SIMPLE EVALUATION OF FRANCK-CONDON FACTORS AND NON-CONDON EFFECTS IN THE MORSE POTENTIAL

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Abstract

The calculation of Franck-Condon factors between different one-dimensional Morse potential eigenstates using a formula derived from the Wigner function is discussed. Our numerical calculations using a very simple program written in Mathematica is compared with other calculations. We show that our results have a similar accuracy as the calculations performed with more sophisticated methods. We discuss the extension of our method to include non-Condon effects in the calculation.

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1 Introduction

The study of complex features of molecular vibrational spectra at high overtones and combinations has become possible by recent advances in optical laser spectroscopy. Rovibrational level structure of small polyatomic molecules has been elucidated in a formerly inaccessible energy range. Transition intensities between these levels can reveal fine aspects of the structure and dynamical properties of these systems. Theoretically, the evaluation of molecular vibrational wave functions has relied upon a number of assumptions and approximations, of which the use of a harmonic normal-mode basis is the best known procedure. At higher energies, however, normal-mode vibrational assignments of individual states becomes more difficult due to anharmonic effects. In this context, Morse potentials [1] have been proposed to more accurately model molecular systems, as they often constitute good approximations to diatomic molecular potentials derived \textit{ab initio} [2]. Even if the general solutions to the corresponding Schrödinger equation cannot be written in analytical form, the case of zero angular momentum can be closely approximated by the one-dimensional analytical solutions [3]. The analytic form of these wave functions has been used not only for the simple diatomic case, but for the analysis of vibrational structure in polyatomic molecules, within a local-mode framework (see eg. [4, 5, 6, 7]). In addition, the connection of the one-dimensional Morse, Poeschl-Teller and other exactly solvable potentials with the $SU(2)$ group has been exploited in the formulation of algebraic models which incorporate the anharmonic character of the local vibrations from the outset (see [8] and references therein).

In recent studies, the Lie-algebraic approach has been also applied to the evaluation of Franck-Condon intensities [9, 10] (FC) in small polyatomic molecules [5, 6, 7]. These studies accurately reproduce the emission spectra of the $S_2O \ C^1 A' - \bar{X}^1 A' (\pi^*-\pi)$ experimental intensities [6], requiring for their calculation a combination of two procedures: a) an accurate fit of the vibrational energy levels in both electronic states using a local-mode algebraic Hamiltonian, and b) an efficient and accurate methodology for the evaluation of one-dimensional Morse wave function overlaps. One possibility to calculate overlaps of Morse wave functions is to use an approximation based on an energy-dependent harmonic approximation where the widths and displacement of the harmonic potentials are adjusted in order to mimic the behavior of the Morse potentials at the corresponding energy levels [4]. Although this method gives explicit formulas for the overlap integrals, and consequently a good accuracy for the low lying vibrational states, it departs from the exact results at higher energies. Other (numerical) methods, like the use of the Configuration Localized States (CLS) formalism and the use of Gaussian quadratures [11, 12] have been proposed as alternative ways to evaluate the overlaps of two Morse functions.

In view of future applications to the evaluation of multidimensional Franck-Condon factors, a simple and reliable method of calculation of one-dimensional Morse functions overlaps has to be devised. In this paper we propose a new method of evaluation based on our recent work on the Wigner function of the Morse potential eigenstates [13]. Our main result contains analytical sums of simple one-dimensional integrals which are not tabulated and which must be evaluated with standard numerical techniques. We make no approximations but must rely on numerical evaluations for part of our calculations. Fortunately, present computational resources (like \textit{Mathematica}) can handle these calculations with very high accuracy in
a simple and efficient way. We show that a short program written in Mathematica (included in an appendix) gives accurate results for several molecular examples. To demonstrate the reliability of the method we compare our results with other calculations and provide estimates for its range of applicability. In the last section we show that the procedure can be extended, with no loss of accuracy, in order to include non-Condon effects.

2 The Morse Potential Eigenstates

In what follows we briefly review the properties of the Morse potential eigenstates and the use of the corresponding Wigner function to evaluate their overlap. We then express our result in terms of the integral $I_a$ (eq. (22)), for which we find a symmetry property and a recurrence relation, which can be used to verify the accuracy of its numerical evaluation. After discussing some particular analytic solutions, we apply our method to several examples and compare our results with more sophisticated techniques [6, 11, 14].

The Morse potential is characterized by two parameters: its depth $D$ (bonding energy), and the inverse of its range $\beta > 0$ (restitution constant in the harmonic approximation). In the one-dimensional version it is given by

$$V(x) = D \left[ (1 - e^{-\beta x})^2 - 1 \right], \quad (-\infty < x < \infty), \quad (1)$$

where $x$ is the position with respect to the equilibrium point.

It is well known that the discrete spectrum of the Morse potential is described by the formula

$$E_\nu = -\frac{\hbar^2 \beta^2}{2\mu} (j - \nu)^2, \quad (2)$$

where

$$j = \frac{\sqrt{2\mu D}}{\beta \hbar} - \frac{1}{2}, \quad (3)$$

while $\nu$ is the number of anharmonic phonons $\nu = 0, 1, \ldots \lfloor j \rfloor$, with $\lfloor j \rfloor$ being the largest integer not exceeding $j$, and $\mu$ the reduced mass of the molecule.

If $j$ takes an integer or half integer value, it determines the irreducible representation $D^j$ of the $SU(2)$ algebra which is the dynamical algebra of the Morse potential. In general there are $\lfloor j \rfloor + 1$ bound states, except when $j$ is an integer, in which case one state has zero energy.

