

Calculation of Franck-Condon factors and r -centroids using isospectral Hamiltonian approach

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The calculation of Franck-Condon factors is of interest to study the vibrational transitions in diatomic molecules. Morse potential is one of the commonly used models for these calculations. Using isospectral Hamiltonian approach, a family of isospectral potentials, which have the same energy eigenvalues as that of Morse potential has been obtained. The eigenfunctions for this family of isospectral potentials are different from that of the original potential. The Franck-Condon factors and r -centroid values obtained using the deformed wavefunctions can be varied to match the experimental data.

Keywords: Isospectral Hamiltonian, Franck-Condon factor, r -Centroid

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1 Introduction

The Franck-Condon (FC) principle is one of the central concepts in the description of transition probabilities between bound molecular states. This explains the spectral intensity distribution for the vibrational transitions between two different electronic states of a molecule. The quantum mechanical basis for the FC principle is the extent of overlap between the vibrational wavefunctions of the two electronic states. These factors give the molecular structure information required to evaluate the band intensities in emission and absorption. The calculation of FC factors is based on the model potential for which the Schrödinger equation can be solved¹⁻³. Morse potential⁴ is one of the most realistic potential models. Energy eigenvalues and eigenfunction dependent quantities (like FC factors, values of r -centroids) can be calculated and compared with the corresponding experimental data. Consider the situation where the energy eigenvalues are in good agreement with experimental data and there is still room for improvement in FC factors agreement. In such a case, one would normally, add an additional term to the potential, which may spoil the agreement of energy eigenvalues already reached with the data. The strictly isospectral Hamiltonian approach has the advantage that without destroying the agreement already achieved between experimental and calculated energy eigenvalues, the wavefunction dependent quantities can be varied. We present the calculations

for FC factors and r -centroids using isospectral Hamiltonian approach for Morse potential.

Two Hamiltonians are said to be strictly isospectral, if they have exactly the same eigenvalue spectrum and S-matrix. The wavefunctions and their dependent quantities are different but related. This has been used to different physical situations, which are of interest to various fields^{5,6}. Though the idea of generating isospectral Hamiltonians using the Gelfand-Levitan approach⁷, Darboux procedures^{8,9} were known for some time, the supersymmetric quantum mechanical techniques (which deals with first order operators) make the procedure look simpler¹⁰⁻¹². When one deletes a bound state of a given potential $V(x)$ and re-introduce the state, it involves solving a first order differential equation, which admits a free parameter. Thus, a set of one-dimensional family of potentials $\hat{V}(x, \lambda)$ can be constructed which have exactly the same energy spectrum as that of $V(x)$. In general, for any one dimensional potential (full line or half-line) with n bound states, one can construct an n -parameter family of strictly isospectral potentials, i.e. potentials with eigenvalues, reflection and transmission coefficients identical to those for original potential¹². Using this formalism, we make a one-parameter deformation of the one-dimensional Morse potential. The deformed wavefunctions are then used to calculate the FC factors. The FC factors thus obtained can be made to match experimental data by a suitable choice of the deformation parameter (λ).

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2 Isospectral Hamiltonian Approach

The connection between the bound state wavefunctions and the potential is one of the key ingredients in solving exactly for the spectrum of one-dimensional potential problems. Once we know the ground state wavefunction (ψ_0) and choose its energy to be zero, we can factorize the Hamiltonian¹³ as $H_1=A^\dagger A$, (in units $\hbar=2m=1$), where $A=(d/dx)+W(x)$ and $A^\dagger=(-d/dx)+W(x)$ are the supersymmetric operators and $W(x)=(-d/dx)[\ln\psi_0(x)]$ is called the superpotential. We have:

$$H_1\psi_n = A^\dagger A\psi_n = \epsilon_n \psi_n \quad \dots(1)$$

Multiplying both sides with A , we get,

$$AA^\dagger(A\psi_n) = \epsilon_n(A\psi_n)$$

$$H_2(A\psi_n) = \epsilon_n(A\psi_n) \quad \dots(2)$$

Here, H_2 is the supersymmetric partner Hamiltonian of H_1 , with eigenfunctions $\chi_n=A\psi_n$. It is obvious that H_2 has the same eigenvalue spectrum as that of H_1 , but for the case $A\psi_0=0$, which is the case of supersymmetry broken. Explicitly, the relation between Hamiltonians reads,

