Second Order Reduction Factors for T ⊗ (e ⊕ t) Jahn-Teller Systems

Faten E. Al-Hazmi and Colin A. Bates

Physics Department, Science College, King Abdulaziz University, Jeddah, Saudi Arabia
School of Physics and Astronomy, University of Nottingham, University Park, Nottingham, UK
Fialhazmi@kau.edu.sa

Abstract. Second-order reduction Factors (SORF) are important as they can generate contributions to the effective Hamiltonian which may be significantly larger than and different from those of first order. The aim of this proposal is to calculate analytical values for the second-order reduction factors by using a new general method which is developed by Nottingham group in 2003. non-Condon corrections to the standard Franck-Condon (FC) calculations for T ⊗ (e ⊕ t) Jahn-Teller (JT) Systems. The validity of this non-Condon correction approximation is first tested in the cubic T ⊗ t JT system. It found that the non-Condon corrections are a valid improvement on the standard FC results and provide an accurate estimate of the SORF for T⊗t JT systems. This proposal gives the results of calculations of the second-order JT reduction factors for T ⊗ (e ⊕ t) JT systems.

Keywords: Second-order reduction factors, orthorhombic Jahn-Teller Systems, Franck-Condon approximation, non-Condon correction approximation, Vibronic Hamiltonian.

1. Introduction

The Jahn-Teller effect is usually observed via the analysis of electronic parameters appearing in the effective Hamiltonian for the system[1,2]. A first-order JT effect reduces the size of some of the terms, whilst a second-order effect introduces new terms. In strong coupling the reduction of first-order terms can be very large and consequently the second terms may dominate[3].
It is therefore important to be able to calculate the magnitude of the SORF for such systems.

The aim of this proposal is to obtain analytical values for the SORF for $T \otimes (e \oplus t)$ JT systems. The calculations of the SORF in many papers have been published either numerically or analytically in the case of spin-orbit coupling\cite{[4-7]}. In the latter, the Nottingham group has developed an analytical method for the calculation of such factors by using non-Condon corrections to the standard FC calculations for cubic and icosahedral systems\cite{[8-11]}.

However, this proposal extends the calculations to the $T \otimes (e \oplus t)$ JT systems by using the new analytical methods. SORF will then be calculated for the important case of a spin-orbit coupling perturbation by FC approximation. This approximation is valid in the strong coupling limit. It is assumed that virtual transitions between the ground and excited states take place so rapidly that the nuclei do not change their positions during a transition. In order to extend the FC approximation to finite coupling strengths, we modify the basic theory by introducing non-Condon corrections into the theory.

The proposal will be organised as follows: After the above introduction, the following Section 2 introduces the vibronic Hamiltonian for the tetrahedron. The general expressions for the SORFs are given in Section 3 followed by a summary of the principles involved in applying the FC method to this problem (Section 4). The Non-Condon corrections to the FC results in the SORF calculations for the $T \otimes (e + t_2)$ system are given in Section 5 while Section 6 concludes with a discussion of the main points that arise in the calculations.

2. Vibronic Hamiltonian of $T \otimes (e \oplus t)$ JT systems

The basic JT Hamiltonian for a $T_1$ ion in a tetrahedral cluster coupled linearly to an $e$ ($Q_g, Q_e$) and $t_2$ ($Q_4, Q_5, Q_6$) displacement of the cluster\cite{[12, 13]}.

The interaction Hamiltonian has the form:

$$ H_{\text{int}} = V_E (Q_g E_g + Q_e E_e) + \sum_{i=1,5,6} V_T (Q_i T_i) + \sum_{i=\delta, \epsilon, A, 5, 6} \left[ \frac{1}{2} (\mu \omega_i^x Q_i^x) T_0 + P_j^z / (2 \mu) \right] $$

where $T_0$ is the $3 \times 3$ identity matrix and $V_E$ and $V_T$ are the E- and T-type coupling constants respectively. The orbital operators represented in matrix form are:
The $Q_i$ are the collective displacements of the $t_2$ mode, the $P_j$ is the momentum conjugate to $Q_i$, and $\mu$ is the mass and $(\omega_E, \omega_T)$ the frequencies of the modes such that $\omega_\theta = \omega_\epsilon = \omega_E$ and $\omega_4 = \omega_5 = \omega_6 = \omega_T$. The last terms in Eq. (1) represent the Hamiltonian describing the kinetic and elastic energies for the harmonic lattice.