The eigenfunctions corresponding to the eigenvalue (2) are given by

$$\psi_{j,\nu}^\beta(\xi) = N_{j,\nu} e^{-\xi^2/2} \xi^{j-\nu} L_{\nu}^{2(j-\nu)}(\xi), \quad (4)$$

where a new variable (the Morse coordinate)

$$\xi = (2j + 1)e^{-\beta x}, \quad (5)$$
has been introduced. The wave function (4) includes the associated Laguerre polynomials [15]

\[
L^{\alpha}_{\nu}(\xi) = \sum_{k=0}^{\nu} (-1)^k \frac{\Gamma(\nu + \alpha + 1)}{k!(\nu - k)!\Gamma(k + \alpha + 1)} \xi^k ,
\]

normalized by the condition

\[
\int_{-\infty}^{\infty} dx |\psi_{j\nu}^{\beta}(x)|^2 = 1 ,
\]

when the normalization factor is taken in the form

\[
(N_{j\nu}^{\beta})^2 = \frac{\beta \nu ! 2(j - \nu)}{\Gamma(2j - \nu + 1)} .
\]

The eigenvalues (2) can be written as

\[
E_{\nu} = -D + \hbar \omega_e (\nu + 1/2) - \hbar \omega_e \chi(\nu + 1/2)^2 ,
\]

where

\[
\hbar \omega_e = \beta \hbar \sqrt{\frac{2D}{\mu}} ,
\]

\[
\hbar \omega_e \chi = \frac{\hbar^2 \beta^2}{2\mu} .
\]

These relations relate the parameters of the Morse potential with the standard spectroscopic parameters \(\omega_e\) and \(\omega_e \chi\) [16]. In particular we have

\[
2j + 1 = \frac{\omega_e}{\omega_e \chi} = 4 \frac{D}{\hbar \omega_e} ,
\]

and

\[
\beta = \sqrt{\frac{4\pi c}{\hbar} \mu \omega_e \chi} .
\]

### 3 Franck-Condon factors for the Morse Potential

Molecular Franck-Condon factors describe, in first approximation, the dependence on the vibrational wave functions of transition intensities between vibrational states in different electronic configurations. Assuming that the electronic wave functions are independent of the vibrational states (Condon approximation [10]), the Franck-Condon factors are given by the square of the overlap integral between initial and final wave functions in the transition

\[
F_{1,2} \equiv |f_{1,2}|^2
\]
where
\[ f_{1,2} = \langle \psi_{j_1,v_1}^{\beta_1} (x - R_1) | \psi_{j_2,v_2}^{\beta_2} (x - R_2) \rangle, \] (15)
and \( R_1 \) and \( R_2 \) are the equilibrium distances of the nuclei in the initial and final electronic states, respectively. Relative transition intensities, in the Condon approximation, are simply related to the Franck-Condon factors (14) by [6]
\[ I_{1,2} \propto \nu^4 |f_{1,2}|^2, \]
where the frequency dependent factor \( \nu^4 \) (\( \nu \) is essentially the difference between vibrational energies of the initial and final states in the transition), is introduced for calibration with experimental data.

In a higher approximation (Non-Condon), the electric dipole operator for transitions is expressed as a series expansion on the interatomic coordinates [17] or, equivalently, as a series expansion in one of the Morse coordinates \( \xi_1(x) \) or \( \xi_2(x) \). Our method can be adapted to include such effects in a straightforward manner (see discussion below).

A simple way to calculate the FC factors arises from the Wigner function of two Morse wave functions, which we define in the form [13]
\[ W(\psi_{j_1,v_1}^{\beta_1} | x, p) = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} dr \psi_{j_1,v_1}^{\beta_1}(x - \frac{1}{2}r) e^{-ipr/\hbar} \psi_{j_2,v_2}^{\beta_2}(x + \frac{1}{2}r). \] (16)
Making the change of variable \( z = \frac{1}{2}r \) and taking into account that
\[ \psi_{j_1,v_1}^{-\beta_1}(x - z) = \left( \frac{\mathcal{N}_{j_1,v_1}^{(-\beta_1)}}{\mathcal{N}_{j_1,v_1}^{\beta_1}} \right) \psi_{j_1,v_1}^{\beta_1}(z - x) = \psi_{j_1,v_1}^{\beta_1}(z - x), \] (17)
where \( \psi_{j_1,v_1}^{-\beta_1}(x) \) is the wave function corresponding to the mirror image of the Morse potential (1) whose normalization \( \mathcal{N}_{j_1,v_1}^{(-\beta_1)} \) is clearly also given by (8).

We then find the expression
\[ W(\psi_{j_1,v_1}^{-\beta_1}, \psi_{j_2,v_2}^{\beta_2} | x, p) = -\frac{1}{\pi \hbar} \int_{-\infty}^{\infty} dz \psi_{j_1,v_1}^{-\beta_1}(x - z) e^{-2ipz/\hbar} \psi_{j_2,v_2}^{\beta_2}(z + x). \] (18)
If we evaluate the integral at \((x = \frac{1}{2}(R_2 - R_2), p = 0)\) we get precisely the overlap integral between \( \psi_{j_1,v_1}^{\beta_1} \) and \( \psi_{j_2,v_2}^{\beta_2} \), and thus
\[ f_{1,2} = -\pi \hbar W(\psi_{j_1,v_1}^{-\beta_1}, \psi_{j_2,v_2}^{\beta_2} | x = \frac{1}{2}(R_2 - R_2), p = 0). \] (19)

In Appendix A we calculate the Wigner function corresponding to two different Morse potential states (4), leading to the following expression for the Franck-Condon factor:

