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ANHARMONIC REDUCTION FACTOR FOR OCTAHEDRAL SYSTEM WITH E⊗e COUPLING

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Abstract:
Following the Öpik and Price method for harmonic vibration of a physical system (molecule, crystal), in this paper we calculate the new equilibrium position of the system due to anharmonic vibronic interaction. We consider a system with ochaedral symmetry for which double degenerate electronic state are coupled to double degenerate anharmonic vibrations of the nuclei. For such system we studied the quenches. of the orbital angular momentum and Jahm Teller interaction using for vibrations the clasical Morse wave function and also anharmonic coherent states. The liniar approximation of the vibronic coupling were used to obtain orbital reduction factor for the considered system.
Key words: reduction factor, vibronic interaction, Jahn - Teller effect, Morse oscillator

1. Introduction

The vibronic coupling between degenerate electronic states and degenerate vibrations of a physical system (molecules, crystals) with octahedral symmetry has been explored using for the vibrations the classical wavefunctions of the harmonic oscillator in a lot of papers [1-5]. This effect was investigated also using coherent states [6-8].

In order to obtain more accurate theoretical results in order to describe the molecular vibrations it can be used the model of Morse oscillator [9]. This model was used to calculate Franck-Condon factors [10]. Recently we have been built the anharmonic coherent states and we used them to study vibronic interaction E ⊗ ε and T ⊗ ε coupling [11]. The Jahn - Teller interaction quenches the orbital angular momentum even though it is insufficiently strong to produce static distortion. The partial quencing shows us as a reduction in the magnitude of the spin-orbit interaction, in the reduction of the orbital contribution of the magnetic moment, etc. This contribution acts as *orbital reduction factors* (*Ham factors*) in the matrix elements of the

angular momentum or of the spin orbit interaction [12]. This effect was also discussed in connection with the experimental results [13,14,15]. In this paper, in order to obtain more accurate results the vibrations will be described by classical Morse wavefunctions, and secondly by the anharmonic coherent states. The linear approximation of the vibronic coupling will be used. We will use the *Opik and Price* method [16] to calculate the new equilibrium positions due to the vibronic interaction, for the case of a system with octahedral symmetry for which the double degenerate electronic states are coupled to double degenerate vibrations of the nuclei and will calculate the vibronic reduction factor (Ham factor).

2. Anharmonic vibronic interaction

We consider the Jahn - Teller interaction in a $E \otimes \varepsilon$ system for the case of anharmonic molecular vibrations described by Morse potential. The vibronic Hamiltonian consists in a double Morse oscillator and the Jahn – Teller interaction Hamiltonian:

$$H = H_e + H_{v1} + H_{v2} + H_{JT} = H_e + \sum_{\lambda=\theta,\varepsilon}\left[\frac{p_\lambda^{\,2}}{2m} + V_0\left(e^{-2\alpha x_\lambda} - 2e^{-\alpha x_\lambda}\right)\right] + k_{JT_A} x_A I + k_{JT_E}\left(x_\theta U_\theta + x_\varepsilon U_\varepsilon\right), \quad (1)$$

(interaction with fully symmetric mode is taken into account as well)

where x_θ, x_ε are the coordinate operators and p_θ, p_ε the momentum operators, α- the anharmonicity constant, V_0 the anharmonic potential energy, and k_{JTE} and k_{JTA} are the Jahn - Teller coupling constants with *a* and *e* modes. *I* stands for a unit 3 x 3 matrix and U_λ, where ($\lambda = \theta, \varepsilon$) are the following matrices:

$$U_\theta = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad U_\varepsilon = \begin{pmatrix} -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (2)$$

H_e represents the electronic energy levels and k_{JT} the Jahn -Teller interaction energy.

We will denote by H:

$$\mathrm{H} = \sum_{\lambda=\theta,\varepsilon}\left[\frac{p_\lambda^{\,2}}{2m} + V_0\left(e^{-2\alpha x_\lambda} - 2e^{-\alpha x_\lambda}\right)\right] + k_{JT_A} x_A I + k_{JT_E}\left(x_\theta U_\theta + x_\varepsilon U_\varepsilon\right) \qquad (3)$$

where the sum over λ contains the Hamiltonian of two anharmonic oscillators, described by the Morse potential $V_0\left(e^{-2\alpha x_\lambda} - 2e^{-\alpha x_\lambda}\right)$ [17], where $\alpha > 0$ is the anharmonicity parameter, V_0>0. In (3) k_{JT} represents the Jahn-Teller coupling constant.