3. General Background to Second order Reduction Factors

The main definition of SORF can be found in the general theory presented in\cite{14}, outlined in\cite{15}, and used to construct the FC approximation\cite{16}. The necessary background for the SORF within the FC approximation is thus presented below. The real Hamiltonian for a perturbation of symmetry $\Gamma$ is written in general terms as:

$$\mathcal{H}^{(1)}(\Gamma) = \sum_\gamma W_{\Gamma, \gamma} C_{\Gamma, \gamma}$$

Where $W_{\Gamma, \gamma}$ are coefficients and

$$C_{\Gamma, \gamma} = \sum_{\gamma_1 \gamma_2} \langle \Gamma_{\gamma_1} | \Gamma_{\gamma_2} \rangle \langle \Gamma_{\gamma_2} | \Gamma_{\gamma_1} \rangle$$

are general expressions for the orbital operators in terms of Clebsch-Gordon (CG) coefficients\cite{17}, where $\gamma_1$ and $\gamma_2$ are components. The Hamiltonian that is generated by the second order perturbation theory is:
\[ \mathcal{H}^{(2)}(\Gamma_i \otimes \Gamma_m) = \mathcal{H}^{(1)}(\Gamma_i) G(T_1) \mathcal{H}^{(1)}(\Gamma_m) \]  

(5)

where \( G(T_1) \) is the Green operator

\[ G(T_1) = \sum_{n,m} \frac{|\Psi^{(m)}; n\rangle \langle \Psi^{(m)}; n|}{\Delta E_{\text{vert}}} \]  

(6)

and \( \Delta E_{\text{vert}} \) is the difference in energy between the excited well states \( |\Psi^{(m)}; n\rangle \) and the ground vibronic symmetry-adapted states. The SORF, which essentially incorporate all the vibronic effects can be written as:

\[ K_{M}^{(2)}(\Gamma) = \frac{\langle 0 \Gamma_{ly_l} | \mathcal{L}_{M\mu}^{(2)}(\Gamma_i \otimes \Gamma_m) | 0 \Gamma_{ly_k} \rangle}{\langle \Gamma_{ly_l} | L_{M\mu}^{(2)}(\Gamma_i \otimes \Gamma_m) | \Gamma_{ly_k} \rangle} \]  

(7)

with

\[ \mathcal{L}_{M\mu}^{(2)}(\Gamma_i \otimes \Gamma_m) = \sum_{\gamma_j \gamma_k} C^{*}_{\gamma_j \gamma_k} G(T_1) C_{\gamma_m} \langle \Gamma_{\gamma_j} \Gamma_{\gamma_k} | M\mu \rangle \]  

(8)

and

\[ L_{M\mu}^{(2)}(\Gamma_i \otimes \Gamma_m) = \sum_{\gamma_j \gamma_k} C^{*}_{\gamma_j \gamma_k} C_{\gamma_m} \langle \Gamma_{\gamma_j} \Gamma_{\gamma_k} | M\mu \rangle \]  

(9)

In the above expression \( \Gamma_i \) and \( \Gamma_m \) are any two different perturbation acting on the vibronic symmetry-adapted ground state. The label \( M \in \Gamma_i \otimes \Gamma_m \) and \( \mu \) over all the components of the irreducible representation \( M \).

Many additional points are required before defining the FC approximation itself\(^{[18]}\). In many systems wells labelled \( p, q \ etc \) are the minima of the lowest adiabatic potential energy surface or sheet (APES)\(^{[9,10]}\). It is then necessary to take into account all possible overlaps between the states located in different wells. Symmetry-adapted vibronic ground states \( |0 T_1 \sigma_i \rangle \) are derived using projection operator techniques. This gives a linear combination of the vibrational ground states \( |\Psi'_p; 0\rangle \) located in the wells such that:

\[ |0 T_1 \sigma_i \rangle = \sum_p \alpha^p_i |\Psi'_p; 0\rangle. \]  

(10)
\(\alpha_i^p\) are appropriate coefficients following normalization \(\sum_p |\alpha_i^p|^2 = 1\). The prime in \(|\Psi'_p;0\rangle\) indicates that these states are the appropriate untransformed vibronic ground state for well \(p\) and the “0” indicates that the localized oscillators are in their ground states.