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5These coordinates are the natural coordinates appearing in the eigenfunctions of the Morse potential and are defined as \( \xi_1(x) = (2j_1 + 1) \exp(-\beta_1 x_1) \) and \( \xi_2(x) = (2j_2 + 1) \exp(-\beta_2 x_2) \) (see Eq. (5))
\[ f_{1,2} = 2 \sqrt{\frac{\nu_1!\nu_2!(j_1 - \nu_1)(j_2 - \nu_2)}{\Gamma(2j_1 - \nu_1 + 1)\Gamma(2j_2 - \nu_2 + 1)}} y_1^{j_1 - \nu_1} y_2^{j_2 - \nu_2} \]

\[ \times \sum_{\ell_1, \ell_2=0}^{\nu_1, \nu_2} \frac{(-1)^{\ell_1 + \ell_2}}{\ell_1!\ell_2!} \left( \frac{2j_1 - \nu_1}{\nu_1 - \ell_1} \right) \left( \frac{2j_2 - \nu_2}{\nu_2 - \ell_2} \right) y_1^{\ell_1} y_2^{\ell_2} \]

\[ \times J_a(j_1 - \nu_1 + \ell_1, j_2 - \nu_2 + \ell_2, y_1, y_2) \] \hspace{1cm} (20)

where

\[ y_1 = (2j_1 + 1)e^{-\beta_1(R_2 - R_1)/2}, \]
\[ y_2 = (2j_2 + 1)e^{+\beta_2(R_2 - R_1)/2}, \] \hspace{1cm} (21)

and

\[ J_a(k_1, k_2, y_1, y_2) = \int_{0}^{\infty} du \, u^{k_1 + a - 1} e^{-\frac{1}{2}(y_1 u + y_2 u^a)}, \] \hspace{1cm} (22)

with \( a = \frac{\beta_2}{\beta_1}, \) \( k_1 = j_1 - \nu_1 + \ell_1 \) and \( k_2 = j_2 - \nu_2 + \ell_2. \)

Overlap integrals of the type (22) were previously encountered in ref.[18], where it is stated that they “cannot be evaluated exactly in general (for \( a \neq 1 \))” and “it is necessary to resort to a valid approximation”. In addition, it was stated that the alternating sums involved in (20) may give unstable results as a consequence of the numerical error accumulation when the sums are performed over very large numbers, a situation that can arise for realistic calculations involving large values of \( j_1 \) or \( j_2. \)

As mentioned in the introduction, several approaches have been proposed to find FC factors (20) in analytic form, including the use of different versions of the harmonic oscillator approximation of the Morse wave functions [4, 5, 6, 19, 20], the expansion of the integral (22) into series containing polygamma functions [21], the use of a Laguerre quadrature [11], and others. We now show that the integral (22), although not tabulated, is an analytical well-behaved function which satisfies relations which can be used for its reliable evaluation using a personal computer. In particular we have found that the program *Mathematica* can be applied to calculate those integrals with high accuracy in an efficient way.

We start our study by stating the following properties of the integral \( J_a \):

1. Symmetry property:

\[ J_a(k_1, k_2, y_1, y_2) = \frac{1}{a} J_{1/a}(k_2, k_1, y_2, y_1), \] \hspace{1cm} (23)

which follows from (22) and the change of variables \( u' = u^a. \)

As an application of (23) we can check the accuracy of the integration appearing in the transition \( A^1\Sigma_u^+(\nu = 0) \rightarrow X^1\Sigma_g^-(\nu = 0) \) of the \( ^7\text{Li}_2 \) molecule (Table 4). In
this case the difference of both calculations \( J_a - \frac{1}{a} J_{1/a} \) is \(-1.71551 \times 10^{-67}\) where \( J_a \approx \frac{1}{a} J_{1/a} \approx 1.14752 \ldots \times 10^{-53}\). This shows the typical precision in the computations of integrals (22). In order to get such an accuracy we have used a scaling method for the integral. This procedure is discussed below.

2. Recurrence relation:

\[
J_a(k_1, k_2, y_1, y_2) = \frac{1}{y_1} [2(k_1 + a k_2 - 1) J_a(k_1 - 1, k_2, y_1, y_2) - a y_2 J_a(k_1 - 1, k_2 + 1, y_1, y_2)] + \delta_{\alpha, 1},
\]

(24)

where \( \alpha = k_1 + a k_2 \). This property follows by carrying out the integration by parts. Note that \( \alpha = 1 \) can only occur for the case \( a = 1 \) (\( \beta_1 = \beta_2 \)).

Regarding the application of the three-term recurrence relation (24), we observe that it can be used to find one such integral if the other two included in this relation are known. It is therefore possible to find a full set of integrals (22) with all possible values of \( k_1 = 1, \ldots, N_1, k_2 = 1, \ldots, N_2 \) if the integrals \( J_a(k_1 = 1 \ldots N_1, k_2 = 1, y_1, y_2) \) and \( J_a(k_1 = 1, k_2 = 1 \ldots N_2 + 1, y_1, y_2) \) are known for given \( a, y_1, \) and \( y_2 \). The relation (24) can be used in two ways: to check the accuracy of the numerical integrations and to calculate the values of the other integrals.

