Second-order vibronic reduction factors for orbital triplet Jahn–Teller systems in cubic and icosahedral symmetry

# Second-order vibronic reduction factors for orbital triplet Jahn–Teller systems in cubic and icosahedral symmetry

**Colin A Bates**[1]**, Michel Abou-Ghantous**[2]**, Janette L Dunn**[1]**,
Faten Al-Hazmi**[1]**, Victor Z Polinger**[1] **and Elie A Moujaes**[2,3]

[1] School of Physics and Astronomy, University of Nottingham, University Park,
Nottingham NG7 2RD, UK
[2] Department of Physics, American University of Beirut, PO Box 11-0236, Riad El-Solh,
Beirut 1107-2020, Lebanon

E-mail: Colin.Bates@nottingham.ac.uk and Janette.Dunn@nottingham.ac.uk

## Abstract

It is well-known that vibronic interactions can be modelled in terms of an
effective Hamiltonian incorporating first and second-order reduction factors
(RFs), particularly when analysing the spectroscopic properties. Measurements
and calculations of the RFs as a function of the strength of vibronic coupling are
therefore of much interest. In this paper, we develop a new general method for
determining second-order RFs (soRFs) from the strength of the Jahn–Teller (JT)
coupling for systems in which electron orbital degeneracy or pseudo-degeneracy
exists. These include in particular the fullerene molecule $C_{60}$, pseudo-Jahn–
Teller molecules and impurity centres in crystals. In order to calculate the
important soRFs for intermediate to strong coupling, it is necessary to determine
non-Condon corrections to the strong coupling values obtained using the
Franck–Condon (FC) approximation. This gives an additional contribution
to the nuclear polarizability of the system, thus enabling the electrons to
follow the nuclear vibrations. These non-Condon corrections are derived using
perturbation theory and are found to be inversely proportional to the square of
the JT energy. The validity of the approximation is first tested in the cubic
$T \otimes t_2$ JT system due to its relative simplicity. It is found that the results are
closer to those obtained earlier by numerical methods than the analytical FC
values alone. Results are then presented that are applicable to $C_{60}^-$ anions.

(Some figures in this article are in colour only in the electronic version)

[3] Present address: School of Physics and Astronomy, University of Nottingham, University Park, Nottingham NG7
2RD, UK.

## 1. Introduction

During the last decade, there have been numerous investigations on the role played by vibronic coupling between the electrons and the nuclei in determining many of the electronic properties of crystals and molecules. This coupling is most commonly observed in spectroscopic experiments (such as optical absorption and emission, infrared spectroscopy, electron paramagnetic resonance) [1, 2] and is usually described as a Jahn–Teller (JT) effect. It is especially important in high-symmetry systems such as those arising in cubic and icosahedral environments as they frequently contain orbitally degenerate electronic states. The effect of this coupling in the latter systems is usually observed through the sizes and character of many of the electronic perturbations that may also be present. Many calculations have been undertaken to highlight these vibronic effects in the fullerenes and in $C_{60}^{\pm}$ ions in particular [3]. For example, analytical methods have been used to calculate the effects of this interaction in these systems which frequently show degenerate electronic ground states of $T$, $G$ or $H$ symmetries [4–7].

A recent review of JT effect theory highlighting application to molecular problems has been given by Bersuker [8]. Many examples of the results obtained in cubic and icosahedral systems are discussed in detail. Much of our understanding is based on quantum mechanical principles involving effective Hamiltonians as they frequently form a bridge between experimental and theoretical investigations. Of particular relevance to this study are then the vibronic reduction factors (RFs); those of first-order (foRF) are relatively simple to calculate and to measure directly by experiment but those of second-order (soRF), which are derived from using second-order perturbation theory, generally involve coupling to an infinite set of excited vibronic states. They are consequently much more difficult to calculate and at the same time their relevance in experiment is not always readily apparent. Nevertheless, if the required information is available they often provide much more information than the foRFs about the physics of the system being investigated. The reason why a lot of attention is focused on the soRFs is that foRFs can quench the effects of a perturbation drastically as the coupling constant increases. This is because in intermediate-to-strong coupling the overlap integral decreases rapidly from unity to zero. In contrast, the overlap integral is not present in soRFs and they can remain important up to higher values of the coupling constants [2] and usually dominate the terms involving the foRFs. A second point is that soRFs can introduce terms of different symmetries into the effective Hamiltonian. However, no new terms are introduced into the effective Hamiltonian from third or higher orders terms and thus foRFs and soRFs are sufficient in most cases. The actual parameter of the theory is the ratio of the vibrational quantum to $E_{JT}$.

Originating from the pioneering work of Ham [9] in 1965, effective Hamiltonians involving both foRFs and soRFs have been used frequently to help interpret data on a wide range of vibronic systems. These RFs are constants for a given system and contain within them the effects of the vibrations of the surroundings. They are usually encountered when the system is described by an effective Hamiltonian. They appear as constants multiplying purely electronic operators involved in various perturbations (such as externally applied magnetic or electric fields, uniaxial stress or random strain). Such constants reflect the symmetry of both the perturbation and the JT centre itself. The approach frequently used as a first attempt at modelling experimental data is to treat all RFs as free parameters in a fitting procedure. However, an important result of theoretical modelling is that these RFs are not truly free parameters but they are intimately related to the vibronic coupling strength(s), which in turn are related to the JT energy and the vibrational frequencies. By determining these RFs by fitting the data obtained from any system to the effective Hamiltonian, they can then be used in principle to determine the strength of the vibronic coupling provided knowledge of the analytical expressions for the RF is available for any strength of the vibronic coupling.

In icosahedral symmetry, expressions for the soRFs have been derived using a shift transformation method for the $T \otimes h$ JT system [6] on the assumption that the ground states with and without the inclusion of vibronic coupling have the same symmetries. Thus only one linear coupling constant was used. (The role played by the quadratic coupling terms in this system was merely to localize the system around the minima in the APES and to prohibit any pseudo-rotation around the trough.) The most important physics of vibronic coupling was then found through the knowledge of the RFs and particularly those of second order.

Most of the JT centres in insulating or semiconducting systems were identified by combining the effects of strain with various perturbations through the determination of the RFs. The soRFs were fundamental to this understanding and identification. It took many years to reach this achievement in cubic symmetry but icosahedral symmetry still remains at an early stage of development. This arises because the soRFs have a complicated nature and also through the lack of sufficiently good interplay between the experimental and theoretical aspects of the problem.

soRFs have been calculated for the $T \otimes h$ JT system in intermediate to strong coupling using a shift transformation (ST) method [6], and in the strong coupling limit using the Franck–Condon (FC) approximation [10]. In the latter, the soRFs were calculated using the Born–Oppenheimer approximation in order to extract the adiabatic wavefunctions. The procedures for determining the soRFs depend critically on the particular JT system and on the vibronic coupling strength. In the FC method, the major contributions to the soRFs originate from virtual vertical transitions between the ground and excited vibronic states within the upper sheets in the APES. In the strong coupling limit, all other transitions may be neglected and the result is consequently very accurate. The FC results were compared with the strong coupling limit of the results obtained using the ST method, and satisfactory agreement was obtained. However, inaccuracies remain in the intermediate to strong coupling regimes in these systems. The aim of this work is to extend the region of validity by correcting the FC values by using a non-Condon, non-adiabatic approach in which first-order non-vertical transitions are also included. To test this correction, we consider, firstly, the well known example of the cubic $T \otimes t_2$ JT system. The numerical results of O'Brien [11] and the analytical expressions of Bates *et al* [12] for the soRFs including anisotropy will be used to show the validity of this correction in this simple system from very strong to intermediate vibronic coupling strengths. The second aim of this paper is to correct the FC values obtained in [10] for $T \otimes h$ icosahedral JT systems using the non-Condon correction.

