A thesis
submitted in partial fulfilment
of the requirements for the Degree
of
Doctor of Philosophy
in the
University of Canterbury
Christchurch, New Zealand.

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1981
A novel method is developed for the description and calculation of Ham reduction factors in 'Jahn-Teller active' systems which are weakly coupled to many lattice modes. Diagrammatic many-body perturbation theory for finite temperatures is combined with diagrammatic group theory into a coherent formalism, whose essential features are readily visualized. The method lends itself to economical calculation of reduction factors (given the recent availability of 6j symbols for crystal point group) and also to generalization of the traditional single multiplet 'Jahn-Teller problem'. Multimode effects may be distinguished experimentally by searching for particular combinations of reduction factors, associated with particular Feynman diagrams, that vanish to all orders in systems with a continuous symmetry group and to fourth order in all systems, within a single-mode coupling model. General expressions for reduction factors are derived for octahedral systems up to at least fourth order, and including lattice anharmonicity and non-linear electron-phonon coupling. The effects of symmetric vibrations and intermultiplet coupling on reduction factors, and generalization to second order reduction factors, are investigated.
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INTRODUCTION

When the coupling of an impurity ion to a host crystal lattice is not so strong, that the Jahn-Teller instability of degenerate electronic states lowers the site symmetry of the ion, the system is said to exhibit the dynamic Jahn-Teller effect (DJTE), (Ham (1972), Englman (1972)). The coupling between the lattice vibrations and the electronic states now modifies the energy levels of the combined (vibronic) system in a non-trivial manner, even for weak coupling. Ham first recognized the import of the DJTE for the interpretation of EPR and optical spectra of impurities: when a symmetry lowering perturbation is applied to the ionic levels, it is the vibronic, and not the electronic states, which determine the response. He introduced the concept of reduction factors (RFs) to describe the (observed) reduction of electronic matrix elements of the perturbation, as a result of the vibronic coupling. Since the magnitudes of the RFs contain details of the ion-lattice interaction, their measurement, and the theoretical models advanced for their interpretation, have played important roles in the understanding of impurity-host systems. It is these models that are our concern.

Ham's (1965, 1968) initial model for RFs, was based on the coupling of the ion to the linear (symmetrized) displacements of the nearest neighbours, assuming a single frequency for this vibration. For example, for the case of an electronic doublet in cubic symmetry, $\Gamma_3$, coupled to a $\Gamma_3$-type vibration, $\Gamma_3 \times \epsilon$, the vibronic ground states related the two RFs, $p,q$ for this system, as $q = \frac{3}{4}(1+p)$. This simple model was used with reasonable success, and held sway until 1973, when Englman and Halperin and, simultaneously, Gauthier and Walker, showed the above relation to be incorrect when the coupling was to more than one mode frequency. Experimental confirmation of their prediction followed (Abou-Ghantous et al. (1974)). Bates and co-workers (Bates (1978) - this article reviews theoretical treatments) have also developed a multimode coupling model for some Jahn-Teller (JT) systems. The methods of calculating RFs, used by the above authors and others, can be divided into three categories:

(i) Construction of the eigenstates of the vibronic Hamiltonian (e.g. Ham, Halperin and Englman) - the standard method. It lends itself to a determination of the relations between RFs that can follow from symmetry arguments (e.g. Leung and Kleiner (1974)).
(ii) Transformation of the vibronic Hamiltonian and external perturbation (Bates) - applicable for linear ion-lattice coupling of JT ions in certain symmetries (it is only exact for one system).

(iii) Green function methods (Gauthier and Walker) - valid for weak coupling.

Though each of the three methods has its limitations, the first is inferior to the other two, because the dependence of the RFs on temperature, and on the coupling of the ion to the continuum of lattice modes, cannot be easily calculated. However, despite the work of the above authors and others, several important problems remain outstanding: a unified approach to RF calculations for JT systems of any symmetry, has yet to be given; the coupling of the ion to the lattice has usually been considered in some restricted form; temperature effects, in combination with the continuum coupling, have not been examined carefully; nor has there been a general formulation to allow the treatment of other considerations, such as coupling between separated electronic states and higher order RFs. With the restriction to a weak coupling solution, we redress this situation. We follow Gauthier and Walker's initiative, and use the thermal Green function method. This borrows the techniques of quantum field theory: perturbative expansions in any interaction are conveniently represented as Feynman graphs. Relevant physical quantities can then be calculated to desired orders, by summing the appropriate graphs. In our case though, these graphs are not merely useful visual aids. Unlike Gauthier and Walker, we represent all algebraic aspects of the formalism by diagrams, as the details of the symmetry constraints on the ion-lattice and the perturbing interactions are latent in these diagrams, and can be extracted with the aid of Stedman's (1975, 1976) diagram technique for groups. We use this technique to maximum advantage to reduce computations. The result is a systematic, and novel, method for the calculation of RFs for any JT system.