As example we use the recurrence relation (24) to check the accuracy of the integrations involved in the transition \( A^1 \Sigma_u^+(\nu = 6) \rightarrow X^1 \Sigma_g^+(\nu = 6) \) of \( ^7 \text{Li}_2 \) molecule (see Table 4). Let us consider the integral \( J_a \) (Eq. 22) with \( (\ell_1 = 0, \ell_2 = 1) \) and compute it by numerical integration and with the recurrence relation (24). For this we need to compute integrals with \( (\ell_1 = 0, \ell_2 = 0) \) and \( (\ell_1 = 0, \ell_2 = 1) \). The absolute difference of both calculations is \( 3.17601 \times 10^{-67} \), being \( J_a \approx 2.07527 \ldots \times 10^{-53} \), in agreement with the estimated precision obtained with the symmetry relation.

Relations (23) and (24) led to a simple method to verify the accuracy of the numerical integration. We are currently studying other properties of the function (22), which is a generalization of the \( \Gamma \) function, to which it reduces in the case \( a = 1 \).

In realistic cases, quite often the overlaps must be calculated for states with rather large values of the parameters \( j_1 \) or \( j_2 \) (or equivalently for large bonding energies, see Eq. (3)). In this cases the numerical integration of (22) requires a special treatment in order to achieve high accuracy. Although the integrand is a well behaved function of \( x \) having a single maximum and going to zero at \( x \to 0 \) and \( x \to \infty \), the resulting integral, being a very small number, could be difficult to evaluate due to the limited precision of the numerical calculations. One way to deal with such complications is to perform a change of variables in order to scale the integrand in such a way that the integrand at the maximum acquires a unit value at \( x = 1 \). In all cases studied, we have found that the best procedure to evaluate (22) is by carrying out a scaled integration. Our tests showed that the relative differences of the integrals calculated using formula (22) and the symmetry relation (23) are very small (\( \lesssim 10^{-13} \)) when the scaled
integrations are used in both cases.

As our first example we have calculated Franck-Condon factors for the $S - S$ mode in the $S_2O$ molecule (Table 1). We found a maximal relative difference $\simeq 3.14 \times 10^{-14}$ between the scaled integrals (22) and the scaled integration using the symmetry relation (23). Despite the fact that the numerical integration can be calculated with high accuracy, it is not always enough to compensate for the loss of accuracy due to the alternating sums involved in (20). This becomes more apparent in the cases in which we have a significant number of terms in the summations. We can see this effect in the results of Table 1 (e.g. for $\tilde{\nu}_X = 7$ and $\tilde{\nu}_C = 6$). The use of logarithms to evaluate the products (and divisions) of the very large numbers appearing in (20) is usually a good strategy to avoid some problems. However we have also calculated the FC factors using this strategy and found no significant improvement in the results.

In Table 1 we compare our results with calculations using the method of quadratures proposed in [11, 12], and with the algebraic formulation using modified harmonic functions of ref. [4]. Our results are in excellent agreement with the results of ref. [11] except for the corner in the table close to $\tilde{\nu}_X = 7$ and $\tilde{\nu}_C = 6$ where the calculations exhibit some deviations due to the above mentioned loss of accuracy in the sums.

The approach using modified harmonic functions is in this case expected to be a good approximation (at least for the overlaps between the lowest-lying states) since we have large values of the parameters $j_1, j_2$ (large depths $D_1, D_2$). However, there are significant deviations with respect to our results even for this extreme case.

For the sake of completeness we now discuss some exactly solvable examples of the FC formula (20):

1. $\beta_1 = \beta_2$  ($a = 1$). In this case we have [11]:

\[
J_{\alpha=1}(j_1 - \nu_1 + \ell_1, j_2 - \nu_2 + \ell_2, y_1, y_2) = \int_0^\infty du \exp \left[ -\frac{1}{2}(y_1 + y_2)u \right] u^{\alpha-1} = \Gamma(\alpha) \left( \frac{y_1 + y_2}{2} \right)^{-\alpha} \tag{25}
\]

with $\alpha = k_1 + k_2 = j_1 - \nu_1 + \ell_1 + j_2 - \nu_2 + \ell_2$, and thus

\[
f_{1,2}^{\alpha=1} = 2 \sqrt{\frac{\nu_1!\nu_2!(j_1 - \nu_1)(j_2 - \nu_2)}{\Gamma(2j_1 - \nu_1 + 1)\Gamma(2j_2 - \nu_2 + 1)}} y_1^{j_1 - \nu_1} y_2^{j_2 - \nu_2} \times \sum_{\ell_1, \ell_2 = 0}^{\nu_1, \nu_2} \frac{(-1)^{\ell_1 + \ell_2}}{\ell_1!\ell_2!} \left( \begin{array}{c} 2j_1 - \nu_1 \\ \nu_1 - \ell_1 \end{array} \right) \left( \begin{array}{c} 2j_2 - \nu_2 \\ \nu_2 - \ell_2 \end{array} \right) y_1^{\ell_1} y_2^{\ell_2} \left( \frac{2}{y_1 + y_2} \right)^{\alpha} \Gamma(\alpha). \tag{26}
\]

\[
7
\]
If we define:
\[ \zeta = \frac{2j_2 + 1}{2j_1 + 1} e^{-\beta(R_2 - R_1)} = \frac{y_2}{y_1}, \]
we obtain the same expression as Eq. (4.5) in Ref. [11]. The results for the Franck-Condon factors obtained through the numerical integration of (22) and with the analytic formula (26) are of comparable accuracy. This gives another indication that the main source for the loss of accuracy is due to the alternating sums appearing in (20), (26). To check the accuracy of the numerical integration (22), we have calculated its relative difference with the analytical result (25) for a broad range of values (e.g. for \( y_1 = y_2 = 100 \) and \( \alpha \equiv k_1 + k_2 = 1\ldots200 \)) and found a maximal relative difference of \( \Delta(\beta_\alpha) \lesssim 5 \times 10^{-13} \). However we should note that the analytical result for the integration (25) can also lead to uncertainties when it is numerically evaluated, specially for large values of \( \alpha \) and/or \( y_1, y_2 \).