The FC approximation applies to the infinitely strong coupling limit. We will start by replacing the vibronic well states \(|\Psi'_p;0\rangle\) in Eq. (10) by a product of electronic and nuclear wave functions with the latter function centred at the bottom of the well. A new Green operator \(G^p(T_1)\) is expressed for a general well \(p\) in the FC approximation as:

\[
G^p(T_1) = \sum_i \frac{|i,p\rangle\langle i,p|}{\Delta E_{\text{vert}}^{(i,p)}}
\]  

(11)

The energy \(\Delta E_{\text{vert}}^{(i,p)}\) in the Green operator is independent of the well label \(p\) and thus simplifies to \(\Delta E_{\text{vert}}\). By replacing the Green operator given in Eq. (11) by the contribution of the well electronic FC Green operator is defined as follow:

\[
G_{\text{FC electronic}} = \sum_i \frac{|e_i^p\rangle\langle e_i^p|}{\Delta E_{\text{vert}}}
\]

(12)

where \(|e_i^p\rangle\) are the excited electronic well states. We note that the ground state involved in the determination of the reduction factors encompasses the ground states for each well described by Eq. (10). The transition is vertical starting from a certain well and ending up within the same well. The physical meaning of all this has been lately stated: Nuclei are much heavier than electrons so that during a specific time, electrons make transitions during which nuclei do not move at all.

The FC expression for the SORF then becomes:

\[
K^{(2)\text{FC}}_{M} (\Gamma_i \otimes \Gamma_m) = \sum_{pq} \alpha_i^p \alpha_q^q \langle \Psi'' | \mathcal{Z}^{(2)p}_{M\mu} (\Gamma_i \otimes \Gamma_m) | \Psi'q \rangle
\]

(13)

\[
= \frac{L^{(2)}_{M\mu} (\Gamma_i \otimes \Gamma_m) | T_i \sigma_j \rangle}{(T_j \sigma_j) | L^{(2)}_{M\mu} (\Gamma_i \otimes \Gamma_m)| T_i \sigma_j \rangle}
\]

The FC approximation is an accurate analytical method in the strong coupling regime. However, it does not take into account the mixing of the
ground states in each well with the excited states in the same well by the JT interaction.

4. Non-Condon Corrections of the FC Values

Now we want to introduce the non-Condon corrections to the electron wave functions which provide the electronic wave functions with an additional flexibility, namely the ability to follow the nuclear vibrations. An important advantage of this approach is that we work with the limited size for the electron basis functions and not with the infinite basis of the vibrational states. This makes the problem solvable in simple terms. The numerator of the Eq. (13) for the SORF includes the three factors namely the bra $\left\langle \Psi'^p \right\rangle$, the operator $\mathcal{L}^{(2)}_{\mu}(\Gamma_i \otimes \Gamma_m)$ and the ket $\left| \Psi'' q \right\rangle$. In principle, corrections to all three factors are necessary and the final result for the second-order correction to a RF is obtained by multiplying them together. Thus we write $U(Q)$ in the general form\(^{[19]}\):

$$U(Q) = U(Q_o) + \sum_j \frac{\partial U(Q_j)}{\partial Q_j} q_p + \frac{1}{2} \sum_{j,j'} \frac{\partial^2 U(Q_j)}{\partial Q_j \partial Q_{j'}} q_p q_{p'} + \ldots$$

$$= U(Q_o) + U_1 + U_2$$

(14)

where $U(Q)$ is the vibronic Hamiltonian and $Q_o$ is defined as the coordinate of the bottom of the well $p$. $U_1$ and $U_2$ are first-order and second-order perturbation terms in the potential. The corrections of the states either to first or second order will generate a second-order contribution. A correction of first order may give contributions of odd or even degree of new displacement coordinates defined by $q_p$ and measured from the positions of the bottoms of the wells where $q_p = Q_j - Q_o$. As we are interested only in the low energy states close to the bottom of the wells, the $q_p$ are small compared to the average value of the nuclear displacements. Instead, the criterion for smallness comes from the small deviation $q_p$ of the displacement from the bottom of the minimum point.