This paper is organized as follows: section 2 introduces the general theory of soRFs and summarizes the principles involved in the application of the FC method. In section 3, the non-Condon perturbative method is presented in general terms. The application of the ideas to the octahedral and tetrahedral $T$-type states is summarized in section 4 while the non-Condon corrections applied to icosahedral $T \otimes h$ JT systems are reported in section 5. Section 6 discusses the results obtained and their application to real systems.

## 2. The Franck–Condon approximation in the theory of soRFs in orbital triplet JT systems

The general vibronic Hamiltonian for a JT system consisting of a single electronic $T_1$ orbital triplet ground state interacting with its immediate surroundings can be written as:

$$\mathcal{H} = \frac{1}{2} \sum_{\Gamma\gamma} \left( \frac{P_{\Gamma\gamma}^2}{\mu} + \mu\omega_\Gamma^2 Q_{\Gamma\gamma}^2 \right) C_{0\Gamma} + V_\Gamma \sum_\gamma Q_{\Gamma\gamma} C_{\Gamma\gamma} \tag{1}$$

where $Q_{\Gamma\gamma}$ are the collective vibrational coordinates of the surroundings, $P_{\Gamma\gamma}$ are the corresponding momenta and $V_\Gamma$ and $\omega$ are the coupling constant and oscillator frequency, respectively. $C_{\Gamma\gamma}$ are the appropriate Clebsch–Gordan (CG) operators transforming like the row $\gamma$ of the irreducible representation $\Gamma$ such that

$$C_{\Gamma\gamma} = \sum_{\sigma_i,\sigma_j} |T_1\sigma_i\rangle\langle T_1\sigma_j| \langle \Gamma\gamma T_1\sigma_i | T_1\sigma_j\rangle \tag{2}$$

where $\sigma_i$ and $\sigma_j$ are components of $T_1$. The $C_{\Gamma\gamma}$ can be expressed in terms of CG coefficients $\langle \Gamma\gamma T_1\sigma_i | T_1\sigma_j\rangle$ found in [13]. Also $C_{0\Gamma}$ is the unit matrix of dimension $\Gamma$. Neglecting the first term in equation (1), which describes the kinetic energy, the energy of the remaining terms generates a set of adiabatic potential energy surfaces with corresponding states $|i, n\rangle$. The parameter $i$ labels these surfaces, or sheets, while $n$ gives the number of phonon excitations.

The definition of the soRFs $K_M^{(2)}(\Gamma_l \otimes \Gamma_m)$ involving two perturbations of symmetries $\Gamma_l$ and $\Gamma_m$ can be found in the general theory presented in [14] and outlined in [6]. Their evaluation within the FC approximation for the icosahedral $T_1 \otimes h$ JT system has been described in detail in [10] and summarized below for a general electronic perturbation having symmetry $\Gamma$. The corresponding first-order-perturbation Hamiltonian within the orbital $T_1$ state is

$$\mathcal{H}^{(1)}(\Gamma_l) = \sum_{\gamma} W_{\Gamma\gamma} C_{\Gamma\gamma} \tag{3}$$

where $W_{\Gamma\gamma}$ are coefficients. The sum $\gamma = \theta, \epsilon, 4, 5, 6$ for coupling to vibrational $h$-modes, and $\gamma = 4, 5, 6$ for coupling to $t_2$ modes.

Second-order perturbation theory generates a second-order Hamiltonian

$$\mathcal{H}^{(2)}(\Gamma_l \otimes \Gamma_m) = \mathcal{H}^{(1)}(\Gamma_l) G(T_1) \mathcal{H}^{(1)}(\Gamma_m) \tag{4}$$

where the Green operator $G(T_1)$ is defined by

$$G(T_1) = \sum_{i,n} \frac{|i, n\rangle\langle i, n|}{\Delta E_{\mathrm{vert}}^{(i,n)}} \tag{5}$$

where $\Delta E_{\mathrm{vert}}^{(i,n)}$ is the energy measured relative to the ground APES for which $i = 0$.

In many systems of interest and those to be considered here, the ground APES contains minima (or wells) labelled $p, q, \ldots$. It is then necessary to take into account all possible overlaps between the states located in different wells. A convenient procedure is to construct symmetry-adapted vibronic ground states $|0T_1\sigma_i\rangle$ derived from projection operator techniques. This gives a linear combination of the vibrational ground states $|\psi'_p; 0\rangle$ located in the wells such that

$$|0T_1\sigma_i\rangle = \sum_p \alpha_i^p |\psi'_p; 0\rangle. \tag{6}$$

The prime in the well state $|\psi'_p; 0\rangle$ indicates that these states have been transformed back from a local oscillator picture for well $p$ to the global frame, and the '0' indicates that the localized oscillators in the wells are in their ground states. The $\alpha_i^p$ are appropriate coefficients. (Full details of this notation are given in [6] and [15].)

The soRF can then be derived from the relation

$$K_M^{(2)}(\Gamma_l \otimes \Gamma_m) = \frac{\langle 0T_1\sigma_i | \mathcal{L}_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m) | 0T_1\sigma_j\rangle}{(T_1\sigma_i | L_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m) | T_1\sigma_j)} \tag{7}$$

with

$$\mathcal{L}_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m) = \sum_{\gamma_l,\gamma_m} C_{\Gamma_l\gamma_l} G(T_1) C_{\Gamma_m\gamma_m} \langle \Gamma_l\gamma_l \Gamma_m\gamma_m | M\mu\rangle \tag{8}$$

and

$$L_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m) = \sum_{\gamma_l, \gamma_m} C_{\Gamma_l \gamma_l} C_{\Gamma_m \gamma_m} \langle \Gamma_l \gamma_l \Gamma_m \gamma_m | M\mu \rangle. \tag{9}$$

In the above expressions, the label $M \in \Gamma_l \otimes \Gamma_m$ while the states $|T_1 \sigma_i\rangle$ are combinations of pure electronic states obtained from the symmetry-adapted ground states given by equation (6). We note that in calculations of the soRFs using the ST method of [6], the number of phonon excitation used was chosen to give a convergent result; 300 phonon excitations were found to be sufficient for accurate results over the range of coupling strengths considered.

As the FC approximation applies to the infinite coupling limit, we replace the vibronic well state $|\psi_p'; 0\rangle$ in equation (5) by a product of electronic and nuclear wavefunctions with the latter function centred at the bottom of the well. The basic ideas can be best understood in terms of WKB wavefunctions. Detailed calculations given in [10] show that this leads on to the FC Green operator in which each well is considered separately. The effective virtual transitions are vertical in a FC diagram. They originate from the vibrational ground state in one of the wells on the lowest APES and end up at the turning point of the excited vibrational state of energy $n\hbar\omega$ associated with another well in an upper sheet lying exactly above the bottom of the minimum on the lowest sheet. A new Green operator $G^p(T_1)$ is thus introduced for well $p$ in the FC approximation where

$$G^p(T_1) = \sum_i \frac{|i, p\rangle \langle i, p|}{\Delta E_{\text{vert}}^{(i,p)}}. \tag{10}$$

In equation (10), all overlaps between the wells are neglected and the system is localized in any one well in this limit. The FC expression for the soRF then becomes

$$K_M^{(2)\text{FC}}(\Gamma_l \otimes \Gamma_m) = \sum_{p,q} \frac{\alpha_i^p \langle \psi'^p | \mathcal{L}_{M\mu}^{(2)p}(\Gamma_l \otimes \Gamma_m) | \psi'^q \rangle \alpha_j^q}{(T_1 \sigma_i | L_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m) | T_1 \sigma_j)} \tag{11}$$

with the Green operator given by equation (10). The energy $\Delta E_{\text{vert}}^{(i,p)}$ in the Green operator is independent of the well label $p$ and thus simplifies to $\Delta E_{\text{vert}}^{(i)}$. In calculating the FC limiting values of the soRFs, equations (10) and (11) were used. The FC approximation is an accurate analytical technique in the strong coupling regime. As emphasized in [10, 16] for the octahedral $T \otimes t_2$ and icosahedral $T \otimes h$ JT systems, respectively, the underlying physics is clearly exposed.