2. \( \beta_2 = 2\beta_1, \quad (a = 2) \). In this case we have
\[
\begin{aligned}
I_{a=2}(j_1 - \nu_1 + \ell_1, j_2 - \nu_2 + \ell_2, y_1, y_2) &= \int_0^\infty du \exp \left[ -\frac{1}{2}(y_1u + y_2u^2) \right] u^{\alpha-1} \\
&= (y_2)^{-\frac{\alpha}{2}} \Gamma(\alpha) \exp \left( \frac{y_1^2}{16y_2} \right) D_{-\alpha} \left( \frac{y_1}{2\sqrt{y_2}} \right),
\end{aligned}
\]
\( D_{-\alpha} \) being the cylindrical functions [15] with \( \alpha = j_1 - \nu_1 + \ell_1 - 2j_2 - 2\nu_2 - 2\ell_2 \), and thus

\[
\begin{aligned}
f_{1,2}^{a=2} &= 2 \sqrt{\frac{2\nu_1\nu_2!(j_1 - \nu_1)(j_2 - \nu_2)}{\Gamma(2j_1 - \nu_1 + 1)\Gamma(2j_2 - \nu_2 + 1)}} y_1^{j_1 - \nu_1} y_2^{j_2 - \nu_2} \\
&\times \sum_{\ell_1, \ell_2 = 0}^{\nu_1, \nu_2} \frac{(-1)^{\ell_1 + \ell_2}}{\ell_1!\ell_2!} \left( \frac{2j_1 - \nu_1}{\nu_1 - \ell_1} \right) \left( \frac{2j_2 - \nu_2}{\nu_2 - \ell_2} \right) \\
y_1^{\ell_1} y_2^{\ell_2} (y_2)^{-\frac{\alpha}{2}} \Gamma(\alpha) \exp \left( \frac{y_1^2}{16y_2} \right) D_{-\alpha} \left( \frac{y_1}{2\sqrt{y_2}} \right).
\end{aligned}
\]

3. \( \beta_2 = \frac{1}{2}\beta_1, \quad a = \frac{1}{2} \)
In this case we have
\[
\begin{aligned}
I_{a=\frac{1}{2}}(j_1 - \nu_1 + \ell_1, j_2 - \nu_2 + \ell_2, y_1, y_2) &= \int_0^\infty du \exp \left[ -\frac{1}{2}(y_1u + y_2\sqrt{u}) \right] u^{\alpha-1} \\
&= 2J_2(j_2 - \nu_2 + \ell_2, j_1 - \nu_1 + \ell_1, y_1, y_2),
\end{aligned}
\]
where we have used the symmetry property (23), and therefore
\[
\begin{aligned}
f_{1,2}^{a=\frac{1}{2}} &= 4 \sqrt{\frac{2\nu_1\nu_2!(j_1 - \nu_1)(j_2 - \nu_2)}{\Gamma(2j_1 - \nu_1 + 1)\Gamma(2j_2 - \nu_2 + 1)}} y_1^{j_1 - \nu_1} y_2^{j_2 - \nu_2}
\end{aligned}
\]
\[
\sum_{\ell_1, \ell_2 = 0}^{\nu_1, \nu_2} \frac{(-1)^{\ell_1 + \ell_2}}{\ell_1! \ell_2!} \left( \begin{array}{cc} 2j_1 - \nu_1 & 2j_2 - \nu_2 \\ \nu_1 - \ell_1 & \nu_2 - \ell_2 \end{array} \right) \\
y_1^{\ell_1} y_2^{\ell_2} \left( \frac{y_2}{\gamma} \right)^{-\alpha} \frac{\Gamma(\alpha)}{2} \exp \left( \frac{y_1^2}{16y_2} \right) D_{-\alpha} \left( \frac{y_1}{2\sqrt{y_2}} \right), \tag{31}
\]

with \( \alpha = 2j_1 - 2\nu_1 + 2\ell_1 + j_2 - \nu_2 + \ell_2 \).

These particular cases can also be used to check the accuracy of the general result (20, 22).

### 4 Examples

Continuing with our comparison with other approaches, we have considered (i) the case of two identical (but displaced) Morse potentials and (ii) the case of two different Morse potentials. We have taken these examples from ref. [11]. Our results are identical to those obtained in [11] where an analytical approximation for the Morse functions overlaps based on the use an integration by quadratures was used (see Tables (2) and (3)). Perhaps this is not surprising since the corresponding values of \( j_1, j_2 \) are small. The accuracy of the numerical calculations is high given that the effects of the numerical instabilities coming from the alternating sums are relatively small. The relevant point, as observed in [11], is that the deviations in the results obtained from harmonic functions relative to those using the Morse functions are larger when the depths \( D \) (and correspondingly the \( j \) values) are small.

As a next set of examples we have considered the vibrational transitions studied by Ley-Koo and collaborators [14]. In ref. [14] Franck-Condon factors of diatomic molecules were calculated by means of 3-dimensional Morse functions via the method of confinement in a box. The solutions of the radial Schrödinger equation were found by diagonalization of the Hamiltonian in a large basis (\( N \sim 600 \)) of free-particle eigenfunctions with appropriate boundary conditions. We have borrowed some tables from ref. [14] to facilitate the comparisons. Our results for the Franck-Condon factors are in excellent agreement with those of Ley-Koo and collaborators (see Tables 4, 5, 6, 7). This shows on the one hand that in spite of the fact that we use 1-dimensional Morse functions, the contributions coming from the unphysical region \( (-\infty < x < 0) \) are entirely negligible, and on the other, that our simple procedure achieves results with a similar accuracy as those arising from the numerically intensive and sophisticated methods.