Ultimately, we should include nuclear motion as a part of the dynamic problem so that the parameter $q_p$ becomes a dynamic variable associated with the ground harmonic oscillator state $|0\rangle$ in well $p$. However, $U_2$ and higher order terms in the expansion do not give any contribution because these are constants and thus cannot admix the ground electronic well states
\[ |\Psi'^p\rangle \] with the excited electronic well states \[ |e_m^p\rangle \] and can therefore be neglected. In fact, this term mixes the ground electronic states \[ |\Psi'^p\rangle \] in a well \( p \) with the excited states \[ |e_m^p\rangle \] in that well (i.e. \( \langle \Psi'^p | U_1 | e_m^p \rangle \neq 0 \)). Although it has zero expectation values within the ground electronic well states \( |\Psi'^p\rangle \) (i.e. \( \langle \Psi'^p | U_1 | \Psi'^p \rangle = 0 \)), it gives a correction \[ |\Delta \Psi^1_{1p}\rangle \] of the well ground states for each well such that:

\[
|\Psi^p_c\rangle = |\Psi'^p\rangle + |\Delta \Psi^1_{1p}\rangle
\]

(15)

where

\[
|\Delta \Psi^1_{1p}\rangle = \sum_m \frac{\langle \Psi'^p | U_1 | e_m^p \rangle}{\Delta E_{\text{vert}}} |e_m^p\rangle
\]

(16)

The Non-Condon perturbation thus gives a correction to the well ground state proportional to \( q_p \). The Non-Condon perturbation also gives a correction to the two excited well states, which also involve \( q_p \). The excited states are then no longer degenerate. The next step is to insert the new \( |\Psi^p_c\rangle \) in the expression of the Green operator, but the closure relation does not hold in the non-Condon correction as in the original FC approximation. It is therefore necessary to define a corrected Green operator \( G^p(T_1) \):

\[
G^p(T_1) = \sum_m \frac{|e_m^p\rangle \langle e_m^p|}{\Delta E_{m}^p}
\]

(17)

where \( \Delta E_{m}^p \) is the appropriate energy denominator including the non-Condon element. The SORF within the corrected FC approximation then become

\[
K^{(2)FC}_{M_l} (\Gamma_l \otimes \Gamma_m) = \sum_{p,q} \alpha_i^p \alpha_{i'}^q \langle \Psi'^p | \mathcal{L}_{M_l}^{(2) p} (\Gamma_l \otimes \Gamma_m) | \Psi'^{p'} \rangle \langle T_1 \sigma_{i'} | L_{M_l}^{(2)} (\Gamma_l \otimes \Gamma_m) | T_1 \sigma_{j} \rangle
\]

(18)

with \( \mathcal{L}_{M_l}^{(2) p} (\Gamma_l \otimes \Gamma_m) \) calculated using the corrected Green operator. The calculations can all be undertaken in one well only because all wells are equivalent. The final results are made up of two terms: one is the original
constant term obtained before (the standard FC results) and it is independent of $q_p$. The second term (the non-Condon correction) contains terms which are of order $q_p^2$. Higher order terms of order $q_p^4$ and $q_p^2 q_p'$ may be neglected.

5. Results

Calculations of the SORF are much more complicated than first-order, as they generally involve coupling to an infinite set of excited vibronic states for which details are often unknown. They can therefore only be calculated exactly in a pure adiabatic case, such as that found in the $T \otimes (e \oplus t)$ system in which the electronic states are not mixed. All calculations of the SORF will be carried out by using the Mathematica programs. The calculations begin with the vibronic Hamiltonian for $T \otimes (e \oplus t)$ JT system. The unitary shift transformation method\[^3\] is used to find the electronic eigenstates and normalisation factors. The work includes calculating energies and vibronic well states. SORF are evaluated by using FC approximation for strong coupling. Finally, the analytical values for the SORF by using non-Condon corrections to the standard FC calculations.