In Chapter I, we give the most general formulation of RFs that follows from a knowledge of the symmetry of the system eigenstates alone. Previous treatments are insufficient for our purposes. Relations between RFs for multiplets in octahedral symmetry, the systems of later interest, are calculated. The Green function formalism is presented in Chapter II, our diagram method developed, and RFs defined in an analogous manner to that in Chapter I. In Chapter III, we derive analytic expressions for the RFs for the electronic doublet, $\Gamma_3$, as functions of coupling type, lattice frequencies, and temperature. The basic group-theoretic structures of Feynman diagrams are examined.
This analysis is extended to the more complicated octahedral systems in Chapter IV. For all systems, we examine the implications of our formulae for the interpretation of RFs. Comparisons with previous theoretical treatments are made throughout. Appendices of tables and diagrams are included so that our calculations may be followed.

As additional examinable material, we present at the end of the above work, a paper which considers some consequences of ion-lattice coupling for the JT system, Fe$^{2+}$: MgO.
CHAPTER I

VIBRONIC REDUCTION FACTORS

We give a general group-theoretic construction for the eigenstates of the vibronic Hamiltonian. Following a generalization of Ham's definition of reduction factors it is shown how to extract the symmetry information in them with a knowledge of the \( j \) symbols of the invariance group of the Hamiltonian. We introduce the diagram method for groups for this. We then determine the relations between reduction factors for isolated multiples in cubic symmetry and review the work which has been done in this area. Lastly we remark on systems that have a more complicated energy level structure.

1. CONSTRUCTION OF EIGENSTATES

We shall describe the electronic energy level scheme of an impurity ion in the perfect host crystal by the eigenvalue equation,

\[
H_e \psi_\alpha (q) = E_\alpha \psi_\alpha (q)
\]

(1-1)

where \( q \) represents the electronic coordinates. The precise form of the electronic Hamiltonian, \( H_e \), is not of interest, but it will contain all terms (free ion, static crystal field, spin-orbit etc.) which are larger in magnitude than the dynamic interaction between the ion and the lattice.

The complete set of eigenfunctions \( \{ \psi_\alpha \} \) will then form a good basis for a linear vector space \( V_q \) (a subspace of Hilbert space). The energy levels of the host lattice vibrations (phonons) can be described similarly - a Hamiltonian \( H_p \) with eigenfunctions \( \chi_\beta (Q) \) (\( Q \) the vibrational coordinates) spanning a vector space \( V_Q \).

The vibronic Hamiltonian for the interacting electron-phonon system is written as

\[
H = H_e + H_p + V(qQ)
\]

(1-2)
We need not specify the interaction \( V \) at this stage either. To construct the eigenfunctions of (I-2) we form the set of all possible products \( \{ \psi_{\alpha} x_{\beta} \} \). This set is complete for a function of the coordinates \( (q, \bar{Q}) \) and a linear combination of these products will form a basis for a vector space \( V_{q} \times V_{\bar{Q}} \) the tensor product of \( V_{q} \) and \( V_{\bar{Q}} \) (Messiah (1965)). Thus the most general eigenfunctions of (I-2) have the form

\[
\psi_{\gamma}(q, \bar{Q}) = \sum_{\alpha \beta \gamma} \psi_{\alpha}(q) x_{\beta}(\bar{Q}) C_{\alpha \beta}^{\gamma}
\]

(1-3)

Now if the ion is situated at a lattice site of symmetry corresponding to some point group \( G \), \( H_{e} \) is invariant with respect to the symmetry operations of \( G \), the eigenvalues \( E_{\alpha} \) take on degeneracies, and the eigenfunctions \( \psi_{\alpha}(q) \) may be relabelled by the components of the irreducible representations (irreps) of \( G \). Similarly for the \( x_{\beta} \). The same relabelling occurs for the vibronic eigenfunctions (I-3) since, as Ham (1972) pointed out, although the electronic degeneracy is lifted by the inclusion of \( V \), (I-2) remains invariant with respect to \( G \) under simultaneous transformations of the coordinates \( q, \bar{Q} \).

Changing to bra-ket notation we introduce symmetrized orthonormal bases for the irrep spaces \( V_{\lambda}, V_{\nu} \) of \( G \) and choose them to be eigenvectors of the Hamiltonians \( H_{e}, H_{p} \) by the relabelling (kept throughout our work)

\[
\psi_{\alpha} \leftrightarrow |x_{\lambda}X> \quad \chi_{\beta} \leftrightarrow |y_{\nu}V>
\]

(1-4)

Here \( l, n \) are the components of the irreps \( \lambda, \nu \) of \( G \) and \( x, y \) represent all other labels necessary to specify the eigenstates completely (all definitions and properties of group-theoretic quantities that we use can be found in Butler (1975, 1981)). So,

\[
H_{e} |x_{\lambda}X> = E_{x_{\lambda}X} |x_{\lambda}X>
\]

and \( E_{x_{\lambda}X} \) has degeneracy \( |\lambda| \) (dimension of \( \lambda \)). The tensor product space \( V_{\lambda} \times V_{\nu} \) will in general decompose into a sum of irreducible spaces \( \sum_{\sigma} V_{\sigma} \) of \( G \) and the product of the kets (1-4) can be written

\[
|x_{\lambda}X>y_{\nu}V> = \sum_{\sigma} \langle x_{\lambda}X,y_{\nu}V| \sigma \rangle \langle \sigma |x_{\lambda}X,y_{\nu}V>
\]

(1-5)