$$E_n^{(2)} = E_{n+1}^{(1)}; \quad E_0^{(1)} = 0$$

$$\psi_n^{(2)} = [E_{n+1}^{(1)}]^{-1/2} A\psi_{n+1}^{(1)}$$

$$\psi_{n+1}^{(1)} = [E_n^{(2)}]^{-1/2} A^\dagger\psi_n^{(2)}$$

The superpotential relates the supersymmetric partner potentials $V_1(x)$ and $V_2(x)$ as:

$$V_{1,2}(x) = W^2(x) \mp \frac{dW}{dx} \quad \dots(3)$$

It is well known that for the potential $V_2(x)$, the original potential $V_1(x)$ is not unique^{10,11}. The argument is as follows. Suppose H_2 has another factorization BB^\dagger , where $B=(d/dx)+\hat{W}(x)$, then, $H_2=AA^\dagger=BB^\dagger$ but $H_1=B^\dagger B$ is not $A^\dagger A$ rather it defines a certain new Hamiltonian. For superpotential $\hat{W}(x)$, the partner potential $V_2(x)$ is

$$V_2(x) = \hat{W}^2(x) + \hat{W}'(x) \quad \dots(4)$$

Consider the most general solution as $\hat{W}(x) = W(x) + \phi(x)$, which demands that,

$$\phi^2(x) + 2W(x)\phi(x) + \phi'(x) = 0. \quad \dots(5)$$

The solution of Eq. (5) is $\phi(x) = (d/dx)\ln[I(x) + \lambda]$, where $I(x) = \int_{-\infty}^x \psi_0^2(x') dx'$ and λ is a constant. Therefore, we obtain,

$$\hat{W}(x) = W(x) + \frac{d}{dx} \ln[I(x) + \lambda] \quad \dots(6)$$

The corresponding one-parameter family of potentials $\hat{V}_1(x, \lambda)$ is given as:

$$\hat{V}_1(x, \lambda) = V_1(x) - 2 \frac{d^2}{dx^2} [\ln(I(x) + \lambda)]. \quad \dots(7)$$

The normalized ground state wavefunction corresponding to the potential $\hat{V}_1(x, \lambda)$ reads,

$$\hat{\psi}_0(x, \lambda) = \frac{\sqrt{\lambda(1+\lambda)}\psi_0(x)}{I(x) + \lambda}, \quad \dots(8)$$

where $\lambda \notin (0, -1)$. The excited state eigenfunctions for the potential $\hat{V}_1(x, \lambda)$ are given by¹²,

$$\hat{\psi}_{n+1}(x, \lambda) = \psi_{n+1}(x) + \frac{1}{E_{n+1}} \left(\frac{I'(x)}{I(x) + \lambda} \right) \left(\frac{d}{dx} + W(x) \right) \psi_{n+1}(x). \quad \dots(9)$$

The Eqs (7-9) represent the one-parameter family of isospectral potentials and wavefunctions, which shall be used to calculate the FC factors and r -centroids.

3 FC Factors and r -Centroids for Morse Potential

Morse potential is characterized by two parameters, depth of the potential minimum D and inverse of its range $\beta > 0$, [$\beta = (k/2D)^{1/2}$, k being the bond force constant]. The one-dimensional Morse potential is

$$V(x) = D[1 - \exp(-\beta x)]^2 - 1 \quad \dots(10)$$

where x is the position with respect to equilibrium point. The discrete spectrum of the potential is given as

$$E_v = -\frac{\hbar^2 \beta^2}{2\mu} (j - v)^2 \quad \dots (11)$$

where $j = [(2\mu D)^{1/2} / \beta \hbar] - 1/2$, μ is the reduced mass of the molecule and $v = 0, 1, 2, \dots, |j|$. The eigenfunctions corresponding to the eigenvalue (11) are obtained as³

$$\psi_{j,v}^\beta(\xi) = N_{j,v}^\beta \exp(-\xi/2) \xi^{j-v} L_v^{2(j-v)}(\xi) \quad \dots (12)$$

where $\xi = (2j + 1) \exp(-\beta x)$ and L_v^α is the associated Laguerre polynomial given by,

$$L_v^\alpha = \sum_{k=0}^v (-1)^k \frac{\Gamma(v + \alpha + 1)}{k!(v - k)! \Gamma(k + \alpha + 1)} \xi^k \quad \dots (13)$$

