(1-\alpha^2)^{(n-k)/2}(\alpha^2-1)^{(n'-k)/2}\alpha^k}{k!\left(\frac{n-k}{2}\right)!\left(\frac{n'-k}{2}\right)!} \quad (3.18)$$

In order to obtain the complete result, one must combine the matrix elements of the translation and dilatation operators. The complete Franck−Condon overlap integral is

$$\int\psi_n(\alpha;x)\psi_{n'}(\alpha';x-\Delta)\,dx = \langle n|D(\alpha)^\dagger T(-\Delta)D(\alpha')|n'\rangle \quad (3.19)$$

Noting that $T(\Delta)D(\alpha) = D(\alpha)T(\alpha\Delta)$, $D(\alpha)^\dagger = D(\alpha)^{-1} = D(1/\alpha)$, and $D(\alpha)D(\alpha') = D(\alpha\alpha')$, one may rewrite (3.19) as

$$\langle n|D(\alpha)^\dagger T(-\Delta)D(\alpha')|n'\rangle = \langle n|T(-\bar{\Delta})D(\bar{\alpha})|n'\rangle \quad (3.20)$$

with $\bar{\Delta} = \alpha\Delta$ and $\bar{\alpha} = \alpha'/\alpha$.

Using the BCH factorizations of (3.8) and (3.17), the matrix elements become

$$\langle n|T(\Delta)D(\alpha)|n'\rangle = \frac{e^{-\Delta^2/4}}{\sqrt{\cosh\beta}}\langle n|e^{-(\Delta/\sqrt{2})a^\dagger}\, e^{(\Delta/\sqrt{2})a}e^{-\gamma a^{\dagger 2}}e^{-\eta a^\dagger a}e^{\gamma a^2}|n'\rangle \quad (3.21)$$

where

$$\eta = \ln\cosh\beta,\quad \gamma = (\tanh\beta)/2,\quad \text{and}\quad \beta = \ln\alpha \quad (3.22)$$

The computation of the matrix element $\langle n|T(\Delta)D(\alpha)|n'\rangle$ in terms of finite sums is still nontrivial. The calculation is simplified by using the BCH formula in its most general form

$$e^{A}e^{B} = \exp\left(A + B + \frac{1}{2}[A,B] + \frac{1}{12}([A,[A,B]] + [B,[B,A]]) + \ldots\right) \quad (3.23)$$

to obtain the result

$$e^{-\lambda\theta a^\dagger}e^{\lambda a}e^{\theta a^{\dagger 2}} = e^{\lambda^2\theta}e^{\lambda\theta a^\dagger}e^{\theta a^{\dagger 2}}e^{\lambda a} \quad (3.24)$$

valid for any arbitrary numbers θ and λ. Using (3.24) to reorder the exponentials in (3.21) the matrix elements become

$$\frac{e^{(-\Delta^2/4)(1+\tanh\beta)}}{\sqrt{\cosh\beta}}\langle n|e^{-(\Delta/\sqrt{2})(1+2\gamma)a^\dagger}e^{-\gamma a^{\dagger 2}}e^{(\Delta/\sqrt{2})a}e^{-\eta a^\dagger a}e^{\gamma a^2}|n'\rangle \quad (3.25)$$

Expanding the exponentials and simplifying as before, we obtain the final result

$$\int \psi_n(x)\psi_{n'}(\alpha; x-\Delta)\,dx = \langle n|T(-\Delta)D(\alpha)|n'\rangle = \exp\left[-\frac{\Delta^2}{2}\frac{\alpha^2}{\alpha^2+1}\right]\left(\frac{n!n'!}{2^{n+n'}}\frac{2\alpha}{\alpha^2+1}\right)^{(1/2)}\left(\frac{1}{\alpha^2+1}\right)^{(n+n')/2} \times \sum_{0\le l\le \min(n,n')} \frac{1}{l!\left(-\dfrac{\alpha^2\Delta^2}{\alpha^2+1}\right)^l} \times \sum_{\substack{l\le k\le n, k=n\bmod 2\\ l\le k'\le n', k'=n'\bmod 2}} \left[\frac{(\alpha^2-1)^{(n'-k')/2}(1-\alpha^2)^{(n-k)/2}}{(\alpha^2+1)^{(k+k')/2}} \times \frac{\alpha^{k'}(-\alpha^2)^k(-2\Delta)^{k+k'}}{(k-l)!(k'-l)!\left(\dfrac{n-k}{2}\right)!\left(\dfrac{n'-k'}{2}\right)!}\right] \quad (3.26)$$

Letting $\Delta \to \alpha\Delta$ and $\alpha \to \alpha'/\alpha$ verifies that this result is identical to that given in (2.9).