## 3. The non-Condon perturbative method

The FC approximation is strictly only applicable for the calculation of soRFs in the adiabatic strong coupling limit such that transitions take place so rapidly that the nuclei do not move during the transition. The polarizability is then due to the electrons only. Coulomb attraction between the electrons and the rigid nuclear frame then links the electrons to the rigid lattice. Therefore the freedom of the electron cloud to distort under external perturbations is limited by the nuclear frame and thus, by allowing the nuclei to move, we enhance the polarizability of the molecular system. This is the main improvement we obtain in the theory from such non-Condon terms.

An alternative description is to suppose that the adiabatic wavefunctions are frozen at the bottom of the minima. Thus we need only consider a very limited number of electron basis functions. However, in real systems involving finite coupling strengths, the nuclear frame is not completely frozen. To include such contributions it is necessary to lift the restriction of the rigid frame approximation by providing, for example, the electron wavefunctions with an
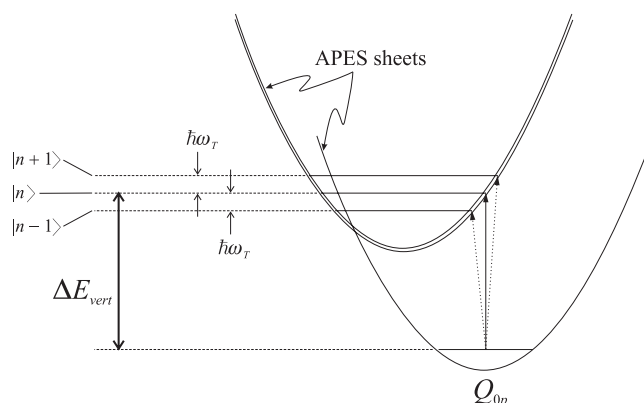
**Figure 1.** A cross-section of the lowest adiabatic potential energy surface for the $T \otimes t_2$ JT system through one of the original wells centred on $Q = Q_{0p}$. Some non-vertical transitions to excited vibrational states separated by $\hbar\omega_T$ above the energy gap $\Delta E_{\text{vert}}$ arising from the non-Condon correction are also shown.

additional flexibility by allowing them to follow the nuclear vibrations. This gives rise to the non-Condon corrections. The physical processes involved are similar to those encountered in Raman spectroscopy where the electric field part of the perturbation acts simultaneously on the nuclei frame and electron charge cloud giving rise to a generalized polarizability of the system. It distorts the electron cloud and moves the nuclei thus providing a coupling between the electrons and nuclei.

The effect of such non-Condon corrections is to modify the diagram used to illustrate the standard Franck–Condon approximation. The transitions between the sheets are then no longer vertical as transitions to excited oscillator states in the wells may occur. This is illustrated qualitatively in figure 1 for the $T \otimes t_2$ JT system. It shows transitions from the ground sheet to the excited sheets supplemented by a number of vibrational levels superimposed on the excited sheets through the non-Condon correction. Not shown but equally likely are transitions from excited vibrational levels at energies $n\hbar\omega_T$ above the basis sheet to the excited sheets. Both sets of transitions take place simultaneously.

The underlying theory for the non-Condon corrections may be deduced by considering the corrections to all the electronic well states used in equation (11) for the soRF within the FC approximation to take into account the effect of non-rigidity of the nuclear frame. We first of all simplify our notation by replacing the general collective coordinate $Q_{\Gamma\gamma}$ in equation (1) by $Q_j$ and define $Q_j = Q_{0p}$ as the coordinate of the bottom of the well $p$. To reach a second-order contribution, we must correct the states either to first or second order. A correction of first order may give contributions of odd or even degree of new displacement coordinates defined by $q_p$ measured from the positions of the bottoms of the wells where $q_p = Q_j - Q_{0_p}$. As we are interested only in those low energy states close to the bottom of the wells, the amplitudes of the nuclear displacements from the bottom of the wells are small compared to the average value of the nuclear displacements (i.e. $q_p \ll Q_j$). Thus the criterion for smallness comes from the small deviation $q_p$ of the displacement from the bottom of the minimum point. Ideally, we should include the nuclear motion as a part of the dynamic problem so that the parameter $q_p$ becomes a variable associated with the ground harmonic oscillator state $|0\rangle$ in the well $p$.

It is necessary next to relate these small displacements to the collective coordinates $Q_j$ from a Taylor expansion of the general potential energy $U(Q_j)$ of the system. In the adiabatic approximation, the nuclear coordinates $Q_j$ are free parameters and can be used as a basis for

the Taylor expansion. Thus we re-write the vibronic Hamiltonian $U(Q_j)$ given in equation (1) in the general form [2, chapter 3]

$$
\begin{aligned}
U(Q_j) &= U(Q_{0p}) + U_1 + U_2 \\
U_1 &= \sum_j \left[ \frac{\partial U(Q_{0_p} j)}{\partial Q_j} \right]_{Q_j = Q_{0_p}} q_p \\
U_2 &= \frac{1}{2} \sum_j \sum_{j'} \left[ \frac{\partial^2 U(Q_j)}{\partial Q_j \partial Q'_j} \right]_{Q_j = Q_{0_p}} q_p q'_p.
\end{aligned}
\tag{12}
$$

In this equation, $U_1$ and $U_2$ are the first- and second-order terms in the potential.

On acting with equation (12) on the ket and bra, corrections to the potential energy of the system are

$$
\begin{aligned}
U_1 &= \sum_j \left( \mu \omega^2 Q_{0p} C_{0j} + V_j C_{\Gamma\gamma} \right) q_p \\
U_2 &= \mu \omega^2 C_{0\Gamma} q_p q'_p.
\end{aligned}
\tag{13}
$$

Now $U_2$ is clearly a constant and thus as it cannot admix the ground electronic well state $|\psi'^p\rangle$ with the excited electronic well states $|e'^p\rangle$ it can be neglected. However, $U_1$ cannot be neglected. 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 admixes the ground electronic well states with the electronic excited well states $|e'^p_m\rangle$ (i.e. $\langle \psi'^p | U_1 | e'^p_m \rangle \neq 0$). This thus gives a correction of the well ground state such that the new ground state is

$$
|\psi'^p_c\rangle = |\psi'^p\rangle + |\Delta\psi^{1p}\rangle
\tag{14}
$$

where

$$
|\Delta\psi^{1p}\rangle = \sum_m \frac{|e'^p_m\rangle \langle \psi'^p | U_1 | e'^p_m \rangle}{\Delta E_{\text{vert}}}.
\tag{15}
$$

The non-Condon perturbation thus gives a correction $|\Delta\psi^{1p}\rangle$ to the well ground state proportional to $q_p$. The non-Condon perturbation also gives a similar correction to the two excited well states, which also involve $q_p$, and mixes the two excited well states. The excited states are then no longer degenerate. We simplify the problem by excluding the mixing of the excited well states.