5.1 The Ground and Excited States Energy

The mathematical treatments used to calculate the vibronic states in this proposal were written using a “Mathematica” program. Using the Gram-Schmidt and projection operator procedures, one obtains a linear combination of the ground states in the orthorhombic wells (labelled by $p$). We found that six orthorhombic wells which are equivalent to each other and thus energies of the ground and excited vibronic states are the same. In each well $p$, we have a singlet electronic state, $|\Psi'^p\rangle$, and doubly degenerate excited electronic states ($|e'^p_1\rangle, |e'^p_2\rangle$) obtained by solving the well Hamiltonian in strong coupling. The energies of the electronic ground and excited states in the trigonal wells are found in Table 1. A new coupling constants $K_E$ and $K_T$ is defined by $K_T = \sqrt{3} \hbar/8 \mu \omega_t V_T$ and $K_E = \sqrt{\hbar/8 \mu \omega_E} V_E$\[^{[12,20]}\]. The energy gap between the ground and doublet excited vibronic states are thus:

$$\Delta E_1 = - \frac{6 K_E^2}{\hbar \omega_E} - \frac{2 K_T^2}{\hbar \omega_T} \quad (19)$$
\[ \Delta E_2 = 3E_{JT}^T = -\frac{4K_T^2}{3\hbar\omega_T} \]  

(20)

with \( E_{JT}^T \) defined as the JT energy.

**Table 1. The ground and excited states in the wells for the \( T \otimes (e \oplus t) \) JT system.**

| Well | Ground state \( |\Psi'^p\rangle \) | Excited state \( |e_1^p\rangle \) | Excited state \( |e_2^p\rangle \) |
|------|-------------------------------|---------------------------------|---------------------------------|
| 1    | \( \left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right\} \) | \( \{0, 0, 1\} \) | \( \left\{ -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right\} \) |
| 2    | \( \left\{ -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right\} \) | \( \{0, 0, 1\} \) | \( \left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right\} \) |
| 3    | \( \left\{ 0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\} \) | \( \{1, 0, 0\} \) | \( \left\{ 0, -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\} \) |
| 4    | \( \left\{ 0, -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\} \) | \( \{1, 0, 0\} \) | \( \left\{ 0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\} \) |
| 5    | \( \left\{ \frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}} \right\} \) | \( \{0, 1, 0\} \) | \( \left\{ \frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}} \right\} \) |
| 6    | \( \left\{ -\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}} \right\} \) | \( \{0, 1, 0\} \) | \( \left\{ \frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}} \right\} \) |

**5-2 Evaluation of the SORF Using the FC Approximation**

The FC expression (18) is used to obtain the SORF for this system. In principle, there are four SORF as the label \( M \in T_1 \otimes T_1 = A_1 \oplus E \oplus T_1 \oplus T_2 \), so we get four reduction factors. From Eq. (18) they are:

\[ K^{(2)}_E(T_1 \otimes T_1), K^{(2)}_T(T_1 \otimes T_1), K^{(2)}_{T_1}(T_1 \otimes T_1) \text{ and } K^{(2)}_{T_2}(T_1 \otimes T_1). \]

On substituting the adiabatic electronic state in the expression (17), the FC Green operator \( G^{p}_{FC} \) is obtained. It is then convenient to use the CG coefficients for the \( T_1 \)-type of perturbation, within the \( T_1 \) orbital states, which are:
\[ C_{xz} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix}, \quad C_{yz} = \begin{pmatrix} 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 \end{pmatrix}, \quad C_{xz} = \begin{pmatrix} 0 & 1/\sqrt{2} & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \] (21)

This proposal will evaluate the second order reduction factors for \( T \otimes (e \otimes t) \) in two cases: First; when there is a strong linear coupling to \( t \), weak linear coupling to \( e \) (i.e. \( K_T \gg K_E \)). Second, when there is equal linear coupling to \( e \) and \( t \) vibrations (i.e. \( K_T = K_E = K_{ET} \)).

5.2.1. Equal Linear Coupling to \( e \) and \( t \) Vibration \( K_T = K_E = K_{ET} \)

The FC values are found to be:

\[ K_{A}^{(2)} (T_1 \otimes T_1) = -\frac{3 \omega \hbar}{16 K_{ET}^2} = -\frac{1}{2E_{JT}^{ET}} \quad K_{E}^{(2)} (T_1 \otimes T_1) = 0 \]

\[ K_{T_1}^{(2)} (T_1 \otimes T_1) = 0 \quad K_{T_2}^{(2)} (T_1 \otimes T_1) = -\frac{\omega \hbar}{16 K_{ET}^2} = -\frac{1}{3E_{JT}^{ET}} \]

The results are identical as those obtained previously by analytical methods\(^6\).