The specific transitions which are included for comparisons are:

1. \( A^1\Sigma_u^+ - X^1\Sigma_g^+ \) in \(^7\text{Li}_2\) molecule (Table 4).
2. \( B^1\Pi_u^+ - X^1\Sigma_g^+ \) in \(^7\text{Li}_2\) molecule (Table 5).

\(^6\)In Ref. [11] it was suggested to calculate the Franck-Condon matrix elements using the Laguerre quadrature in order to avoid the calculation of the alternative sum in (20). However this approach may present a similar disadvantage since the calculation involves a sum over all positive and negative nodes of a polynomial.
3. $A^2\Pi_2 - X^2\Sigma^+$ in CN molecule (Table 6).

4. $B^3\Pi_g - A^3\Sigma^+_u$ in N$_2$ molecule (Table 7).

Tables 4, 5, 6, 7 contain results of calculations arising from analyses of experimental data [22, 23, 24, 25, 26], simple harmonic oscillator approximations [27, 28], anharmonic approximations [20, 29], graphical integration [30], asymptotic expansions [31] and by the method of confinement of Morse potentials in a box [14]. We emphasize that we are concerned with an accurate evaluation of the overlap of two Morse functions and thus comparisons have to be done with similar calculations, in particular with the results obtained by Ley-Koo and coauthors [14].

5 Non-Condon Effects

Our method can be generalized to include non-Condon effects by taking into account more terms in the expansion of the electric dipole operator. Assuming a power expansion in terms of one of the Morse coordinates, say $\xi_1$ [32]

$$\mathcal{T}(\xi_1) = \sum_{\eta=0}^{\infty} a_\eta (\xi_1)^\eta,$$

(32)

and following a similar calculation to that leading to (20), we obtain for the dipole transition

$$\langle j_2, \nu_2 | \mathcal{T} | j_1, \nu_1 \rangle \equiv \int_{-\infty}^{+\infty} \psi_{j_2 \nu_2}^*(x) \mathcal{T}(\xi_1(x)) \psi_{j_1 \nu_1}(x) \, dx$$

(33)

$$= 2 \sqrt{a \nu_1! \nu_2! (j_1 - \nu_1)(j_2 - \nu_2)} \frac{y_1^{j_1-\nu_1} y_2^{j_2-\nu_2}}{\Gamma(2j_1-\nu_1+1)\Gamma(2j_2-\nu_2+1)} \sum_{\ell_1, \ell_2=0}^{\nu_1, \nu_2} \frac{(-1)^{\ell_1+\ell_2}}{\ell_1! \ell_2!} \sum_{\eta=0}^{\infty} a_\eta \cdot \left\{ J_a(k_1 + \eta, k_2, y_1, y_2) \right\},$$

with $a = \frac{\partial^2}{\partial \xi_1^2}$, $k_1 = j_1 - \nu_1 + \ell_1$ and $k_2 = j_2 - \nu_2 + \ell_2$. The term $\eta = 0$ corresponds to the FC part. The only difference with (20) is that instead of a single integral $J_a(k_1, k_2, y_1, y_2)$ we have a sum of integrals $J_a(k_1 + \eta, k_2, y_1, y_2)$, each of them multiplied by the corresponding coefficient in the expansion (32). That means that we only have to calculate some more integrals and multiply them by some coefficients which should be chosen in a suitable way.

In Figure 1 we have plotted the calculated emission intensities for the transition $\tilde{C}^1A' - \tilde{X}^1A'$ of the $S_2O$ molecule in the $SS$ mode using (a) a zero order approximation (FC), and (b) including the first correction in (33) for some values of the coefficient $a_1$. The emission intensities were calculated for the transitions $(0 \rightarrow \nu)$ and $(1 \rightarrow \nu)$. We can see that the effect of the first non-Condon term reduces, as expected, the transition intensities to the
higher levels (large $\nu$) being more important for the transitions ($1 \rightarrow \nu$). Although we have not attempted to perform a detailed analysis of these transitions (since in any case a full polyatomic treatment is necessary), it is clear that the present approach can be easily adapted to include non-Condon effects without major changes in the method.

6 Summary and Conclusions

In this paper we have calculated Franck-Condon factors by means of a simple formula (20) (derived from the Wigner function) which can be adapted in a straightforward manner to include non-Condon effects when the transition operator is written as a series expansion in powers of one of the Morse coordinates (33). The formula obtained involves well behaved one-dimensional integrations (22) which are not tabulated, but for which a symmetry property (23) and a three term recurrence relation (24) have been derived to check the accuracy of their numerical evaluation. We found that the best strategy to treat the numerical integrations is by means of a scaling method in which the integral is transformed in such a way that the integrand acquires a unit value at the maximum shifted at $x = 1$. This approach is particularly useful when the transitions involve large bonding energies (or large values of the parameters $j_1, j_2$).

Since the present approach is oriented to possible applications to the calculation of multidimensional Franck-Condon factors, we have confined our study to the calculation of one-dimensional Morse function overlaps by using a simple program written in Mathematica (see appendix B for a listing of the Mathematica program used to calculate the FC factors).