Normalization factor is given as

$$N_{j,v}^\beta = \left[\frac{\beta v! 2(j - v)}{\Gamma(2j - v + 1)} \right]^{1/2} \quad \dots (14)$$

Molecular FC factors describe the dependence on the vibrational wavefunctions of the transition intensities between vibrational states in different electronic configurations. Assuming that the electronic wavefunctions are independent of the vibrational states, the FC factors are given by the square of the overlap integral between initial and final wavefunctions in the transition.

$$q_{1,2} = [\langle \psi_{j_1, v_1}^{\beta_1}(x - R_1) | \psi_{j_2, v_2}^{\beta_2}(x - R_2) \rangle]^2 \quad \dots (15)$$

where R_1 and R_2 are equilibrium distances of the nuclei in the initial and final electronic states. The r -centroid is the unique value of inter nuclear separation, which is given by

$$\bar{r}_{v_1, v_2} = \frac{\langle \psi_{j_1, v_1}^{\beta_1}(x - R_1) | x | \psi_{j_2, v_2}^{\beta_2}(x - R_2) \rangle}{\langle \psi_{j_1, v_1}^{\beta_1}(x - R_1) | \psi_{j_2, v_2}^{\beta_2}(x - R_2) \rangle} \quad \dots (16)$$

We present the calculations for FC factors and r -centroids for Morse potential using $j_1 = j_2 = 5$;

$\beta_1 = \beta_2 = 0.9 \text{ \AA}^{-1}$, $R_1 = 2.67 \text{ \AA}$ and $R_2 = 3.60 \text{ \AA}$, which are given in Table 1.

3.1 FC factors and r -centroids for isospectral Morse potential

Using isospectral Hamiltonian approach, the one-parameter family of isospectral Morse potential is obtained as,

$$\hat{V}(x, \lambda) = V(x) - 2 \left[\frac{I''(x)}{I(x) + \lambda} - \left(\frac{I'(x)}{I(x) + \lambda} \right)^2 \right] \quad \dots (17)$$

where

$$I'(x) = \frac{(2j + 1)^{2j} \beta}{(2j - 1)!} \exp[-2j\beta x - (2j + 1) \exp(-\beta x)].$$

The isospectral potential is plotted for different values of deformation parameter λ in Fig. 1. The potential for $\lambda \rightarrow \infty$ is just the initial potential $V(x)$, whereas for smaller values of λ , the well becomes deep and a local maxima develops in the potential. Similar analysis holds for $\lambda < -1$. After some straightforward calculations, we obtain the normalized ground state wavefunction for the isospectral Morse potential as,

$$\psi_{5,0}^\beta = \frac{\sqrt{\lambda(1 + \lambda)} \left(\frac{\beta}{9!}\right)^{1/2} t_1 \exp[-5\beta(x - R)]}{\lambda + \exp[1 \exp\{-\beta(x - R)\} - 9\beta x] (t_2 + t_3)} \quad \dots (18)$$

where

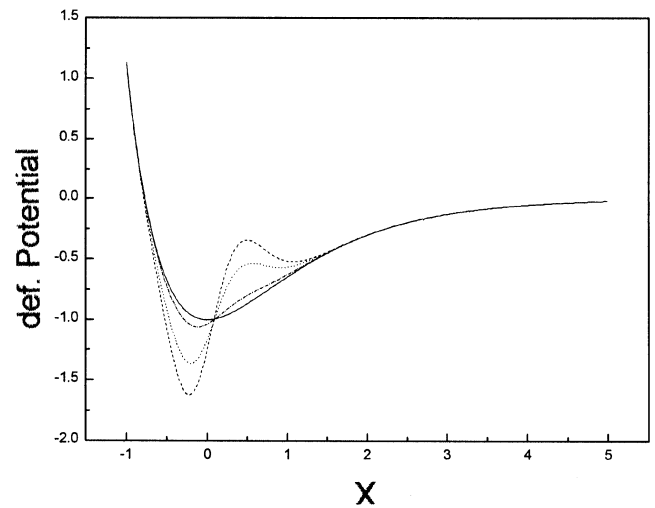


Fig. 1— One-parameter family of strictly isospectral Morse potential for $\lambda=6.0$ (dashed line), $\lambda=10$ (dotted line), $\lambda=50$ (dot-dash line) and solid line represents the undeformed Morse potential