We use the y_λ variable and the notations [17]:

$$v = \sqrt{\frac{8mV_0}{\alpha^2\hbar^2}}\,,\; s_\lambda = \sqrt{\frac{-2mE_\lambda}{\alpha^2\hbar^2}},\; y_\lambda = v\exp\left(-\alpha x_\lambda\right), \qquad (4)$$

where $\lambda = \theta, \varepsilon$.

The eigenfunctions of the Hamiltonian are for the discrete eigenenergy levels ($E_\lambda \in$ [-V_0, 0]) are written in term of confluent hypergeometric functions [17]:

$$\psi_{n\lambda}\left(y_\lambda\right) = c_\lambda\, y_\lambda^{\,s_\lambda} \exp\left(-\frac{y_\lambda}{2}\right) F\left(-n_\lambda, 2s_\lambda + 1; y_\lambda\right). \qquad (5)$$

Solutions correspond to $2s_\lambda + 1 - v = -2n_\lambda$, (where $n_\lambda \in$N). The quantum number must be n_λ= 0, 1, 2, ... , N_{max} = [μ] where [μ] represents the entire part of $\mu = (v-1)/2$. The normalization constant is:

$$c_\lambda = \frac{1}{\Gamma\left(v - 2n_\lambda\right)}\sqrt{\frac{\Gamma\left(v - n_\lambda\right)}{n!}}$$

The wavefunction of the system (1) in absence of Jahn-Teller interaction is a product of the electronic wave function $\Phi(\mathbf{R})$ and a double anharmonic oscillator $\varphi(\mathbf{r}) = \phi_\theta\left(x_\theta\right)\phi_\varepsilon\left(x_\varepsilon\right)$:

$$\Psi(\mathbf{R},\mathbf{r}) = \Phi(\mathbf{R})\phi(\mathbf{r}).$$

The new equilibrium position corresponds to the vibronic wavefunction:

$$\Psi(\mathbf{R},\mathbf{r}) = \Phi(\mathbf{R})\phi_\theta(x_\theta + D_{\theta i})\phi_\theta(x_\varepsilon + D_{\varepsilon i}) \tag{6}$$

The equilibrium position can be established from the condition $\frac{\partial \mathrm{H}}{\partial x_\theta} = \frac{\partial \mathrm{H}}{\partial x_\varepsilon} = 0$. Results:

$$\exp(-2\alpha x_a) - \exp(-\alpha x_a) - \frac{k_{JT_a}}{2\alpha V_0} = 0$$

$$\exp(-2\alpha x_\theta) - \exp(-\alpha x_\theta) - \frac{k_{JT}U_\theta}{2\alpha V_0} = 0,$$

$$\exp(-2\alpha x_\varepsilon) - \exp(-\alpha x_\varepsilon) - \frac{k_{JT}U_\varepsilon}{2\alpha V_0} = 0.$$

The equilibrium position will be:

$$D_{\theta i} = -\frac{1}{\alpha}\ln\left\{\frac{1}{2}\left(1 + \sqrt{1 + 2\frac{k_{JT}U_{\theta i}}{\alpha V_0}}\right)\right\}, \tag{7}$$

$$D_{\varepsilon i} = -\frac{1}{\alpha}\ln\left\{\frac{1}{2}\left(1 + \sqrt{1 + 2\frac{k_{JT}U_{\varepsilon i}}{\alpha V_0}}\right)\right\}, \tag{8}$$

where $U_{i\lambda}$ represents the diagonal element $(U_\lambda)_{ii}$ of the matrix (2), and Ω_0 represents the ground state vibration frequency $\Omega_0 = E_{n_\lambda=0}/\hbar$.

3. The anharmonic reduction factor

The matrix element an observable described by an operator *A* can be calculated

$$\left\langle \Psi_{i,n_\theta n_\varepsilon}(\mathbf{R},\mathbf{r}) \middle| A \middle| \Psi_{j,n'_\theta n'_\varepsilon}(\mathbf{R},\mathbf{r}) \right\rangle = \left\langle \Phi_i(\mathbf{R}) \middle| A \middle| \Phi_j(\mathbf{R}) \right\rangle \left\langle in_\theta \middle| jn'_\theta \right\rangle \left\langle in_\varepsilon \middle| jn'_\varepsilon \right\rangle. \tag{9}$$

In the above equation the vibronic reduction factor (Ham factor) is:

$$\langle in_\lambda | jn'_\lambda \rangle = \int_R \psi_{n_\lambda}(x_\lambda + D_{\lambda_i}) \psi_{n'_\lambda}(x_\lambda + D_{\lambda_j}) dx_\lambda, \quad (10)$$

where *i, j* = 1, 2, 3.