Here \( |x_{\lambda}X,y_{\nu}V> \) is a basis ket in the product space, \( \langle \sigma |x_{\lambda}X,y_{\nu}V> \) is a coupling coefficient for \( G \) and the multiplicity label \( r \) distinguishes the space \( V_{\sigma} \) transforming in the same manner under \( G \). It takes the values \( r = 0, 1, \ldots, R \) where \( R \) is the number of times \( \sigma \) appears in the Kronecker product \( \lambda \times \nu \).
Since the \( \{ \psi_n \} \) also transform irreducibly under \( G \) we may choose eigenvectors \( |z_k\rangle \) of \( H \) and (I-3) becomes

\[
|z_k\rangle = \sum_{\lambda \ell} |x\lambda\ell\rangle |y\nu\rangle <x\lambda\ell; y\nu|z_k\rangle
\]  

(I-6)

The generalized coupling coefficient \( <x\lambda\ell; y\nu|z_k\rangle \) (in general complex) contains the relevant physical information concerning the formation of vibronic eigenstates, given a specific \( H \), as well as a part depending on symmetry considerations alone. To factorize these parts we first invert (I-5) to obtain basis vectors for the space \( V_g \)

\[
|(x\lambda, y\nu)\rangle \sim = \sum_{\lambda \ell n} |x\lambda\ell\rangle |y\nu\rangle <x\lambda\ell; y\nu|\sim\rangle
\]  

(I-7)

An arbitrary linear combination of these must give the eigenvector \( |z_k\rangle \), so with \( \sigma = k \)

\[
|z_k\rangle = \sum_{x} |(x\lambda y\nu)\rangle r_k \langle (x\lambda y\nu) r_k |z_k\rangle
\]  

(I-8)

By considering the action of a group operation \( G_g, g \in G \), on the kets (I-7), (I-8) separately, i.e.:

\[
O_g |z_k\rangle \sim = \sum_{i} |z_{k}\rangle \lambda(g)_{ik}
\]

and using the unitarity of the matrix representation \( \{ \lambda(g)_{ij} \} \), the coefficient in (I-8) becomes \( <(x\lambda y\nu) r_k|z_k\rangle \delta_{sk} \) and is independent of \( k \). Together (I-6, 7, 8) factorize the generalized coupling coefficient into a coupling coefficient for \( G \) and a term independent of the components \( k, l, n \):

\[
<x\lambda\ell; y\nu|z_k\rangle = \sum_{\lambda \ell r} <x\lambda\ell; y\nu|r_k\rangle <x\lambda\ell; y\nu|z_k\rangle \equiv \sum_{\lambda \ell r} <x\lambda\ell; y\nu|r_k\rangle \lambda_{zrk}
\]  

(I-9)

(I-6) with (I-9) gives the most general group-theoretic construction of the eigenstates of the Hamiltonian (I-2) which transform as the \( k \)-th component of the irrep \( \kappa \) of \( G \), the invariance group of (I-2). The summations over \( (x\lambda\ell) \) (\( y\nu \)) ensure that all possible electronic and vibrational states are included in the formation of a single vibronic state characterized by \( (z_k k) \).

Leung and Kleiner (1974) have achieved a similar result by a more circuitous route - their Equn. (1) can always be chosen to transform irreducibly. However, contrary to their statements, the construction of the vibronic eigenstates is not within the Born-Oppenheimer approximation. No assumptions
concerning the relative strengths of $V$ and $H$ have been made in arriving at 

\[(I-6)\]

2. \textbf{REDUCTION FACTORS}

Consider a single electronic multiplet \{\ket{x\lambda\ell}\}. In the absence of electron-phonon coupling, the effect of external perturbations and other interactions involving dynamical operators on this multiplet, can be represented by the Hamiltonian

\[H_s = \sum_{\mu m} h_{\mu m} O^\mu_m\]  \hspace{1cm} (I-10)

$O^\mu_m$ is an electronic operator transforming irreducibly under $G$ and the $h_{\mu m}$ are functions of the external perturbations and other operators (Ham, 1972). ($H_s$ is assumed to have a magnitude much less than $H_e$). However, since in any real experiment it is the vibronic system on which (I-10) acts, then any measured quantities will be related to the matrix elements $\langle \Psi_\gamma | H_s | \Psi_\gamma \rangle$ and not $\langle \Psi_\alpha | H_s | \Psi_\alpha \rangle$. Ham (1965, 1968) restated the problem: for the (multiplicity free) systems he was considering, the ground vibronic multiplet had the same symmetry labels as its electronic parent, for moderate strengths of $V$. Hence the ground state vibronic matrix elements of (I-10) were identical to those of

\[\overline{H}_s = \sum_{\mu m} h_{\mu m} \overline{O}^\mu_m K(\mu)\]

where the bar denotes operators in the vibronic manifold, defined by

\[\overline{\langle z\lambda\ell' | O^\mu_m | x\lambda\ell \rangle} \equiv \langle x\lambda\ell' | O^\mu_m | x\lambda\ell \rangle\]

and $K(\mu)$ is a reduction factor (RF),

\[K(\mu) \equiv \frac{\overline{\langle z\lambda\ell' | O^\mu_m | z\lambda\ell \rangle}}{\langle x\lambda\ell' | O^\mu_m | x\lambda\ell \rangle},\]  \hspace{1cm} (I-11)