4. Anharmonic Morse Oscillator, Approximate Analytic Expressions

For transitions between low-lying states (n, n' small) the harmonic oscillator results are a good approximation to the Franck–Condon overlaps. However, in recent years, measurements of transitions up to very high n ($n \sim 20$) have become available. For these transitions, the harmonic oscillator results are no longer sufficient.

We consider specifically the Morse potential

$$V(x) = D[1 - e^{-a(x-x_0)}]^2 \quad (4.1)$$

shown in Figure 2. The overlap integrals between the eigenfunctions of two Morse potentials, (4.1) and (4.2),

$$V'(x) = D'[1 - e^{-a'(x-x'_0)}]^2 \quad (4.2)$$

differing in strength (D) and location (x_0) but having identical range ($a = a'$) can be calculated analytically.

The wave functions for the Morse potential (4.1) are given by

$$\psi_n(N, a; x-x_0) = \sqrt{a}M_{n,N}\,((N+1)\omega)^{(N/2)-n} \times \exp\left[-\frac{N+1}{2}w\right]L_n^{(N-2n)}[(N+1)w],$$
$$w = e^{-a(x-x_0)}, \quad M_{n,N} = \left(\sum_{j=0}^{n}\frac{\Gamma(N-2n+j)}{j!}\right)^{-1/2} \quad (4.3)$$

where $L_n^{(\alpha)}(x)$ are the generalized Laguerre polynomials and $(N+1)/2 = [D2\mu/(\hbar^2a^2)]^{1/2}$ (N is significant since, when integral, it labels representations of $u(2)$).

Integrals of the type

$$\int \psi_{n'}(N', a; x-x'_0)\psi_n(N, a; x-x_0)\,dx \quad (4.4)$$

may be readily evaluated by substituting in the defining relations of the Laguerre polynomials and recognizing the resulting integrals are simply representations of Gamma functions:

$$\int \psi_{n'}(N', a; x-x'_0)\psi_n(N, a; x-x_0)\,dx = M_{n',N'}M_{n,N}\,\zeta^{(N/2)-n}\left(\frac{2}{1+\zeta}\right)^{[(N+N')/2]-n'-n} \times \sum_{m,m'=0}^{n,n'}\left[\frac{(-)^{m+m'}}{m!m'!}\binom{N'-n'}{n'-m'}\binom{N-n}{n-m}\zeta^m\left(\frac{2}{1+\zeta}\right)^{m+m'} \times \Gamma\left(\frac{N+N'}{2}-n-n'+m+m'\right)\right] \quad (4.5)$$

where

$$\zeta = \frac{N+1}{N'+1}e^{-a(x'_0-x_0)} \quad (4.6)$$

and the binomial coefficient is given by

$$\binom{\alpha}{\beta} = \frac{\Gamma(\alpha+1)}{\Gamma(\beta+1)\Gamma(\alpha-\beta+1)} \quad (4.7)$$

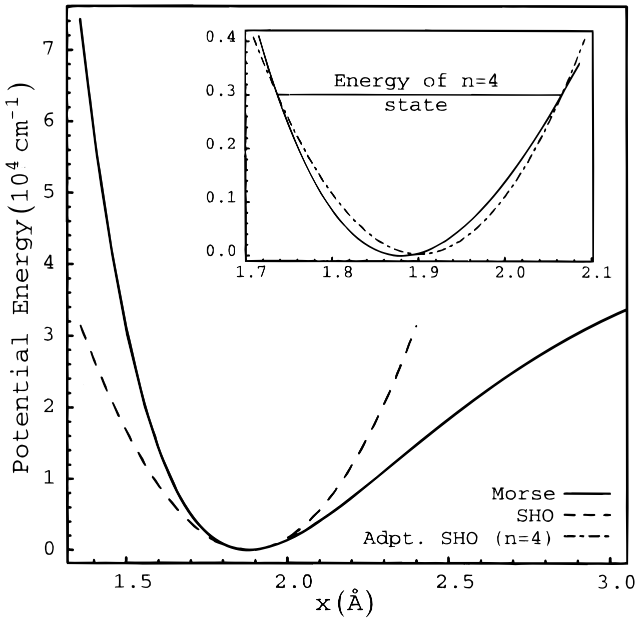

Figure 2. Morse potential corresponding to the first column of parameters in Table 1; the simple harmonic oscillator (SHO) approximating the Morse oscillator to second order, (inset) magnification of the Morse potential near the classical turning points for the $n = 4$ state, (inset) the harmonic oscillator adapted to give the best approximation to the Morse wave function at the $n = 4$ state.