Since the JT systems considered here all involve the orbital triplet terms only, the Green operator can be simplified by writing it in terms of the ground electronic well state $|\psi'^p\rangle$ using the closure relation as in [16]. However, the orbital operators after the introduction of the non-Condon correction do not satisfy the closure relation and thus $G^p(T_1)$ must be replaced by the standard form of second-order perturbation theory namely:

$$
G^p(T_1) = \sum_{m=1,2} \frac{|e'^p_m\rangle \langle e'^p_m|}{\Delta E^p_m}
\tag{16}
$$

where $\Delta E^p_m$ is the appropriate energy denominator including the non-Condon element. The general expression for the soRF within the corrected FC approximation thus becomes

$$
K^{(2)\text{FC}}_{M,\text{corr}}(\Gamma_l \otimes \Gamma_m) = \sum_{p,q} \alpha_i{}^p \frac{\langle \psi'^p_c | \mathcal{L}^{(2)p}_{M\mu,\text{corr}}(\Gamma_l \otimes \Gamma_m) | \psi'^q_c \rangle}{(T_1 \sigma_i | L^{(2)}_{M\mu}(\Gamma_l \otimes \Gamma_m) | T_1 \sigma_j)} \alpha_j^q
\tag{17}
$$

in which $\mathcal{L}^{(2)p}_{M\mu,\text{corr}}(\Gamma_l \otimes \Gamma_m)$ is now calculated with the corrected Green operator in equation (16). In this final result, we have terms independent of $q_p$ (which are the standard

FC results) together with the non-Condon correction containing terms which are of order $q_p^2$. Higher order terms of order $q_p^4$ and $q_p^2 q_{p'}^2$ may be neglected. We conclude that the standard FC approximation for the calculation of the soRFs can be obtained directly by using equations (10) and (11). When the non-Condon corrections are included, the soRFs are given instead by equation (17).

Before presenting details for specific JT systems, we note that $\Delta E_{\text{vert}}$ is proportional to the JT energy $E_{\text{JT}}$. This in turn is proportional to the inverse square of the linear JT coupling constant $V_j$. Thus the non-Condon correction to the standard FC values will be of the order of the inverse square of JT energy (i.e. of the order of $V_j^{-4}$). We also note that, even though all wells are equivalent to each other and the overlaps between different wells are zero, we have retained the labels of the individual wells in equation (17) for symmetry reasons.

## 4. Application to cubic $T \otimes t$ JT systems

We recall first of all some background information related to these important systems. The simplest case of a very strong $T \otimes t$ JT effect in molecular systems is in the molecular cation of methane ($CH_4^+$). The corresponding details of the chemical bonding and the nature of the JT effect were reported in 1962 by Snyder [17]. The importance of this molecular system is in its extensive presence in the so-called methane planets (due to radiolysis of molecular methane) and, also, in interstellar space. Due to the strong JT effect, the methane cation is an extreme example of high chemical reactivity, even higher than that of fluorine. In its turn, the high reactivity provides the ability of the methane cation to initiate the chemical reaction of polymerization and, in the presence of water and/or ammonium, to produce amino acids and sugars, the important elements of biochemistry of life.

In the laboratory, many other examples of the JT effect in orbital triplet states are well known. (See the bibliographic review of Bersuker [18] for further references.) In particular, we mention substitutional impurity ions in various host crystals. The impurity site invariably has either octahedral or tetrahedral symmetry. In octahedral symmetry, the triplet usually appears to involve a stronger coupling to the $e$-type vibrational modes of the surroundings than to the $t_2$-type modes. However, this is not the case in tetrahedral symmetry where the situation is reversed. A possible physical reason for this is that the $t_2$-modes result in a trigonal distortion along the $\pi$ bonds in octahedral symmetry, whereas in tetrahedral symmetry the equivalent distortion is along the $\sigma$ bonds. The corresponding overlap integrals are consequently smaller for $t_2$-modes compared to $e$-modes in octahedral symmetry but larger in the tetrahedral case. Thus the most likely place to find examples of a $T \otimes t$ JT system is in III–V and II–VI semiconductors (such as GaAs, GaP and InP) doped with $(3d)^n$ transition metal ions such as $Cr^{2+}$, $Cr^{3+}$, $Fe^{2+}$ and $V^{3+}$. Many of these impurities generate deep levels within the semiconductor band gap, and they frequently form the basis of semi-insulating device material which has been of significant importance during the last two decades.

We know that GaAs:$V^{3+}$ has been identified as an example of such a system from an analysis of the structure observed in optical data [19]. It was shown there that the structure of the accompanying zero-phonon line could be explained in terms of the effects of spin–orbit coupling as a second-order perturbation through the soRFs [20, 21]. However, although the literature contains many examples of JT effects in such systems, there are relatively few other cases known in which the existence of a $T \otimes t$ JT systems has been clearly verified. One basic problem is that the appearance of soRFs often complicates the interpretation of the experimental data. This emphasizes the importance of our study.

We consider now the general determination of soRFs for the $T \otimes t$ system. The Hamiltonian given in equation (1) applies with $\Gamma = T$ and $\gamma = 4, 5, 6$. Thus $Q_i$ ($i = 4$–6)

are the usual collective displacements of the $t_2$-mode. In the cubic $x$, $y$, $z$ basis, the matrices of the $C_{\Gamma}\gamma$ operators within the $T_2$ orbital ground states are

$$C_{T_{2x}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & 0 \end{pmatrix}; \qquad C_{T_{2y}} = \begin{pmatrix} 0 & 0 & -\sqrt{3}/2 \\ 0 & 0 & 0 \\ -\sqrt{3}/2 & 0 & 0 \end{pmatrix}$$

$$C_{T_{2z}} = \begin{pmatrix} 0 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}; \qquad C_{T_{20}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{18}$$

(Note that the factor $\sqrt{3}/2$ has been included in the above $\Gamma\gamma$ matrices for later convenience.) A four-dimensional APES is thus formed comprising the energy (along the vertical axis) and the three-$t_2$ displacement coordinates $Q_4$, $Q_5$ and $Q_6$. Within this space, the lowest APES contains four minima (or wells) labelled $p = 1$–4 centred on $Q_i = Q_{0p}$, as discussed in standard texts (e.g. [2, 8]). To a first approximation, the vibrational states within each well are equally spaced with a separation $\hbar\omega_T$. The ground $|\psi'^p\rangle$ and excited electronic states $|e_1^p\rangle$ and $|e_2^p\rangle$ in each well are well known (see, for example, [2, 4, 22, 23]).

The energy gap between the ground and doublet excited vibronic states is thus

$$\Delta E_{\text{vert}} = 3E_{\text{JT}}^{Tt} \equiv \frac{4K_T^2}{\hbar\omega_T} \tag{19}$$

with $-E_{\text{JT}}^{Tt}$ defined as the JT energy, and where a new coupling constant $K_T$ has been defined by

$$K_T^2 = \frac{3V_T^2\hbar}{8\mu\omega_T}. \tag{20}$$

In our previous work describing the FC approximation for soRFs [10], we replaced the vibronic well state $|\psi'^p; 0\rangle$ by the product

$$|\psi'^p; 0\rangle = |\psi'^p\rangle|0\rangle \tag{21}$$

where $|0\rangle$ is the associated three-dimensional oscillator wavefunction centred about $Q = Q_{0p}$. The nuclear frame wavefunction is thus given by

$$|0\rangle = \left(\frac{2\tau}{\pi}\right)^{1/4} \exp[-\tau q_p{}^2] \tag{22}$$

with $\tau = \mu\omega_T/(2\hbar)$.