a ratio of the matrix elements in the two manifolds, independent of the component labels. Arguing that the overlap of the vibrational wavefunctions would make $K(\mu) < 1$ Ham deduced that a measurement of the response of the ground state of the system to an electronic perturbation would yield values reduced from those in the absence of electron-phonon coupling.
An assumption made in writing (I-11) is that other vibronic/electronic levels are sufficiently separated in energy from the multiplets under consideration that the perturbation does not mix them. Nevertheless, general matrix elements $<z'k'k'|O^\mu_m|zkk>$ (and hence their corresponding reduction factors) will be required to describe the system as the interaction $V$ increases in strength, in particular the transition from the dynamic to the static JTE. This then will be our first generalization of Ham's notation. Our second is the relaxation of the multiplicity restriction in his definitions. We take $O^\mu_m$ to be an irreducible tensor operator whose matrix elements between either electronic or vibronic states may be factorized by the Wigner-Eckart theorem into a sum of independent constants (with respect to $G$), the reduced matrix elements. Thus a vibronic matrix element becomes

$$<z'k'k'|O^\mu_m|zkk> = \sum_k |k|^{-\frac{1}{2}} <z'k'k'\mu_m|zkk><z'k'|O^\mu_t|zkk>$$

(I-12)

(We discard the idea of an operator $\bar{O}$ acting entirely within the vibronic manifold). A different set of constants, $<x'\lambda'|O^\mu_p|x\lambda>$, is produced by the electronic matrix elements. Consider now the matrix elements of (I-6). A general element is;

$$<z'k'k'|O^\mu_m|x\lambda k> = \sum_{x'\lambda'\ell'}<x'\lambda'\ell'|O^\mu_m|x\lambda\ell><y'\nu'n'>|y\nu>$$

$$\times <z'k'k'|x'\lambda'\ell'; y'\nu'n'>|x\lambda\ell; y\nu|z\times k>$$

(I-13)

where the sum is over all repeated labels. Using the orthonormality of $\{|y\nu>\}$ and (I-9) the right hand side is;

$$\sum_{x'\lambda'\ell'}<x'\lambda'\ell'|O^\mu_m|x\lambda\ell> \left( A^*_{x'\lambda'y\nu} \right)_{z'rf'^k}$$

$$\times <z'k'k'|x'\lambda'\ell'; y\nu|z\times k>$$

(I-14)

We cannot take the ratio of the matrix elements on both sides of (I-13) directly. But as the (multiplicity free) definition of (I-11) is just the ratio of two reduced matrix elements, the obvious generalization of Ham's method is to define a RF,

$$K_{\mu\nu}^{\gamma\alpha}(\mu), \quad \alpha = (x\lambda), \quad \gamma = (z\kappa), \text{ by}$$

$$<z'k'|O^\mu_t|z\kappa> = \sum_{\mu\nu\alpha\gamma} K_{\mu\nu}^{\gamma\alpha}(\mu) <x'\lambda'|O^\mu_p|x\lambda>$$

(I-15)
This will serve to relate the two arbitrary matrix elements in (I-13), independently of the component of the irreps. Note, however, that in general, an operator as simple as $\bar{H}_s$ can never be written.

To help obtain a simple form for the RF we digress to the diagrammatic techniques of Stedman (1975), (1976) — where the details of the following can be found. The left hand side of (I-13) is depicted by Fig. 1(a). The stub on the line labelled $\kappa'k'$ is a 2 jm symbol and $z,z'$, though not group labels, are left on the lines. The circle labelled $O$ is an invariant subdiagram with three external legs and therefore application of the JLV3n theorems for $n=3$ will reproduce the result of (I-12), Fig. 1(b). The top and bottom parts of this diagram are respectively, a coupling coefficient and a reduced matrix element, summed over multiplicity indices $s,t$ (dotted lines). The central part is a permutation matrix or 3 jm symbol, $m(13), \kappa'\mu \kappa$ st', inserted to produce an 'untwisted' version of the Wigner-Eckart theorem. The diagram definitions of the two coupling coefficients in (I-14) allow the latter to be represented by Fig. 1(c) with the circles labelled A, depicting those factors in (I-14). All summations in (I-14) are implied by the diagram. Since there is a stub on each internal line of Fig. 1(c) the whole diagram is an invariant and the JLV3 theorem may be applied twice, first to the external legs labelled $\kappa'\mu \kappa$, and then to the legs $\lambda'\mu \lambda$ to produce Fig. 1(d). Comparison with Fig. 1(b) and (I-15) yields the diagram definition of the RF, Fig. 1(e), where we have untwisted the line labelled by irrep $v$. This figure involves a summation over four 3jm vertices and is thus expressible as a 6j symbol. To obtain the latter in its standard form we introduce further 3j symbols, the result of the Derome-Sharp lemma, the reality of the 2 jm symbols and the 2j symbol, $\phi_v$, (double stubs). The result is Fig. 1(f) with the corresponding algebraic expression:

$$R^{\gamma'\alpha'\alpha}_{\kappa\kappa'}(\mu) = \sum_{\kappa'\kappa} \left[ m((13)\mu^*\kappa\kappa')_{tt'} m((12)\nu^*\kappa'\kappa^*)_{r's'} m((13)\nu^*\kappa^*)_{rs} \right] (I-16)$$