$$t_1 = (11)^5 \exp[-11 \exp\{-\beta(x - R)/2\}]$$

$$t_2 = 6497 \exp(9\beta R) + \exp(9\beta x) + 2460 \exp[3\beta(x + 2R)] \\ + 5316 \exp[\beta(x + 8R)] + 221 \exp[3\beta(2x + R)] \\ + 11 \exp[\beta(8x + R)]$$

and

$$t_3 = 3866 \exp[\beta(2x + 7R)] + 1342 \exp[\beta(4x + 5R)] \\ + 610 \exp[\beta(5x + 4R)] + 60 \exp[\beta(7x + 2R)].$$

Similarly, we obtain the higher excited state wavefunctions and calculate the FC factors and *r*-centroids using the relation:

$$\hat{q}_{1,2}(\lambda) = [\langle \hat{\Psi}_{j_1, v_1}^{\beta_1}(x - R_1, \lambda) | \hat{\Psi}_{j_2, v_2}^{\beta_2}(x - R_2, \lambda) \rangle]^2 \quad \dots(19)$$

The FC factors and *r*-centroids are calculated for each transition, which include the deformation parameter. The four values of FC factors ($\hat{q}_{0,0}$, $\hat{q}_{2,0}$, $\hat{q}_{0,2}$, $\hat{q}_{0,1}$) show the similar variation with deformation parameter $\lambda > 0$ and are plotted in Fig. 2. The FC factors increase monotonically for small values of λ and reach their respective saturation values (the undeformed values), which are presented in Table 1. The values of $\hat{q}_{1,1}$ (and $\hat{q}_{2,2}$) plotted in Fig. 3 show a different feature of initially increase (decrease) and then decrease (increase) to their respective saturation value. Similarly, the FC values can also be varied with negative $\lambda < -1$ which increases our freedom to choose the value of λ

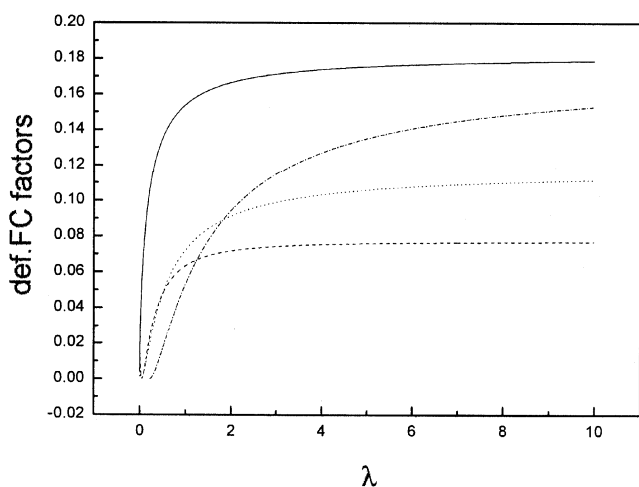


Fig. 2— Franck-Condon factors $\hat{q}_{0,0}$ (solid line), $\hat{q}_{2,0}$ (dot-dash line), $\hat{q}_{0,1}$ (dotted line) and $\hat{q}_{0,2}$ (dashed line) as a function of λ

matching with the experimental data. The values of *r*-centroids are plotted for both positive and negative values of deformation parameter in Fig. 4. It is clear from these plots that for large values of λ (as $\lambda \rightarrow \pm\infty$), we get the undeformed values of FC factors and *r*-centroids. Therefore, one can choose a particular value of λ , for which the FC factors match with the experimental values. Further, notice that the variation of FC factors as a function of the deformation parameter is more prominent in Fig. 3. The relative transition intensities are related to FC factors as $I_{1,2} \propto \nu^4 q_{1,2}$, where ν is the difference between vibrational energies of the initial and final states in the transition. Thus, a suitable choice of value for deformation parameter will reduce the discrepancy between the theoretical and experimental values of transition intensities.