As far as we only require transitions between the lowest-lying states in each Morse potential (up to $\nu_1 \approx \nu_2 \approx 10$) our results have a similar accuracy as those obtained through more sophisticated methods. Although in this work we have included only a few examples, we were able to reproduce all results in [14] with high precision. Only for cases involving long summations we observe some isolated small deviations. We emphasize that in the above transitions we are dealing with rather large values of the bonding energies in the Morse potentials (i.e. large summations in eq. (20)), which suggests that our procedure can be reliably applied to a wide variety of physical examples. On the basis of these results, it is our impression that the inaccuracies arising from the alternating sums in (20) have been overestimated. Such sums can be calculated by Mathematica with no significant loss of precision for a wide range of problems of physical interest. However, for transitions involving higher-states a more elaborate programming of our formula is required in order to avoid the loss of accuracy. This is beyond the objective of the present work and will be studied elsewhere.

In conclusion, Franck-Condon factors for the Morse potential and corrections including non-Condon effects can be calculated with high accuracy by means of a very simple program suggesting that this approach is very convenient, since it can be implemented in any personal computer.
A Derivation of Franck-Condon overlaps for Morse Potential eigenfunctions

Let’s consider the Wigner function of two different Morse wavefunctions \( \psi_{j_1\nu_1}^\beta_1(x) \) and \( \psi_{j_2\nu_2}^\beta_2(x) \) (16),

\[
W(\psi_{j_1\nu_1}^\beta_1, \psi_{j_2\nu_2}^\beta_2 | x, p) = \frac{N_{j_1\nu_1}^\beta_1 N_{j_2\nu_2}^\beta_2}{2\pi\hbar} \int_{-\infty}^{\infty} dr \exp \left\{ -\frac{1}{2} (2j_1 + 1) e^{-\beta_1(x - \frac{1}{2} r)} \right\} \int_{-\infty}^{\infty} du \exp \left\{ -\frac{1}{2} (2j_2 + 1) e^{-\beta_2(x + \frac{1}{2} r)} \right\} \frac{N_1}{N_2} \psi_{j_1\nu_1}^\beta_1(x) \psi_{j_2\nu_2}^\beta_2(x),
\]

from which we obtain the Franck-Condon factors (20).
B The Mathematica program for the calculation of the Franck-Condon factors with wave functions of the Morse potential.

FCFact[j1_,nu1_,beta1_,R1_,j2_,nu2_,beta2_,R2_,flag_]:=Module[
{y1,y2,a},
(* --------------------------------------------------------------------- *)
(* This program computes the Franck-Condon factor of two Morse functions *)
(* Usage: *)
(* FCFact[j1,nu1,beta1,R1,j2,nu2,beta2,R2,flag] *)
(* flag=0 computes the FC factor *)
(* flag=1 computes the square of the FC factor *)
(* --------------------------------------------------------------------- *)
(* Definition of Local Variables *)
Acc=12;
AccN=100;
a=SetAccuracy[beta2/beta1,AccN];
y1=SetAccuracy[(2*j1+1)*Exp[-beta1*(R2-R1)/2],AccN];
y2=SetAccuracy[(2*j2+1)*Exp[-beta2*(R1-R2)/2],AccN];
Fcsum=0;
fac0a=SetAccuracy[2*Sqrt[a*FullSimplify[nu1!*(j1-nu1)*nu2!*(j2-nu2)/
(Gamma[2*j1-nu1+1]*Gamma[2*j2-nu2+1])]],AccN];
fac0b=SetAccuracy[y1^(j1-nu1)*y2^(j2-nu2),AccN];
fac0=fac0a*fac0b;
Do[ (* Do loops for summations *)
fac1a=SetAccuracy[(2*j1+1)^(l1)*(2*j2+1)^(l2),AccN];
fac1b=SetAccuracy[Exp[-beta1*(R2-R1)*(l1)/2]*Exp[-beta2*(R1-R2)*(l2)/2],AccN];
fac1=SetAccuracy[fac1a*fac1b,AccN];
fac2=SetAccuracy[(-1)^(l1+l2)/(l1!*l2!),AccN];
fac3=SetAccuracy[FullSimplify[Binomial[2*j1-nu1,nu1-l1]*
Binomial[2*j2-nu2,nu2-l2]],AccN];
Fcaux=SetAccuracy[fac0 *fac1*fac2*fac3,AccN];
(*================================================================**)
(* Integration Section. Integral Ia. Calculation with scaling *)
(*================================================================**)
Lambda=SetAccuracy[j1-nu1+l1 + a*(j2-nu2+l2),AccN];
(* Integrand *)
integr=x^(Lambda-1)*Exp[-(y1*x+y2*x^a)/2];
finteg[xx_]:=xx^(Lambda-1)*Exp[-(y1*xx+y2*xx^a)/2];
(* Looking for position of maximum *)
aux=FindMinimum[-integr,{x,1,0,1000},PrecisionGoal->10];
peak=aux[[2]][[1]][[2]];
xatmax =SetAccuracy[peak,AccN]; (* Position of maximum *)
(* Integrand value at maximum *)
}
fatmax=SetAccuracy[finteg[peak],AccN];
finteg2=SetAccuracy[(1/fatmax)*(X*xatmax)^((Lambda-1)*
    Exp[-(y1*(X*xatmax)+y2*(X*xatmax)^a)/2],AccN];
res=SetAccuracy[fatmax*xatmax*NIntegrate[finteg2,{X,0,Infinity},
    PrecisionGoal->Acc,AccuracyGoal->Acc,
    Method->GaussKronrod],AccN];
(* Adding terms *)
Fcsum=Fcsum*SetAccuracy[Fcaux*res,AccN]
   ,{l1,0,nu1},{l2,0,nu2}];
(* Choosing Output *)
If[flag==0, FCfactor=Fcsum];
If[flag==1, FCfactor=Fcsum^2];
N[FCfactor,15]
}
References