This result is valid for an arbitrary compact group $G$. However for our problems a simplification follows immediately. All the crystallographic point groups are simple phase (Stedman (1975)). For these Butler has shown
the 3j symbols to have a simple form: for an interchange, i, of the columns of the 3jm symbol \((\lambda_1, \lambda_2, \lambda_3)_{r_1r_2r_3}\),

\[
m(i \lambda_1, \lambda_2, \lambda_3)_{rs} = (\lambda_1, \lambda_2, \lambda_3) \delta_{rs}
\]

with \((\lambda_1, \lambda_2, \lambda_3)\) = ± 1. Thus the diagrams Fig. 1(g) are equivalent. For a cyclic interchange,

\[
m(c \lambda_1, \lambda_2, \lambda_3)_{rs} = \delta_{rs}
\]

and we can neglect the diagrams Fig. 1(h) altogether. (Thus the exact position of a multiplicity line at a 3jm vertex is irrelevant). Even for groups which are not simple phase it may be that for the irreps of interest one can still make the above choices for the 3j symbols. This is the case for the groups \(S_0^2, S_0^3, S_0^5\) which have been found to be invariance groups of the vibronic Hamiltonian in special JT systems.

Now, (I-16) becomes

\[
k_{tp}^{y'u'u}(\mu) = \sum_{y'v'rr'} \begin{pmatrix} x' y' v' \\ z' r' y v \end{pmatrix} \frac{\chi_{y'v'rr'}^{\lambda_1 \lambda_2 \lambda_3}}{A_{z'r'\kappa'}} \frac{\chi_{\mu_1 \lambda_1 \lambda_2 \lambda_3}^{\lambda_1 \lambda_2 \lambda_3}}{A_{z'r'\kappa'}} \frac{\chi_{\kappa_1 \kappa_2 \kappa_3}^{\lambda_1 \lambda_2 \lambda_3}}{A_{z'r'\kappa'}} \frac{\delta_{\kappa_1 \kappa_2 \kappa_3}}{A_{z'r'\kappa'}} \frac{\delta_{\kappa_1 \kappa_2 \kappa_3}}{A_{z'r'\kappa'}} \frac{\delta_{\kappa_1 \kappa_2 \kappa_3}}{A_{z'r'\kappa'}} \frac{\delta_{\kappa_1 \kappa_2 \kappa_3}}{A_{z'r'\kappa'}}
\]

Thus the most general RF can always be written as the sum of two parts: the first, the A's, contains all the physical information about the electron-phonon interaction necessary to find eigensolutions of (I-2); the second, depends upon the irreps of the group G of (I-2) alone. In particular a knowledge of the 6j, 3j and 2j symbols of G yields all the information about RFs which can follow from a symmetry analysis, independently of both the nature and the strength of the interaction V.

As it is not our intention to attempt a solution of the vibronic problem, for the remainder of the chapter we treat the A's as free parameters to be determined for a particular model. But they are not all independent: orthonormality of the kets (I-6) gives a normalization

\[
\delta_{zz'} = \sum_{x\lambda} \begin{pmatrix} x \lambda y v \\ z' r k \end{pmatrix}^* \begin{pmatrix} x \lambda y v \\ z r k \end{pmatrix} \delta_{zz'}
\]

(I-18)
by the unitarity of the coupling coefficient. If we set $\mu = \Gamma_1$ in (I-17), the $6j$ reduces to $|\lambda \kappa|^{-\frac{1}{2}} (\lambda \kappa \nu r') \delta_{rr'}$, the $3j$ becomes $\phi_\lambda$ and (I-18) is

$$\sum_{\alpha} K_{\Gamma_0}^{\gamma' \gamma \alpha} (\Gamma_1) \cdot |\lambda_{\kappa}|^2 = \delta_{zz'}$$  (I-19)

($\phi_\lambda \phi_\mu \phi_\nu = 1$ for any triple $(\kappa \lambda \nu)$). This result simplifies some of the $RF$s.

3. **JAHN-TELLER SYSTEMS IN OCTAHEDRAL SYMMETRY**

In our later chapters strongly coupled JT systems will not be of interest so we confine our attention to a single degenerate electronic level and its derived ground vibronic level. As most of the studies of the dynamic JTE have been of systems such as this in cubic symmetry we take the group $G$ to be the octahedral (double) group $O$. We investigate the $RF$s which follow for the 2-, 3-, and 4-fold degeneracies that occur, the last of these being sufficiently complex to highlight the need for a formula as simple as (I-17). We reproduce the $3j$ and $6j$ symbols evaluated by Butler for this group in Appendix IA. We also list there the notation used below and throughout our work to designate irreps and various JT systems. Since for any single electronic and vibronic multiplets $x = x'$, $z = z'$ and $\kappa' = \kappa = \lambda' = \lambda$ (certainly for the magnitudes of $V$ we are interested in), we can dispense with most of the labels in (I-17), rewriting it as;

$$K_{\tau \rho}^{\lambda} (\mu) = \sum_{\nu \tau'} \sum_{\gamma} (A_{\tau' \lambda}^{\nu \nu})^* A_{\tau \lambda}^{\nu \nu} \left\{ (\frac{\mu \lambda \nu \lambda}{\nu \lambda})_{\tau \rho} \right\} |\lambda| \phi_\lambda \phi_\mu (I-20)$$

(the only complex irreps for any point group are those corresponding to Kramer's doublets but (I-2) is necessarily invariant under time reversal and so has no matrix elements within these levels, (Abragam and Bleaney (1970)). We also define a positive parameter,

$$b_{\nu \tau}^{\lambda} = \sum_{\gamma} |A_{\tau \lambda}^{\nu \nu}|^2$$  (I-21)
We now list the RFs for $G = 0$, $\lambda = \Gamma_3$, $\Gamma_4$, $\Gamma_5$, $\Gamma_8$ and review previous work connected with them.