Table 1—FC factors and the values of *r*-centroids for Morse potential parameters $j_1=j_2=5$; $\beta_1=\beta_2=0.9\text{\AA}^{-1}$, $R_1=2.67\text{\AA}$ and $R_2=3.60\text{\AA}$. The first line corresponds to FC factors and second line corresponds to *r*-centroid values

ν'/ν''	0	1	2
0	0.182215	0.117157	0.077499
	3.39197	3.07994	2.97364
1	0.624854	0.016319	0.002202
	3.70399	1.86351	2.37762
2	0.173706	0.559484	0.016937
	4.43251	4.20506	0.89537
3	0.016045	0.199030	0.603600
	3.05317	4.98347	4.93540
4	0.000788	0.058937	0.044500
	0.948056	4.11761	6.41066

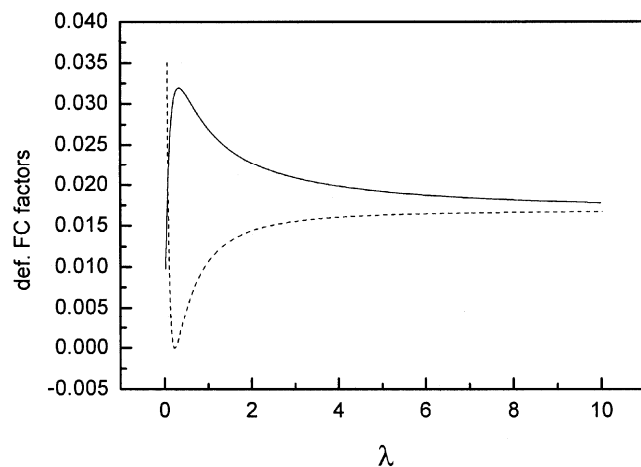


Fig. 3— Franck-Condon factors $\hat{q}_{1,1}$ (solid line) and $\hat{q}_{2,2}$ (broken line) as a function of λ

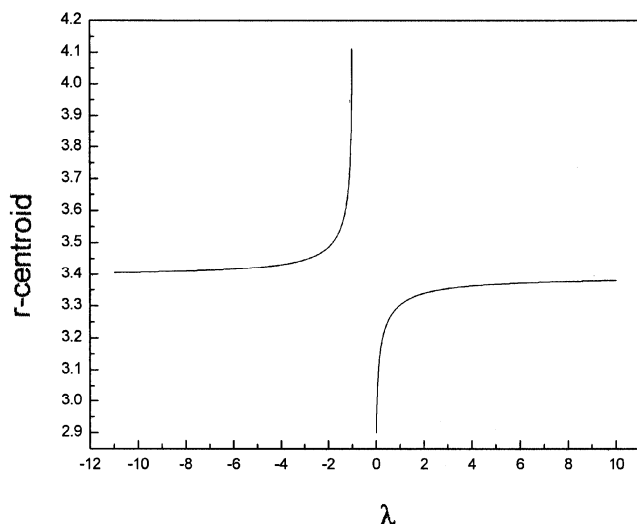


Fig. 4— Values of r -centroids $\bar{r}_{0,0}$ as a function of λ for both positive and negative values

4 Conclusion

In this paper, we have presented the calculations for FC factors and r -centroids using isospectral Hamiltonian approach, which deals with first order differential equations. FC factors represent one of the most useful and pervasive mathematical concepts employed for the study of molecules and their interactions. In case, the calculations for FC factors, r -centroids or transition intensities do not match with experimental data, this approach has benefit to reduce the discrepancy without destroying the energy eigenvalue agreement. We showed in Figs 2 and 3 the dependence of various FC factors on the deformation parameter. Fig. 4 describes the behaviour of r -centroid values as a function of deformation parameter (λ taking both positive and negative

values). By following the work of Keung *et al.*¹⁵, one can also obtain a multi parameter family of isospectral Morse potential $\hat{V}(x, \lambda_1, \lambda_2, \dots, \lambda_n)$, where we can deal with more deformation parameters, increasing the freedom to obtain the values closest to experimental data. The application of this approach to calculate the FC factors and r -centroids for specific diatomic molecules is under progress.

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