We take spin–orbit coupling as our perturbation. It is then necessary to use the appropriate CG coefficients for a $T_1$-type of perturbation within the $T_1$ orbital triplet. In this case, there are in principle four soRFs, as the label $M \in T_1 \otimes T_1 = A_1 \oplus E \oplus T_1 \oplus T_2$. Within the Born–Oppenheimer approximation, the adiabatic electron wavefunctions are frozen at the bottom of the corresponding minima. The FC values are then obtained from the Green operator given by equation (10). 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 as in [6] so that the problem in the strong coupling limit is solvable in simple terms. The FC values obtained are thus given by

$$K_A^{(2)}(T_1 \otimes T_1) = -\frac{1}{3E_{\text{JT}}^{Tt}} \qquad K_{T_2}^{(2)}(T_1 \otimes T_1) = -\frac{2}{9E_{\text{JT}}^{Tt}}$$

$$K_{T_1}^{(2)}(T_1 \otimes T_1) = 0 \qquad K_E^{(2)}(T_1 \otimes T_1) = 0 \tag{23}$$

and agree with those obtained previously by analytical methods [12]. It should be noted that all the contributions to the above soRF come from the identity operator when the Green operator is simplified with the closure relation [10, 16].

The next stage in the analysis is to introduce the non-Condon corrections to the above FC values as discussed in the previous section. However, at the same time it is necessary to include the effects of anisotropy in the problem as their origin closely follows that of the non-Condon correction. The anisotropy arises here because the wells in the lowest APES sheet have trigonal symmetry so that they are not isotropic. Thus the oscillators in the wells have different vibrational frequencies in different directions. The cubic coordinates in a well should thus be re-classified in terms of a trigonal singlet mode and a trigonal doublet mode with associated oscillator frequencies $\omega_A$ and $\omega_E$, respectively. Previous calculations involving anisotropy in the $T \otimes t_2$ JT system [15, 24, 25] have shown that the effective oscillator frequency $\omega_A = \omega_T$ for the soRF $K_A^{(2)}(T_1 \otimes T_1)$ but that for the soRF $K_{T_2}^{(2)}(T_1 \otimes T_1)$ is $\omega_E = \sqrt{2/3}\omega_T$. A more detailed general discussion of the effects of anisotropy in JT systems has been given very recently in Dunn *et al* [26].

The corrections to the soRFs from the non-Condon perturbation $U_1$ are readily obtained using equation (16) and the corrected electronic ground states in the wells. The results obtained for the soRF of $A$-symmetry and for one of the components for each of $T_2$ and $E$-symmetries including the anisotropy corrections are

$$K_A^{(2)}(T_1 \otimes T_1) = -\frac{1}{3E_{JT}^{Tt}} - \frac{\mu\hbar^2\omega_T^4}{96K_T^4}\langle 0|q_4^2 + q_5^2 + q_6^2|0\rangle = -\frac{1}{3E_{JT}^{Tt}} - \frac{\hbar\omega_T}{36E_{JT}^{Tt\,2}}$$

$$K_{T_2}^{(2)}(T_1 \otimes T_1) = -\frac{2}{9E_{JT}^{Tt}} + \frac{\mu\hbar^2\omega_T^4}{216K_T^4}\langle 0|q_4^2 + q_5^2 - 2q_6^2|0\rangle = -\frac{2}{9E_{JT}^{Tt}}$$

$$K_E^{(2)}(T_1 \otimes T_1) = \frac{\mu\hbar^2\omega_T^4}{288K_T^4}\langle 0|q_4^2 + q_5^2 - 2q_6^2|0\rangle = 0 \tag{24}$$

$$K_{T_1}^{(2)}(T_1 \otimes T_1) = 0.$$

The matrix elements in the above expressions involve symmetry-related combinations of the displacements $q_p$. These have then been replaced by the expectation value $\langle q_p^2 \rangle$ over the oscillator ground states, namely $\frac{\hbar}{2\mu\omega_T}$ in this case. It can be seen that the only non-zero non-Condon corrections are to the soRF of $A$-symmetry. However, the correction is proportional to $1/(E_{JT}^{Tt})^2$ which results in a significant modification to the original FC value. (Note that the detailed expressions given in equation (24) are corrected from those given previously in [10].)

The soRFs of $A$ and $T_2$ symmetries are shown in figures 2 and 3, respectively, as a function of the coupling strength $K_T$, and figure 4 shows an alternative plot in the form $K_T^2 K_M^2$ for $M = A$. (With this choice of label for the vertical axis, the standard FC values are represented by horizontal straight lines as seen, for example, in figure 4.) Also included in these figures are the original analytical calculations of Bates *et al* [12] (which also included the anisotropy corrections) together with the numerical results of O'Brien [11]. Figures 2 and 4 clearly show that the non-Condon corrections to the soRFs of $A$ symmetry give values of the soRFs which are significantly closer to the numerical results in the strong coupling regime and thus the inclusion of the non-Condon corrections represents an improvement on the standard FC results for this simple cubic system [10]. These results also indicate that the neglect of the mixing of the excited well states by the non-Condon correction is valid. They are also an improvement on the analytical calculations [12] in the strong coupling regime because they avoid the over counting of the excited states inherent in that work.

## 5. Non-Condon corrections for $T \otimes h$ JT systems

The icosahedral $T_{1u} \otimes h_g$ JT system is generally regarded as a suitable model to describe the vibronic properties of the ground state of the $C_{60}^-$ molecular ion [3]. In this case, the single
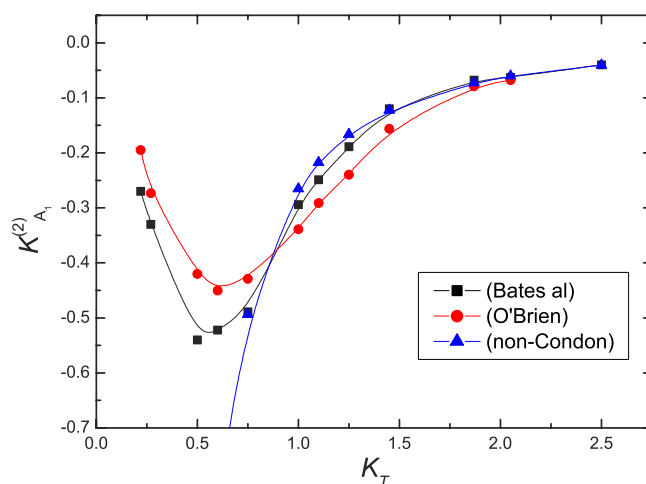
**Figure 2.** Comparative plots of the soRF $K_{A_1}^{(2)}(T_1 \otimes T_1)$ as a function of $K_T$ and in units of $\hbar\omega_T$ for the $T \otimes t$ JT system, showing the results of the analytical calculation based on the shift-transformation method (■) [12], the numerical calculation (●) [11] and this work (▲) including non-Condon corrections.
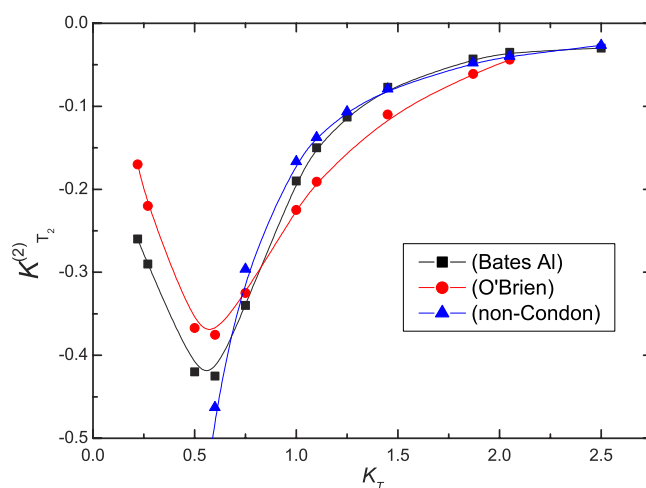