### Doublet States - $\Gamma_3$

$\lambda = \Gamma_3$, $\mu, \nu = \Gamma_1, \Gamma_2, \Gamma_3$. There are no multiplicities. We find

\[ K(\Gamma_1) = b_0 + b_7 + b_4 = 1 \]
\[ K(\Gamma_2) = b_0 + b_7 - b_4 \]
\[ K(\Gamma_3) = b_0 - b_7. \]

(We can always remove the \( \lambda \) label from $b^\lambda_\nu$ without confusion). These equations give,

\[ K(\Gamma_3) = \frac{1}{4} \{1 + K(\Gamma_2)\} - 2b_7 \]  

(I-23)

With the relabelling $q = K(\Gamma_3)$, $p = K(\Gamma_2)$, (I-24) is the most general relation for the RFs of the vibronic doublet, first derived by Abragam and Bleaney and later by Leurg and Kleiner (1974). Ham's (1968) initial treatment of the orbital doublet linearly coupled to a single $\Gamma_3$ phonon (pair) of a cluster of nearest neighbours of the ion, $\Gamma_3 \times \epsilon$, showed that $b_7 = 0$ in the weak and strong coupling limits, a result subsequently generalized by Leung and Kleiner. They and Halperin and Englin (1973), and Gauthier and Walker (1973) have also shown that weak linear coupling to lattice phonons of different frequencies makes $b_7 > 0$. Thus one expects to find for measurements on the vibronic ground state, $q < \frac{1}{4} (1+p)$.

### Triplet States - $\Gamma_5$

$\lambda = \Gamma_5$, $\Gamma_4$, $\mu, \nu = \Gamma_1, \Gamma_3, \Gamma_4, \Gamma_5$. Again there are no multiplicities. The RF's listed below have the same form for $\lambda = \Gamma_5$ and $\Gamma_4$ so we refer to $\Gamma_5$ throughout only. (I-20) gives,

\[ K(\Gamma_3) = b_0 + b_4 - \frac{1}{2} b_2 - \frac{1}{2} b_5 \]
\[ K(\Gamma_4) = b_0 - \frac{1}{2} b_2 + \frac{1}{2} b_4 - \frac{1}{2} b_5 \]
\[ K(\Gamma_5) = b_0 - \frac{1}{2} b_2 - \frac{1}{2} b_4 + \frac{1}{2} b_5 \]

and together with (I-22) yields the relation,
\[ K(\Gamma_3) = 1 - \frac{3}{2}\{\kappa(\Gamma_5) - \kappa(\Gamma_4)\} - 3b_2 \] (I-24)

(I-24) is identical to Equn. (37) of Leung and Kleiner. Bersuker and Polinger (1973) have obtained an equivalent result using the same approach as presented in this chapter.

For the linear coupling of the triplet to a \( \Gamma_3 \)-phonon pair, \( \Gamma_5 \times \epsilon \), Ham (1965) obtained the results,

\[ K(\Gamma_3) = 1, \quad \kappa(\Gamma_4) = \kappa(\Gamma_5) \] (I-25)

Leung and Kleiner have since shown that for arbitrary coupling to (many) \( \Gamma_3 \) phonons, that \( b_2 = b_5 = 0 \), generalizing Ham's result. They also show for weak linear coupling to a \( \Gamma_5 \) phonon triplet, \( \Gamma_5 \times \tau_2 \), that \( b_2 \) becomes non-zero only when its perturbative expansion in \( V \) is taken to tenth order. Ham calculated RFs to second order based on the cluster model, for this system, and Bates et al. (1974) extended his results to full lattice coupling. These authors and Judd (1974) have obtained analytic expressions in the strong coupling limit while the intermediate region has been treated numerically, Caner and Englman (1966), Sakamoto and Muramatsu (1978).

The \( \Gamma_5 \times (\epsilon + \tau_2) \) system, coupling to both phonon symmetries, is more complicated. Originally Bersuker and Polinger obtained RFs on the cluster model for weak \( \tau_2 \) - and arbitrary \( \epsilon \)-type linear coupling. This work has since been generalized by Bates et al. One special system exists however, the equal linear coupling of \( \Gamma_3 \) and \( \Gamma_5 \) phonons of equal frequency to the electronic triplet, \( \Gamma_5 \times (\epsilon = \tau_2) \). The five-fold degeneracy of the vibrational mode results in (I-2) having symmetry higher than cubic, namely \( \text{SO}_3 \) (O'Brien (1971), Romestain and Merle d'Aubigne (1971)). Indeed, as shown most clearly by Judd (1974), the invariance of the vibrational Hamiltonian under the operations of the group \( \text{U}_5 \) allows the eigenstates \( |\gamma \nu \nu> \) to be uniquely labelled by the irreps of the groups in the chain,

\[ \text{U}_5 \supset \text{SO}_5 \supset \text{SO}_3 \supset \text{SO}_2 \]