The sum of (4.5) is finite and thus would seem useful in cases where $a = a'$. Unfortunately, for realistic molecules, N tends to be quite large ($N \sim 200$) and the alternating series of (4.5) becomes quickly unstable due to computational precision errors. Rearrangement of the summation has, as of yet, not significantly decreased these precision errors.

To evaluate overlap integrals for Morse functions with large N values (and in any event for the case $a \neq a'$), one must thus resort either to numerical quadrature or to an approximate analytic or algebraic evaluation. The results of such a numeric calculation are given in Figure 3. The parameters in this figure are taken as those that fit the S–S stretch progression of S_2O[15] (Table 1). The two Morse potentials differ in strength, D, range, a, and location, x_0.

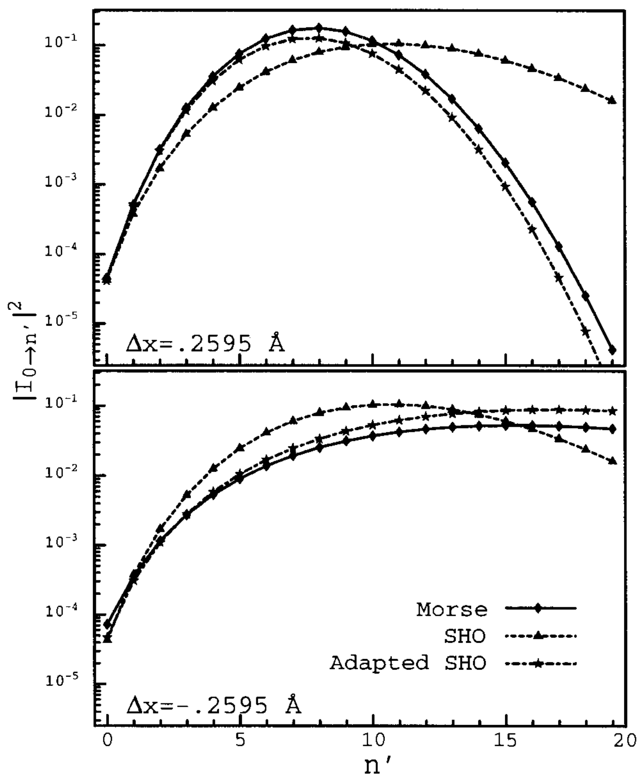

Figure 3. Square of the overlap integrals, $|I_{n\to n'}|^2$, vs n' for $n = 0$ calculated (1) numerically for a Morse potential, (2) analytically for the SHO approximating the Morse, (3) analytically using a dynamically adapted SHO. The top panel corresponds to the data of Table 1. The bottom panel is identical except $x_0 \to -x_0$ and $x_0' \to -x_0'$ (i.e., $\Delta \to -\Delta$).

TABLE 1

		final state	initial state
D	(cm^{-1})	48 151	20 523
a	(Å^{-1})	1.551	1.639
x_0	(Å)	1.8005	2.14
ω_e	(cm^{-1})	680.006	415.2
$\omega_e x_e$	(cm^{-1})	2.4008	2.10

In view of the fact that the Morse potential is not symmetric around x_0, the results depend crucially on whether the shift

$$\Delta = x_0' - x_0 \tag{4.8}$$

is positive or negative (upper and lower panels of Figure 3).

The Morse potential (4.1) can be approximated around its minimum by a harmonic oscillator

$$D[1 - e^{-a(x-x_0)}]^2 \approx Da^2(x - x_0)^2 \tag{4.9}$$

One can use, to this approximation, the formulas derived in sections 2 and 3 to calculate the overlap integrals. The appropriate values of α, α′, and Δ are given by

$$\frac{\hbar^2}{2\mu}\alpha^4 = Da^2, \quad \frac{\hbar^2}{2\mu}\alpha'^4 = D'a'^2, \quad \Delta = x_0' - x_0 \tag{4.10}$$

or, introducing the parameter of anharmonicity x_e

$$\alpha = \frac{a}{\sqrt{2x_e}}, \quad \alpha' = \frac{a'}{\sqrt{2x_e'}}, \quad \Delta = x_0' - x_0 \tag{4.11}$$

The results for the harmonic approximation, which are independent of the sign of Δ, are also shown in Figure 3. One can see that for large n, the results are rather poor. This is expected since as n increases, the Morse potential deviates more and more from the harmonic oscillator. A better approximation can be obtained by considering the classical turning points at energy E given by

$$x_\pm^M = x_0 - \frac{1}{a}\ln(1 \mp \sqrt{(E/D)})$$
$$\Delta x^M = x_+^M - x_-^M \tag{4.12}$$

The wave functions diminish rapidly to 0 outside of the turning points. Hence, at the nth energy level, the Morse wave functions would be best approximated by harmonic wave functions where the harmonic oscillator is adjusted so that its width is equal to the Morse width at the nth level and the minimum of the oscillator is midway between the Morse potential's turning points. In other words, the approximating harmonic oscillator is adapted to the Morse potential at each n.