**Figure 3.** As figure 2 but for the soRF $K_{T_2}^{(2)}(T_1 \otimes T_1)$.

electron attached to the $C_{60}$ cage is coupled to the vibrations of the cage itself rather than to the surrounding lattice. An analytical model for this system was developed in [27] in which both linear and quadratic vibronic coupling was considered. When linear vibronic coupling is considered alone, a trough in the lowest APES was found. Dunn *et al* [28] have shown, for example, how the motion of the system in the five-dimensional coordinate space may be decomposed into vibrations in three directions perpendicular to the trough and rotations in the two directions around the trough. The addition of quadratic coupling generates wells in the trough [27] and it is this aspect of the problem which is our prime concern in this paper.

Calculations of the soRFs were presented in [6], assuming the presence of linear coupling terms only. The role of the quadratic terms was merely to generate either six pentagonal $D_{5d}$
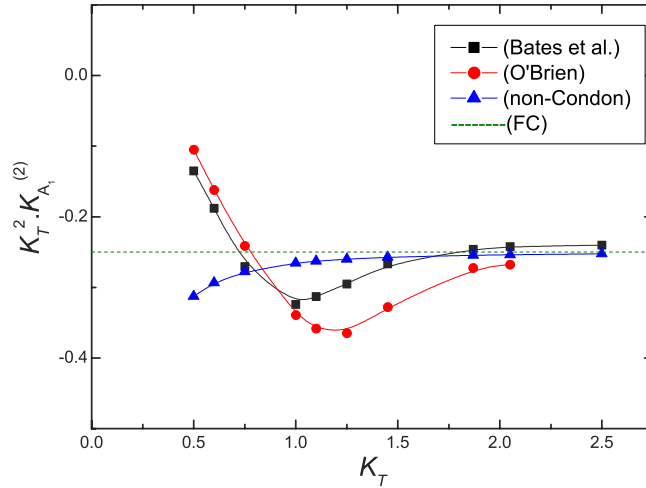
**Figure 4.** As figure 2 but plotting $K_T^2 K_{A_1}^{(2)}$ rather than $K_{A_1}^{(2)}$.

wells or ten trigonal $D_{3d}$ wells in the lowest APES in order to represent more closely a real system. A set of symmetry-adapted states were determined for each case and were used as a basis to calculate analytical expressions of the soRFs in these systems using the ST method. In the latter calculations, an infinite set of vibronic states in each well was used so that the expressions found were expected to cover the whole range of coupling strengths. The limiting case of strongly coupled systems was considered later by using the FC approximation [10]. The FC-values for the soRFs $K_M^{(2)}(T_1 \otimes T_1)$ were generally found to be smaller than those estimated from the ST method in the strong coupling limit by factors of 5/2 and 3/2 for the $D_{5d}$ and $D_{3d}$ type wells, respectively. Possible factors to account for the differences in the results obtained with the two approaches were discussed, such as the neglect of anisotropy in the FC calculations. This could be an important omission but it is unlikely to give a correction of the required magnitude. A further correction arising from the $T_2$ excited tunnelling states is also likely to be unimportant as at moderately strong coupling this tunnelling state is well separated from the ground vibronic triplet. We thus suppose that the most important correction arises from the non-Condon correction to the FC calculations as discussed above in section 3.

We now consider the non-Condon corrections for this $T \otimes h$ JT system. Our starting point is equation (1) with $V_\Gamma \to V_H$ and $\omega \to \omega_H$. The matrices of the CG coefficients $C_{Hi}$ are given explicitly in [6] so that the potential energy part of equation (1) becomes

$$\mathcal{H}_{Th} = \left[ \sum_{i=\theta,\epsilon,4,5,6} \tfrac{1}{2}\mu\omega_H^2 Q_i^2 + V_H Q_i C_{Hi} \right]. \tag{25}$$

In terms of the coupling constant $K_H = -V_H\sqrt{\hbar}/\sqrt{2\mu\omega_H}$, [6] the JT energy $E_{JT}^{Th}$ is given by [10]

$$E_{JT}^{Th} = \frac{2K_H^2}{5\hbar\omega_H}. \tag{26}$$

From this equation, we obtain an expression for $U_1$ and follow the details presented above in section 3. The additional information required consists of the coordinates of the centres of the $D_{3d}$ and $D_{5d}$ wells which are given in [27], for example, and expressions for the doublet excited electronic states $|e_m^p\rangle$ for both types of wells. The latter are given in table 1 of [29],

for example. Each well has a singlet electronic ground state and an excited doublet and their separation is thus $\Delta E_{\text{vert}} = 3E_{\text{JT}}^{Th}$.

Following the procedures given in [10] but modified as given above, expressions for the soRFs including the non-Condon corrections for the $T \otimes h$ JT system have been found for $D_{5d}$ and the $D_{3d}$ wells separately. We recall that $M = A$, $H$ in the soRF $K_M^{(2)}(T_1 \otimes T_1)$ and $M = A$, $T_1$ and two $H$-type components (now labelled $H_a$ and $H_b$) in the soRF $K_M^{(2)}(H \otimes H)$. (We note that $H_a$ and $H_b$ cannot be distinguished on symmetry grounds.) In this system, the averages $\langle q_p^2 \rangle$ evaluate to $\hbar/(2\mu\omega_H)$.

The soRFs involving the perturbations $(T_1 \otimes T_1)$ are, for $D_{5d}$ wells,

$$
\begin{aligned}
K_A^{(2)}(T_1 \otimes T_1)_{\text{D}_{5d}} &= -\frac{1}{3E_{\text{JT}}^{Th}} - \frac{\hbar\omega_H}{12E_{\text{JT}}^{Th\,2}} \\
K_H^{(2)}(T_1 \otimes T_1)_{\text{D}_{5d}} &= -\frac{2}{15E_{\text{JT}}^{Th}}
\end{aligned}
\tag{27}
$$

and for $D_{3d}$ wells,

$$
\begin{aligned}
K_A^{(2)}(T_1 \otimes T_1)_{\text{D}_{3d}} &= -\frac{1}{3E_{\text{JT}}^{Th}} - \frac{\hbar\omega_H}{12E_{\text{JT}}^{Th\,2}} \\
K_H^{(2)}(T_1 \otimes T_1)_{\text{D}_{3d}} &= -\frac{2}{15E_{\text{JT}}^{Th}}
\end{aligned}
\tag{28}
$$

where the suffices $D_{5d}$ and $D_{3d}$ label the well symmetries.