[17] R. Lemus and A. Frank, *(To be published)*


Figure 1: Emission intensities in the $S_2O \tilde{C}^1A' - \tilde{X}^1A'$ transitions (a) $I_{0\rightarrow\nu}$ and (b) $I_{1\rightarrow\nu}$. The calculations in the Condon approximation using Eq. (20) (FC) as well as the calculations with inclusion of the first non-Condon correction as given by Eq. (33) (NC) for $a_1 = 0.01$ and $a_1 = 1$ are displayed. Data from experimental analysis indicated by crosses is from ref.[6]. The parameters for this calculations are $j_1 = 128, \beta_1 = 1.6, j_2 = 79, \beta_2 = 1.8$ and $\Delta = R_2 - R_1 = 0.26$
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Table 1: Franck-Condon factors (20) for $\nu_\tilde{X} = 0 \ldots 7$ and $\nu_\tilde{C} = 0 \ldots 6$ for the $S-S$ stretching degree of freedom in the $S_2O$ molecule. Parameters for overlaps are $j_1 = 128$, $\beta_1 = 1.6$, $j_2 = 79$, $\beta_2 = 1.8$ and $\Delta = R_2 - R_1 = 0.283$. Successive entries correspond to the calculations using formula (20) with a scaled integration (first line), using the Configuration Localized States method of ref.[11, 12] and using the algebraic formula of ref.[4].
Table 2: Franck-Condon overlap integrals $f_{1,2}$ between states in identical Morse potentials displaced one with respect to the other. The Morse parameters are $j_1 = j_2 = 5$, $\beta_1 = \beta_2 = 0.90 \, \text{Å}^{-1}$, $R_1 = 2.67\, \text{Å}$ and $R_2 = 3.60\, \text{Å}$. The first line correspond to the results of formula (20) using numerical integrations (22). Identical results are obtained with the exact formula (26), and are also identical to the results of [11]. Second line corresponds to the calculations using harmonic oscillator wave functions with oscillator length $a_0 = [(j + \frac{1}{2})^{1/2} \beta]^{-1}$, and third line shows the calculations with modified harmonic oscillator wave functions as given in Ref.[4].

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Table 3: Franck-Condon overlap integrals $f_{1,2}$ between states in different Morse potentials. Parameters in potentials are $j_1 = 5$, $R_1 = 2.67\text{Å}$, $\beta_1 = 0.90\text{Å}^{-1}$ and $j_2 = 5$, $R_2 = 3.60\text{Å}$, $\beta_2 = 0.60\text{Å}^{-1}$. Successive entries correspond to results of formula (20) (which agree exactly with the calculations of ref.[11] making the integration of the Morse wave functions), the calculation using harmonic-oscillator wave functions with oscillator length $a_0 = [(j + \frac{1}{2})^{1/2}/\beta]^{-1}$, and the calculation with modified harmonic oscillator wave functions as given in ref.[4].

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Table 4: Franck-Condon (squared) overlap between states involved in the transition \( A^1\Sigma_u^+ \rightarrow \chi^1\Sigma_g^+ \) of \( ^7\)Li\(_2\) molecule. The parameters of this transition are: \( j_1 = 69.494, \beta_1 = 0.326 a_0^{-1}, R_1 = 5.876 a_0, j_2 = 48.106, \beta_2 = 0.459 a_0^{-1}, R_2 = 5.0535 a_0. \) Successive entries correspond to: Kusch[22], Drallos[27], Rivas-Silva[20], Ley-Koo[14] and our results using formula (20) with the scaled integral (22).
Table 5: Franck-Condon (squared) overlap between states involved in the transition $B^1\Pi_u^+ - X^1\Sigma_g^+$ of $^7$Li$_2$ molecule. The parameters of this transition are: $j_1 = 62.05$, $\beta_1 = 0.354 \ a_0^{-1}$, $R_1 = 5.550 \ a_0$. $j_2 = 48.104$, $\beta_2 = 0.459 \ a_0^{-1}$, $R_2 = 5.0535 \ a_0$. Successive entries correspond to: Hessel[23], Drallos[27], Palma[20], Ley-Koo[14] and our results using formula (20) with the scaled integral (22).
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Table 6: Franck-Condon (squared) overlap between states involved in the transition $A^2\Pi_2 \rightarrow X^2\Sigma^+$ of CN molecule. The parameters of this transition are: $j_1 = 60.4084$, $\beta_1 = 1.2167 \, a_0^{-1}$, $R_1 = 2.3308 \, a_0$, $j_2 = 73.5602$, $\beta_2 = 1.227 \, a_0^{-1}$, $R_2 = 2.2152 \, a_0$. Successive entries correspond to: Nicholls[28], McCallum[24], Waldenstrom[25], Rivas[20], Ley-Koo[14] and our results using formula (20) with the scaled integral (22).
Table 7: Franck-Condon (squared) overlap between states involved in the transition $B^3\Pi_g - A^3\Sigma_u^+$ of N$_2$ molecule. The parameters of this transition are: $j_1 = 58.55$, $\beta_1 = 1.301 \ a_0^{-1}$, $R_1 = 2.287 \ a_0$. $j_2 = 50.994$, $\beta_2 = 1.280 \ a_0^{-1}$, $R_2 = 2.420 \ a_0$. Successive entries correspond to: Jarmain [30], Zare [26], Chang [31], Waldenstrom [25], Palma [29], Ley-Koo [14] and our results using formula (20) with the scaled integral (22).
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Table 7: Continued
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- $FC$

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