Using the expression for the Morse energy levels in (4.12),

$$E = \hbar\omega_e\left(n + \frac{1}{2}\right)\left[1 - x_e\left(n + \frac{1}{2}\right)\right]$$
$$\omega_e = a\sqrt{(2D/\mu)} \tag{4.13}$$

and equating Δx^M with the analogous expression for the simple harmonic oscillator,

$$\Delta x^{SHO} = \frac{2\sqrt{2}}{\alpha}\left(n + \frac{1}{2}\right)^{1/2} \tag{4.14}$$

one finds

$$\alpha = \frac{2\sqrt{2}\left(n + \frac{1}{2}\right)^{1/2} a}{\ln\left(\frac{1 + g(x_e,n)}{1 - g(x_e,n)}\right)} \tag{4.15}$$

where

$$g(x_e, n) = 2\left[x_e\left(n + \frac{1}{2}\right)\left[1 - x_e\left(n + \frac{1}{2}\right)\right]\right]^{1/2} \tag{4.16}$$

Similarly, by finding the midpoint of the Morse potential's turning points and equating it with the midpoints of the harmonic oscillators turning points, one finds

$$\Delta = \left[x_0' - \frac{1}{2a'}\ln(1 - g(x_e', n')^2)\right] - \left[x_0 - \frac{1}{2a}\ln(1 - g(x_e, n)^2)\right] \tag{4.17}$$

Using (4.15)−(4.17) in the expressions of section 2 and 3 demonstrates much greater qualitative agreement with the Morse overlap integrals (Figure 3).

Since the anharmonicity is typically small, one may expand (4.15) and (4.17) to lowest order in x_e, x_e',

$$\alpha = \frac{a}{\sqrt{2x_e}}\left[1 - \frac{5}{6}x_e\left(n + \frac{1}{2}\right)\right]$$
$$\alpha' = \frac{a'}{\sqrt{2x_e'}}\left[1 - \frac{5}{6}x_e'\left(n' + \frac{1}{2}\right)\right] \tag{4.18}$$

$$\Delta = \left[x_0' + 2\frac{x_e'}{a'}\left(n' + \frac{1}{2}\right)\right] - \left[x_0 + 2\frac{x_e}{a}\left(n + \frac{1}{2}\right)\right] \quad (4.19)$$

for smaller n and n'. Comparing (4.18)−(4.19) with (4.11) reveals that we may in some sense interpret this approximation as a low-order correction in the anharmonicities. Since the turning point approximation contains all the necessary features of Franck−Condon transitions for anharmonic oscillators, the expression (2.9) with

$$\alpha = \alpha_0\left(1 - \xi\left(n + \frac{1}{2}\right)\right)$$

$$\alpha' = \alpha_0'\left(1 - \xi'\left(n' + \frac{1}{2}\right)\right)$$

$$\Delta = \Delta_0 + \eta\left(n + \frac{1}{2}\right) - \eta'\left(n' + \frac{1}{2}\right) \quad (4.20)$$

where α_0, α_0', ξ, ξ', Δ_0 are parameters (effective parameters which compensate for higher order contributions in (4.18)−(4.19)) and

$$\eta = \frac{2}{\alpha_0}\sqrt{\frac{3}{5}\xi}, \quad \eta' = \frac{2}{\alpha_0'}\sqrt{\frac{3}{5}\xi'}$$

can be used to analyze Franck−Condon transition intensities for stretching vibrations. A similar expression applies to Pöschl−Teller oscillators (appropriate to bending vibrations) except that these potentials are now symmetric about x_0, x_0' and hence $\eta = \eta' = 0$. An analysis of experimental data in S_2O will be presented in a forthcoming publication.[15]

5. Conclusions

In this article, we have given a compact expression for the Franck−Condon overlap integrals between harmonic oscillator wave functions with different frequencies (ω, ω'), which are displaced by an amount Δ. These differ from previous results in that the expression is given as an easily computed finite sum. These results have been obtained by using both analytic and algebraic methods. In particular, the algebraic evaluation is of interest, since it makes use of nontrivial mathematical results to evaluate matrix elements of exponential functions of quadratic operators, $a^2 - a^{\dagger 2}$. We have also presented an approximate expression for the Franck−Condon overlaps of Morse oscillators based on the harmonic expression previously derived but including anharmonic corrections. This form is of great interest for the analysis of experimental data, since it provides an explicit expression, which can be combined with the algebraic wave functions to calculate Franck−Condon intensities in polyatomic molecules.

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