5.2.2. Strong Coupling: \( V_T \) Large

The FC values for \( t \)-mode are found to be:

\[ K_{A}^{(2)} (T_1 \otimes T_1) = -\frac{3 \omega \hbar}{8 K_{T}^2} = -\frac{1}{2E_{JT}^{T}} \quad K_{E}^{(2)} (T_1 \otimes T_1) = 0 \]

\[ K_{T_1}^{(2)} (T_1 \otimes T_1) = 0 \quad K_{T_2}^{(2)} (T_1 \otimes T_1) = -\frac{\omega \hbar}{4 K_{T}^2} = -\frac{1}{3E_{JT}^{T}} \]

(23)

5.3. Evaluation of the SORF including the Non-Condon Corrections to the FC Values.

The second and more interesting part of this proposal is now to correct the FC results by including terms and effects that were not taken into account previously as a perturbation such as the transitions between the ground and excited states within the ground sheet. As described in section 5.1, the excited states are split into excited states \( |e_1^p \rangle \) and \( |e_2^p \rangle \), so the calculation of the SORF by using Eq. (18) requires the correction of the Green operator, which is defined as:
Now the non-Condon corrections to the second order reduction factors involve both ground and excited states. Following exactly the same steps as used previously in the FC approximation where the corrected excited states are substituted in the new Green operator. Running the program gives an expression for the SORF within the corrected FC approximation including the anisotropy corrections containing terms like \( q_p^2 \) and \( q_p' q_p'' \). After substituting \( \langle 0| q_p q_p' | 0 \rangle = 0 \) and \( \langle q_p^2 \rangle = \hbar / 2 \mu \omega_T \), we obtain terms inversely proportional to the square of the JT energy \( 1/(E_{JT}^T)^2 \). As \( \Delta E_{\text{vert}} \) is directly proportional to \( K_T^2 \) and \( K_{ET}^2 \), the product \( K_T^2 K_{M}^{(2)} (T_1 \otimes T_1) \) is a constant in the standard FC approximation\(^{[21]} \). It is therefore convenient to plot this product as a function of \( K_T \).

5.3.1 Equal Linear Coupling to e and t Vibration \( K_T = K_E = K_{ET} \)

The SORF involving the perturbations \( (T_1 \otimes T_1) \) are:

\[
NFCK_A^{(2)} (T_1 \otimes T_1) = -\frac{3 \hbar \omega}{16 K_{ET}^2} - \frac{19 \hbar^3 \omega^3}{12 K_{ET}^4} = -\frac{3}{8 E_{JT}^E} - \frac{19 \hbar \omega}{64 E_{JT}^E} \tag{25}
\]

\[
NFCK_E^{(2)} (T_1 \otimes T_1) = -\frac{3 \hbar \omega}{32 K_{ET}^2} - \frac{5 \hbar^3 \omega^3}{128 K_{ET}^4} = -\frac{3}{16 E_{JT}^E} - \frac{5 \hbar \omega}{32 E_{JT}^E} \tag{25}
\]

\[
NFCK_T^{(2)} (T_1 \otimes T_1) = -\frac{\hbar \omega}{16 K_{ET}^2} - \frac{\hbar^3 \omega^3}{256 K_{ET}^4} = -\frac{1}{8 E_{JT}^E} - \frac{\hbar \omega}{64 E_{JT}^E} \tag{25}
\]

\[
NFCK_T^{(2)} (T_1 \otimes T_1) = 0
\]

The SORF \( K_M^{(2)} \) for \( M = A, E \) and \( T_2 \) as a function of the vibronic coupling \( K_{ET} \) are plotted in Fig. 1.
Fig. 1. A plot of the SORF $K_M^{(2)} (T_1 \otimes T_1)$ as a function of $K_{ET}$.

Figures 2, 3, and 4 show plots of, $K_{ET}^2 K_A^{(2)} (T_1 \otimes T_1)$, $K_{ET}^2 K_E^{(2)} (T_1 \otimes T_1)$, and $K_{ET}^2 K_{T_2}^{(2)} (T_1 \otimes T_1)$ versus $K_{ET}$. The straight lines are the FC results while the curved ones represent the results obtained by the Non-Condon corrections to the second order reduction factors (NFC), where the key is shown as an insert in each figure.