The displaced wavefunction can be expressed in y□ variable as

$$\psi_{n_\lambda}(\sigma_{\lambda_i} y_\lambda) = c_\lambda (\sigma_{\lambda_i} y_\lambda)^{s_\lambda} \exp\left(-\frac{\sigma_{\lambda_i} y_\lambda}{2}\right) F(-n_\lambda, 2s_\lambda + 1; \sigma_{\lambda_i} y_\lambda), \quad (11)$$

for $\lambda = \theta, \varepsilon$, and $\sigma_{\lambda_i} = \exp(-\alpha D_{\lambda_i})$.

Results that (10) can be written:

$$\langle in_\lambda | jn'_\lambda \rangle = \int_0^\infty \psi_{n_\lambda}(\sigma_{\lambda_i} y_\lambda) \psi_{n'_\lambda}(\sigma_{\lambda_i} y_\lambda) dy_\lambda,$$

where $\sigma_{\lambda_i} = \exp(-\alpha D_{\lambda_i})$ and $\sigma_{\lambda_j} = \exp(-\alpha D_{\lambda_j})$ represents scale factors.

Results finally:

$$\langle in_\lambda | jn'_\lambda \rangle = c_{n_\lambda} c_{n'_\lambda} \sigma_{\lambda_i}^{s_\lambda} \sigma_{\lambda_j}^{s'_\lambda} \times \int_{R_+} y_\lambda^{s_\lambda + s'_\lambda} \exp\left(-\frac{\sigma_{\lambda_i} + \sigma_{\lambda_j}}{2}\right) F(-n_\lambda, 2s_{n_\lambda} + 1, \sigma_{\lambda_i} y_\lambda) F(-n'_\lambda, 2s_{n'_\lambda} + 1, \sigma_{\lambda_i} y_\lambda) dy_\lambda, \quad (13)$$

where s'□ corresponds to n'□. We can also express the confluent hypergeometric function in terms of Laguerre L_n^{2s} polynomials [18]:

$$F(-n, 2s+1, y) = \frac{n!\Gamma(2s+1)}{\Gamma(n+2s+1)} L_n^{2s}.$$

Results, expanding L_n^{2s} polynomials [18]:

$$F(-n, 2s+1, y) = n!\Gamma(2s+1) \sum_{m=0}^{n} \frac{(-1)^m}{(n-m)!\Gamma(m+2s+1)} y^m. \quad (14)$$

This expansion can be used, replacing in (13) one of the confluent hypergeometric polynomial. Results:

$$\langle in_\lambda | jn'_\lambda \rangle = c_{n_\lambda} c_{n'_\lambda} \sigma_{\lambda_i}^{s_\lambda} \sigma_{\lambda_j}^{s'_\lambda}$$
$$\times n_\lambda! \Gamma(2s_\lambda + 1) \sum_{m=0}^{n_\lambda} \frac{(-1)^m \sigma_{\lambda_i}^m}{(n_\lambda - m)! \Gamma(m + 2s_\lambda + 1)} \tag{15}$$
$$\times \int_{R_+} y_\lambda^{m+s_\lambda+s'_\lambda} \exp\left(-\frac{\sigma_{\lambda_i} + \sigma_{\lambda_j}}{2}\right) F(-n'_\lambda, 2s_{n'_\lambda} + 1, \sigma_{\lambda_i} y_\lambda) dy_\lambda.$$

The integral can be evaluated using the equation [18]

$$\int_0^\infty e^{-\lambda y} y^v F(a,b,ky) dy = \frac{\Gamma(v+1)}{\lambda^{v+1}} F\left(a, v+1, b, \frac{k}{\lambda}\right). \tag{16}$$

After calculations results that the Ham factor is:

$$\langle in_\lambda | jn'_\lambda \rangle = c_{n_\lambda} c_{n'_\lambda} \sigma_{\lambda_i}^{s_\lambda} \sigma_{\lambda_j}^{s'_\lambda}$$
$$\times n_\lambda! \Gamma(2s_\lambda + 1) \sum_{m=0}^{n_\lambda} \frac{(-1)^m \sigma_{\lambda_i}^m}{(n_\lambda - m)! \Gamma(m + 2s_\lambda + 1)} \tag{**17**}$$
$$\times \frac{\Gamma(m + s_\lambda + s'_\lambda + 1)}{\left(\frac{s_\lambda + s'_\lambda}{2}\right)^{m+s_\lambda+s'_\lambda+1}} F\left(-n'_\lambda, m + s_\lambda + s'_\lambda + 1, 2s_{n'_\lambda} + 1, \frac{\sigma_{\lambda_j}}{\frac{s_\lambda + s'_\lambda}{2}}\right).$$

This integral can be particularized for $\lambda = \theta, \varepsilon$.