Similarly, for perturbations $(H \otimes H)$ for which the five matrices of the CG coefficients are given by equation (30) in [13], the results for $D_{5d}$ wells are

$$
\begin{aligned}
K_A^{(2)}(H \otimes H)_{\text{D}_{5d}} &= -\frac{1}{5E_{\text{JT}}^{Th}} - \frac{\hbar\omega_H}{20E_{\text{JT}}^{Th\,2}} \\
K_{H_a}^{(2)}(H \otimes H)_{\text{D}_{5d}} &= -\frac{2}{15E_{\text{JT}}^{Th}} + \frac{2\hbar\omega_H}{45E_{\text{JT}}^{Th\,2}} \\
K_{H_b}^{(2)}(H \otimes H)_{\text{D}_{5d}} &= +\frac{2}{25E_{\text{JT}}^{Th}} - \frac{2\hbar\omega_H}{25E_{\text{JT}}^{Th\,2}}
\end{aligned}
\tag{29}
$$

and the results for $D_{3d}$ wells are:

$$
\begin{aligned}
K_A^{(2)}(H \otimes H)_{\text{D}_{3d}} &= -\frac{1}{5E_{\text{JT}}^{Th}} - \frac{\hbar\omega_H}{20E_{\text{JT}}^{Th\,2}} \\
K_{H_a}^{(2)}(H \otimes H)_{\text{D}_{3d}} &= -\frac{2}{135E_{\text{JT}}^{Th}} - \frac{2\hbar\omega_H}{81E_{\text{JT}}^{Th\,2}} \\
K_{H_b}^{(2)}(H \otimes H)_{\text{D}_{3d}} &= -\frac{2}{15E_{\text{JT}}^{Th}} + \frac{2\hbar\omega_H}{45E_{\text{JT}}^{Th\,2}}.
\end{aligned}
\tag{30}
$$

Unlike the case of the $T \otimes t_2$ JT system, no anisotropy corrections have been included in any of the above expressions for the soRFs in the $T \otimes h$ JT system. The effects of anisotropy in the $T \otimes h$ JT system have been studied by evaluating the curvature associated with the $D_{3d}$ and $D_{5d}$ minima when quadratic coupling is included in the analysis [30, 31]. The frequencies of the local vibrational modes were obtained as a function of the strength of the quadratic coupling constants in the strong linear coupling limit for both types of wells. The original five-fold degenerate oscillators associated with the wells are split into one singlet and two doublets. Further work [29] extended the earlier calculations to less strongly coupled JT systems. However, even with the simplest approximation cited above, it is not straightforward
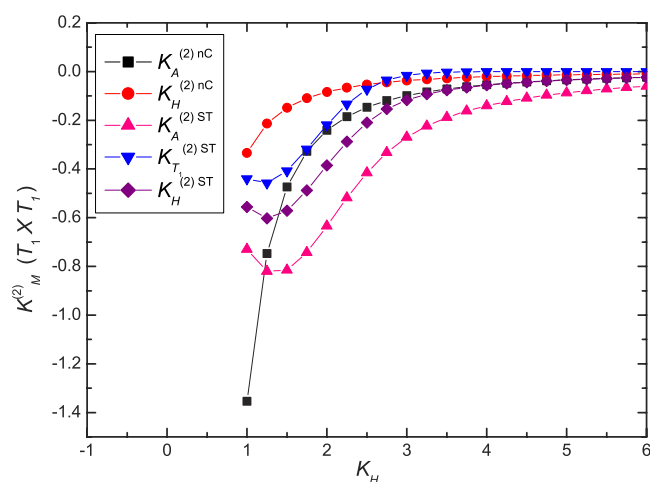
**Figure 5.** The calculated values of the soRFs $K_M^{(2)}(T_1 \otimes T_1)$ as a function of the vibronic coupling coefficient $K_H$, in units of $\hbar\omega_H$, for $D_{5d}$ wells in the $T \otimes h$ JT system. The values obtained by including the non-Condon corrections described here (designated by the suffices nC) and from the original ST approximation (designated by the suffices ST) are both shown.
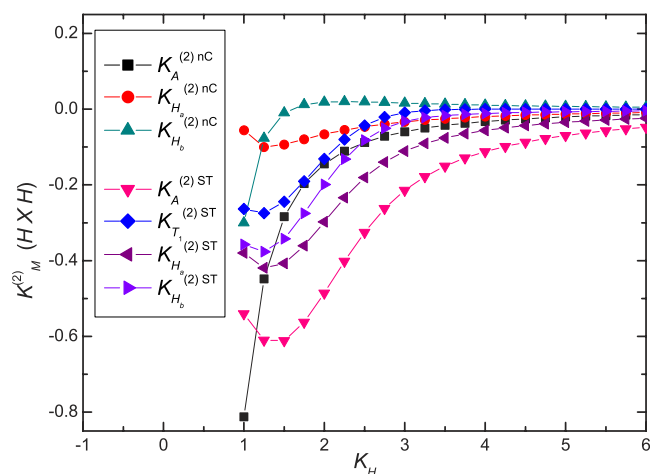


**Figure 6.** As figure 5 but for the soRFs $K_M^{(2)}(H \otimes H)$.

to insert the corrections to the frequencies in the formulae of the soRFs given above, unlike the case of the $T \otimes t$ JT system. As these corrections involve the quadratic coupling constants only, they are small [30].

There are many sets of graphs which can be produced to take into account simultaneously the two types of minima, the two combinations of perturbation $[(H \otimes H)$ and $(T_1 \otimes T_1)]$ and the different values of $M$. Further complications can occur with mixed perturbations such as $T_1 \otimes H$, and because the two components $H_a$ and $H_b$ are not uniquely defined. A few typical results are illustrated in figures 5–8 showing the dependence of the soRFs on the vibronic coupling coefficient $K_H$ for values of $K_H > \hbar\omega_H$; other graphs for other soRFs can usually be obtained directly from the formulae given above. The new graphs shown
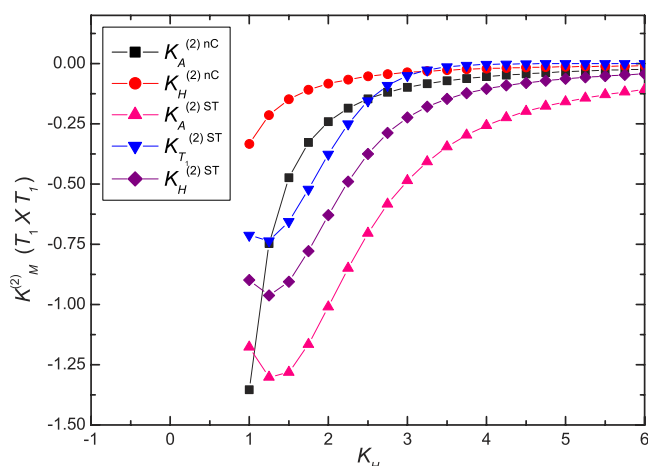
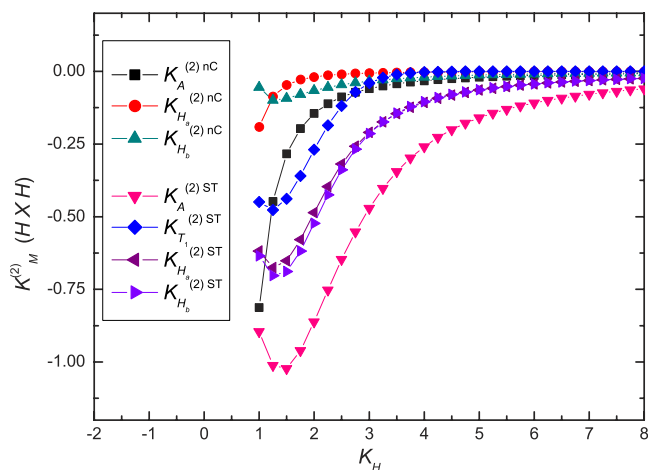**Figure 7.** As figure 5 but for $D_{3d}$ wells.