Fig. 2. A plot of the SORF $(K_{ET})^2 K_A^{(2)} (T_1 \otimes T_1)$ as a function of $K_{ET}$. 
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5.3.2 Strong Coupling: $V_T$ Large

The SORF involving the perturbations $(T_1 \otimes T_1)$ are,

\[
\text{NFCK}^{(2)}_A (T_1 \otimes T_1) = -\frac{3\hbar \omega}{8K^2_T} - \frac{1h^3 \omega^3}{4K^4_T} = -\frac{1}{2E_{JT}} - \frac{4\hbar \omega}{9E_{JT}^2}
\]

\[
\text{NFCK}^{(2)}_E (T_1 \otimes T_1) = \frac{h^3 \omega^3}{32K^4_T} = \frac{\hbar \omega}{18E_{JT}^2}
\]

\[
\text{NFCK}^{(2)}_{T2} (T_1 \otimes T_1) = -\frac{h \omega}{4K^2_T} - \frac{h^3 \omega^3}{8K^4_T} = -\frac{1}{3E_{JT}} - \frac{2h \omega}{9E_{JT}^2}
\]

\[
\text{NFCK}^{(2)}_{T1} (T_1 \otimes T_1) = 0
\]
The SORF $K_M^{(2)}$ for $M = A, E$ and $T_2$ as a function of the vibronic coupling $K_T$ are plotted in Fig. 5.

![Fig. 5. A plot of the SORF $K_M^{(2)} (T_1 \otimes T_1)$ as a function of $K_T$.](image)

Figures 6, 7, and 8, show plots of, $K_T^2 K_A^{(2)} (T_1 \otimes T_1)$, $K_T^2 K_E^{(2)} (T_1 \otimes T_1)$ and $K_T^2 K_{T_2}^{(2)} (T_1 \otimes T_1)$ versus $K_T$. The straight lines are the FC results while the curves ones represent the results obtained by the non-Condon corrections to the second order reduction factors (NFC), where the key is shown as an insert in each figure.

![Fig. 6. A plot of the SORF $(K_T)^2 K_A^{(2)} (T_1 \otimes T_1)$ as a function of $K_T$.](image)
6. Conclusion and Discussions

The purpose of this proposal has been to calculate the analytical values of the SORF for $T \otimes (e \oplus t)$ JT system by using Non-Condon corrections to the standard FC calculations. Second order reduction factors are important as they can generate contributions to the effective Hamiltonian which may be significantly larger than and different from those of first order. The validity of this non-Condon correction approximation is first tested in the cubic $T \otimes t$ JT system. It found that the non-Condon corrections are a valid improvement on the standard FC results and provide an accurate estimate of the second-order reduction factor for cubic and icosahedral systems.
Figs. 6 and 8 show that the non-Condon corrections to the SORF of $A$ and $T_2$ symmetry give values of the SORF which are closer to the analytical calculations\[6\].

Our work makes a further step towards enabling theoretical results to be related to experimental data, as the reduction factors are very important when using the effective Hamiltonian to describe a real system.

References

معاملات الدالة الثانية الاختراقية

جان تيلر

T ⊗ (e ⊕ t)

لأنظمة Jahn-Teller

فاطم إبراهيم الحازمي و كولن بيتس

قسم الفيزياء - كلية العلوم - جامعة الملك عبد العزيز

جدة - المملكة العربية السعودية

قسم الفيزياء والفلك - جامعة نوتنجهام - المملكة المتحدة

Fialhazmi@kau.edu.sa

الخلاصة:

تتغلى معاملات اختزال الدالة الثانية هامة جدا، حيث أنها تولد مساهمات قوية في الهايترنيين الفعالة بشكل مختلف عن تلك الناشئة من الدالة الأولي. الهدف من هذا المشروع هو حساب القيم التحليلية لمعاملات الاختزال من الدالة الثانية باستخدام طريقة تحليلية جديدة تم تطويرها وتطبيقها بواسطة مجموعة جامعة نوتنجهام الفيزيائية وذلك بتقريب قيم لا-كانتن لحسابات فرانك-كندن لنظام جان-تيلر. وإثبات صحة هذا التصحيح تم اختياره على نظام جان-تيلر لبسيطته وشهرته. واتضح من نتائج هذا الاختبار أن تقريب لا-كانتن تعطي نتائج صحيحة ودقيقة أكثر من غيرها لهذا النظام. وفي هذا البحث استجفت قيمة معاملات الاختزال من الدالة الثانية لنظام جان-تيلر T ⊗ (e ⊕ t).