Thus the irreps \( \lambda, \mu, \nu \) are those of \( \text{SO}_3 \) and are labelled by the \( J \) values. For the triplet, \( \lambda = 1 \), and \( \mu, \nu = 0, 1, 2 \). Using \( \phi_\lambda = (-1)^2\lambda \), \( (\lambda_1 \lambda_2 \lambda_3 0) = (-1)^{\lambda_1+\lambda_2+\lambda_3} \) and the 6j tables of Rotenberg et al. (1959), the RFs are
\[ K(0) = b_0 + b_1 + b_2 = 1 \]
\[ K(1) = b_0 + 2b_1 - b_2 \]
\[ K(2) = b_0 - 2b_1 + \frac{1}{10} b_2 \]

or
\[ 5K(2) - 3K(1) = 2 - 6b_1 \]  \hspace{1cm} (I-26)

We could have obtained this directly from (I-24) since the 0 irreps are competitive labels for the \( SO_3 \) irreps so,
\[ K(1) = K(\Gamma_4), \quad K(2) = K(\Gamma_3) = K(\Gamma_5) \]  \hspace{1cm} (I-27)

(I-26) reduces to O'Brien's result only when \( b_1 = 0 \). But she restricted the vibrational quintets to a common frequency. The labelling of the \( U_3 \) irreps then insured that \( J=1 \) of \( SO_3 \) never occurred in the group - subgroup reduction (Judd). As no-one has presented the argument clearly we show in Appendix II that this restriction is removed for quintets of different frequency.

3.3 Quartet States - \( \Gamma_8 \)

\( \lambda = \Gamma_8 \). The symmetric and antisymmetric parts of the product \( \lambda \times \lambda \) are respectively,
\[ (\Gamma_8 \times \Gamma_8)_s = \Gamma_2 + 2\Gamma_4 + \Gamma_5 \]
\[ (\Gamma_8 \times \Gamma_8)_A = \Gamma_1 + \Gamma_3 + \Gamma_5 \]

Thus a multiplicity of two exists whenever \( \mu, \nu \) equal \( \Gamma_4 \) or \( \Gamma_5 \) and complex parameters in addition to (I-21) must be defined,
\[ b^3_{\nu} = \sum_{y} \left( A_{x3yv}^* A_{z13}^{x3y} \right) R_{r} \nu = 2, 5 \text{ only} \]  \hspace{1cm} (I-28)

They do not appear in the normalization (I-22). Consider now the consequences of a multiplicity for the matrix element of an operator. We write this element symbolically as,
\[ \sum_{r} \left( \begin{array}{c} \nu \\ \lambda \end{array} \right) _{r} R_{r} \]  \hspace{1cm} (I-29)

where the bracket denotes a 3jm symbol and \( R_{r} \) is a reduced matrix element.

There is a freedom in the way one performs the factorization in (I-29). One can define a new multiplicity separation,
\[
\begin{align*}
&\begin{pmatrix}
   \quad & \quad & \quad \\
   \quad & \quad & \quad \\
\end{pmatrix}_{r'} = U_{r'r} \begin{pmatrix}
   \quad & \quad & \quad \\
   \quad & \quad & \quad \\
\end{pmatrix}_r \\
\Rightarrow & \begin{pmatrix}
   \quad & \quad & \quad \\
   \quad & \quad & \quad \\
\end{pmatrix}_{s'} = U_{s's} \begin{pmatrix}
   \quad & \quad & \quad \\
   \quad & \quad & \quad \\
\end{pmatrix}_s \\
\end{align*}
\]

(I-30)

where \( U \) is a unitary matrix. Then \( r \rightarrow r' \) in (I-29), the matrix element is unaltered, but the 6j symbols which are formed from the 3jms will be different for the two sets of labels \( \{r\}, \{r'\} \). Now the 6j tables of Appendix IA correspond to one choice for the \( \Gamma_8 \) 3jms. However, Butler first produced a different set of 6js (unpublished) with which we in turn first calculated the general form of the RFs for the quartet. This set is reproduced in Appendix IB (the differences between the two sets only occurs for the triple \( (332r) \)). We shall give our results for both sets of 6js, because, in the first place, we wish to compare them with the only other major attempt at the \( \Gamma_8 \) RFs, that of Ham, Leung and Kleiner (1976) (HLK), and in the second place, besides making clear the arbitrariness of the multiplicity choice we want to show that one set of 6js is preferable for calculations.