**Figure 8.** As figure 6 but for $D_{3d}$ wells.

here containing the non-Condon corrections can be compared directly with the original ST analytical calculations [7] which are reproduced in the figures.

As anticipated from above, the soRFs containing the non-Condon corrections to the Franck–Condon calculations are generally significantly smaller in magnitude than those obtained from the ST approximation alone for large $K_H$ but their relative importance decreases rapidly with increasing $K_H$. Nevertheless, the terms generated by the soRFs in the effective Hamiltonian for any $T \otimes h$ JT system make significant contributions in those regions in which real systems are expected to fall. They thus are important in any modelling of experimental data.

## 6. Discussion

The initial aim of this work was to take the simplest of the possible non-Condon corrections to the standard FC calculations to see if the gap between the numerical calculations of

O'Brien [11], the analytical calculations of Bates *et al* [12] and the FC limiting values could be reduced for the $T \otimes t_2$ JT system. This work represents an improved and corrected version of our preliminary work on this subject described in [10]. The new results obtained and shown in figures 2 and 4 show clearly that the non-Condon corrections indeed give final results closer to the numerical work of O'Brien [11]. Thus the non-Condon corrections are a valid improvement on the standard FC results and provide an accurate estimate of the second-order RFs for this system in strong vibronic coupling for which $K_T > \hbar\omega_T$.

The main part of this work was to extend our calculations of RFs, particularly those of second order to icosahedral JT systems. The simplest of these is $T \otimes h$ which has direct relevance to the ground state of the $C_{60}^-$ molecular ion. Thus the non-Condon correction to the soRFs in this system were obtained, and some of the results have been presented in figures 5–8. The strong coupling limit of the soRFs in these systems have been calculated following the shift-transformation method [7] and the Franck–Condon approximation [2]. The non-Condon corrections lift the assumption of rigid electronic wavefunctions that are assumed in the standard FC approximation. They provide a way for the vibronic wavefunctions to adjust to the effects of electronic perturbations up to and including those of second order. This concept is based on ideas that are similar to those involved in Raman scattering in optical spectra. The comparison made between these different methods has shown that the soRFs are now available and valid from very strong vibronic to intermediate coupling for these systems.

The overall aim of our work is to give a comprehensive account of the basic theory of icosahedral JT systems and thus provide a framework to enable the modelling of real systems to be undertaken. As pointed out earlier, the development of the JT theory for magnetic ion impurities in semiconducting and insulating host crystals provided a most significant step in our understanding of these systems. In turn, this provided much of the basis for the manufacture of device material as well as the contributions to basic science. However, we note that many years passed before JT models in cubic systems could be used with much confidence. Studies of icosahedral systems have had a much shorter history and are usually much more complicated than those of cubic symmetry in terms of interpreting the experimental data. Also, the latter are not usually in a form directly relevant to the theory, and much further work is needed to enable a valid comparison to be made. Here, we have concentrated on the $T \otimes h$ JT system as it is the simplest icosahedral system and it is applicable to the ground state of the $C_{60}$ molecular anion. However, in the modelling of experimental data of the excited states of $C_{60}$ and of multi-electron and/or multi-hole doped fullerene ions [32, 33], it is necessary to also develop equivalent theoretical models for all the other linear icosahedral systems (such as $G \otimes (g \oplus h)$ and $H \otimes (g \oplus h)$). They are also expected to have a role to play in the study of phase transitions and co-operative JT effects in some fullerene solids [34]. A catalogue of theoretical information can now be assembled to assist in the identification of the system being studied.

## References

[1] Bersuker I B 1984 *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry* (New York: Plenum)
[2] Bersuker I B and Polinger V Z 1989 *Vibronic Interactions in Molecules and Crystals* (Berlin: Springer)
[3] Chancey C C and O'Brien M C M 1997 *The Jahn–Teller Effect in $C_{60}$ and Other Icosahedral Complexes* (Princeton, NJ: Princeton University Press)
[4] Dunn J L 1988 *J. Phys. C: Solid State Phys.* **21** 383
[5] Dunn J L 1989 *J. Phys.: Condens. Matter* **1** 7861
[6] Qiu Q C, Dunn J L, Bates C A, Abou Ghantous M and Polinger V Z 2000 *Phys. Rev.* B **62** 16155
[7] Huang R, Abou-Ghantous M, Bates C A, Dunn J L, Polinger V Z and Moate C P 2002 *J. Phys.: Condens. Matter* **14** 1319

[8] Bersuker I B 2001 *Chem. Rev.* **101** 1067
[9] Ham F S 1965 *Phys. Rev.* A **138** 1727
[10] Abou-Ghantous M, Polinger V Z, Dunn J L and Bates C A 2002 *J. Phys.: Condens. Matter* **14** 3115
[11] O'Brien M C M 1990 *J. Phys.: Condens. Matter* **2** 5539
[12] Bates C A, Dunn J L, Hallam L D, Kirk P J and Polinger V Z 1991 *J. Phys.: Condens. Matter* **3** 3441
[13] Fowler P W and Ceulemans A 1985 *Mol. Phys.* **54** 767
[14] Polinger V Z, Bates C A and Dunn J L 1991 *J. Phys.: Condens. Matter* **3** 513
[15] Dunn J L, Bates C A and Kirk P J 1990 *J. Phys.: Condens. Matter* **2** 10379
[16] Al-Hazmi F, Polinger V Z, Dunn J L, Bates C A, Moujaes E A and Abou-Ghantous M 2002 *Adv. Quantum Chem.* **44** 169
[17] Snyder L C 1962 *Phys. Rev.* **66** 2299
[18] Bersuker I B 1984 *The Jahn–Teller Effect. A Bibliographic Review* (New York: Plenum)
[19] Ulrici W *et al* 1987 *Phys. Status Solidi* b **141** 191
[20] Bates C A, Dunn J L and Ulrici W 1990 *J. Phys.: Condens. Matter* **2** 607
[21] Bates C A and Dunn J L 1989 *J. Phys.: Condens. Matter* **1** 2605
[22] Öpik U and Pryce M H L 1957 *Proc. R. Soc.* A **238** 425
[23] Ham F S 1990 *J. Phys.: Condens. Matter* **2** 1163
[24] Jamila S, Dunn J L and Bates C A 1992 *J. Phys.: Condens. Matter* **4** 4945
[25] Dunn J L and Bates C A 1989 *J. Phys.: Condens. Matter* **1** 375
[26] Dunn J L, Bates C A, Moate C P and Liu Y M 2003 *J. Phys.: Condens. Matter* **15** 5697
[27] Dunn J L and Bates C A 1995 *Phys. Rev.* B **52** 5996
[28] Dunn J L, Eccles M R, Liu Y-M and Bates C A 2002 *Phys. Rev.* B **65** 115107
[29] Qiu Q C, Dunn J L, Bates C A and Liu Y M 1998 *Phys. Rev.* B **58** 4406
[30] Liu Y M, Dunn J L, Bates C A and Polinger V Z 1997 *J. Phys.: Condens. Matter* **9** 7119
[31] Liu Y M, Dunn J L, Bates C A and Polinger V Z 1997 *Z. Phys. Chem.* **200** S.111
[32] Sookhun S, Dunn J L and Bates C A *Phys. Rev.* B **68** 235403
[33] Dunn J L and Li H 2004 *Phys. Rev.* B submitted
[34] Dunn J L 2004 *Phys. Rev.* B **69** 064303