An important particular value of the factor corresponds to $n'_\lambda = n_\lambda = 0$. This corresponds to the zero-phonon line. In this case the confluent hyergeometric function becomes $F(0,a,y) = 1$. From Eq. (13) we obtain:

$$\langle i0_\lambda | j0_\lambda \rangle = \langle i0 | j0 \rangle = \frac{1}{v-1} \sigma_{\lambda_i}^{\frac{y-1}{2}} \sigma_{\lambda_j}^{\frac{y-1}{2}} \left(\frac{\sigma_{\lambda_i} + \sigma_{\lambda_j}}{2}\right)^{v-1}, \tag{18}$$

where σ_{λ_i} and σ_{λ_j} are:

$$\sigma_{\lambda_i} = \frac{1}{2}\left(1 + \sqrt{1 + 2\frac{k_{JT} U_{\lambda_i}}{\alpha V_0}}\right), \sigma_{\lambda_j} = \frac{1}{2}\left(1 + \sqrt{1 + 2\frac{k_{JT} U_{\lambda_j}}{\alpha V_0}}\right).$$

An *electronic* operator F_A with only off-diagonal matrix elements has matrix elements within the vibronic ground-state triplet

$$\left\langle \Psi_{i00}\left|F_A\right|\Psi_{joo}\right\rangle = \left\langle \psi_i\left|F_A\right|\psi_j\right\rangle \frac{1}{(v-1)^2}\sigma_{\theta_i}^{v-1}\sigma_{\theta_j}^{v-1}\left(\frac{\sigma_{\theta_i}+\sigma_{\theta_j}}{2}\right)^{2(v-1)}.$$

Another particular factor of interest is:

$$\begin{aligned}\left\langle in_\lambda\left|\, j0_\lambda\right.\right\rangle &= \left\langle in\left|\, j0\right.\right\rangle = c_{n_\lambda}c_0\sigma_{\lambda_i}^{s_\lambda}\sigma_{\lambda_j}^{\frac{v-1}{2}} \\ &\times\int_0^\infty y_\lambda^{\,s_\lambda+\frac{v-1}{2}}\exp\left(-\frac{\sigma_{\lambda_i}+\sigma_{\lambda_j}}{2}y_\lambda\right)F\left(-n_\lambda,2s_{n_\lambda}+1,\sigma_{\lambda_i}y_\lambda\right).\end{aligned} \tag{19}$$

Results according (16):

$$\begin{aligned}\left\langle in_\lambda\left|\, j0_\lambda\right.\right\rangle &= \left\langle in\left|\, j0\right.\right\rangle = c_{n_\lambda}c_0\sigma_{\lambda_i}^{s_\lambda}\sigma_{\lambda_j}^{\frac{v-1}{2}} \\ &\times\frac{\Gamma\left(\sigma_{\lambda_i}+\sigma_{\lambda_j}+1\right)}{\left(s_\lambda+\frac{v-1}{2}\right)^{\sigma_{\lambda_i}+\sigma_{\lambda_j}+1}}F\left(-n_\lambda,\sigma_{\lambda_i}+\sigma_{\lambda_j}+1,2s_\lambda+1,\frac{\sigma_{\lambda_i}}{s_\lambda+\frac{v-1}{2}}\right).\end{aligned} \tag{20}$$

In the second order perturbation theory we can calculate the correction to the ground state in the case of off-diagonal operators F_A and $F_{A'}$:

$$\left\langle \Psi_{i00}\left|F_{AA'}\right|\Psi_{j00}\right\rangle = \sum_{k\neq i,\,j}\sum_{n,m}\frac{\left\langle \Psi_{i00}\left|F_A\right|\Psi_{knm}\right\rangle\left\langle \Psi_{knm}\left|F_{A'}\right|\Psi_{j00}\right\rangle}{E_m-E_n}, \tag{21}$$

where E_k ($k = m, n$) represents the energy levels of the Morse oscillator:

$$E_k = \frac{4V_0}{\alpha}\left(\frac{v-1}{2}-k\right)^2 = \hbar\Omega\left(\frac{v-1}{2}-k\right)^2.$$

Conclusion

The coupling between double degenerate electronic states and double degenerate vibrations for a physical system with octahedral symmetry has been studied in order to calculate vibronic reduction factor (Ham factor). We extended the calculation of the vibronic factor for the case of the harmonic vibrations of a physical system to that of the anharmonic vibrations. First we obtain the general formula for Ham factor using anharmonic vibrations,

described by the wavefunctions of classical Morse oscillator, and then we obtained it with the help of anharmonic coherent states. The results (17) and (18) are generalizations of the well known solutions of the harmonic oscillator model.

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