For our first set of RFs we use the 6js of Appendix IB. Taking account of (I-22) and defining \( B_v = b_v + b_v^* \) from (I-28), we can tabulate the results as:

<table>
<thead>
<tr>
<th>( \Gamma )</th>
<th>1/5</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_2 )</td>
<td>1</td>
<td>-2</td>
<td>-2/5</td>
<td>-8/5</td>
<td>4/5</td>
</tr>
<tr>
<td>( \Gamma_3 )</td>
<td>1</td>
<td>-2</td>
<td>-1</td>
<td>-1/5</td>
<td>-4/5</td>
</tr>
<tr>
<td>( 00' \Gamma_4 )</td>
<td>1</td>
<td>-2/5</td>
<td>-1/5</td>
<td>-13/15</td>
<td>-8/5</td>
</tr>
<tr>
<td>( 11' \Gamma_4 )</td>
<td>1</td>
<td>-8/5</td>
<td>-4/5</td>
<td>-8/5</td>
<td>-4/15</td>
</tr>
<tr>
<td>( 10' \Gamma_4 )</td>
<td>4/5</td>
<td>2/5</td>
<td>-2/5</td>
<td>2/5</td>
<td>-4/15</td>
</tr>
<tr>
<td>( 01' \Gamma_4 )</td>
<td>4/5</td>
<td>2/5</td>
<td>-2/5</td>
<td>2/5</td>
<td>-4/15</td>
</tr>
<tr>
<td>( 00' \Gamma_5 )</td>
<td>1</td>
<td>-2</td>
<td>-6/5</td>
<td>-4/5</td>
<td>-4/15</td>
</tr>
<tr>
<td>( 11' \Gamma_5 )</td>
<td>1</td>
<td>-2</td>
<td>-1</td>
<td>-7/5</td>
<td>-8/5</td>
</tr>
</tbody>
</table>

The two remaining RFs not given in (I-31) but produced by our formula are,

\[
K_{10} (\Gamma_5) = \frac{2}{3} \left( b_2 - b_2^* + (b_5 - b_5^*) \right)
\]

(01)
However, we show in Appendix IIIIA that the $SO_3 \Rightarrow 0$ 3j's require $K_{tp}(\Gamma_5) \sim \delta_{tp}$. Thus the eight RFs for the $\Gamma_8$ multiplet are completely described by eight real parameters (two of unknown sign) and although one can invert (I-31) to obtain all parameters there are no simple relations between the RFs such as we faced previously.

HLK restricted the coupling of the ion to the lattice to be linear (of arbitrary strength) via (many) $\Gamma_3$ and $\Gamma_5$ phonons, $\Gamma_8 \times (\epsilon + \tau_2)$, and expressed their RFs in terms of five parameters. Their (hidden) multiplicity choice corresponds to the conventions of Abragam and Bleaney (1970 - section 18.3) and Koster et al.'s (1963) coupling coefficients. For future reference we show in Appendix IIIB that the following one-to-one correspondence between HLK's labelling of RFs and ours holds as a result:

\[
\begin{align*}
K_{ij}(\Gamma_4) \quad &\rightarrow \quad K_{tp}(\Gamma_4) \\
K(\Gamma_5^e) \quad &\rightarrow \quad K_{oo}(\Gamma_5) \\
K(\Gamma_5^o) \quad &\rightarrow \quad K_{ll}(\Gamma_5)
\end{align*}
\]

K($\Gamma_2$), K($\Gamma_3$) are the same in both. (Hereafter we use our labelling only). We can also relate two of our parameters to theirs directly (by comparing (I-6,-9) to their Eqns. (1,5) and using Koster et al's tables),

\[p' = 1 - 2b_4 \quad b^2 = b_7\]

(1-32)

(The numerical coefficients of $b_4$ and $b_7$ obtained from their RF expressions agree with those of (I-31) with one exception - see below). However, three relations must exist for the $b_{vr}$, $B_v \nu = 2, 5$ to obtain their remaining parameters. One follows immediately from their results and implies a correction to one of their formulae without much work on our part: if $K_{10}(\Gamma_4)$ is to depend on the same parameters as the other RFs, as their results suggest, then we can set $B_5 = 0$ in (I-31) in which case we find $K_{10}(\Gamma_4) = K_{01}(\Gamma_4)$, contrary to HLK. However, as they have this equality to within a factor of 25/9, and their coefficients of $p'$, $b^2$ are out by a factor of 3/5 we believe they should have,
\[ K_{10}(\Gamma_4) = K_{01}(\Gamma_4) = \frac{1}{5} (1-p') - \frac{2}{15} (1-q') - \frac{1}{5} a^2 + \frac{4}{5} b^2 \] (I-33)

We now turn to the presentation of our second set of RFs using the 6js of Appendix IA. We first explain why these 6js are a better set to work with and what effects the transformation between the two sets have.

Amongst the 6js responsible for the formulae (I-31) are those of the type, 
\begin{align*}
\{11 & 33\} \\
233 & \text{trsp}
\end{align*}
Here the 'off-diagonal' multiplicity pairs \((rs) = (10), (01)\) complicate the summations in (I-30). If one could remove such pairs then unnecessary work would be eliminated and, as one simplification, \(B_2\) would not appear in \(K_{tt}^{(\mu)}\). Butler noticed that for some pairs \((t,p)\) such a transformation of the 6js of Appendix IB was indeed possible. Denoting the transformed set by primed quantities, it takes the form,
\[ \{ \} \text{tr} 's' \]
\[ U_{r'r} U_{s's} \] (I-34)
where the left hand side is chosen to be diagonal in \((r's')\). \((U\) is derived in Appendix IIIIC). Notice that this transformation only affects the original set of 6js whenever the triple \((233)\) is involved. It follows from (I-30) that any quantity depending upon this triple will also be altered in the multiplicity separation. Thus in our new set of RFs there will appear new parameters \(b'_{2r},\ B'_{2}\), which can be related to the originals by,
\[ \left( \begin{array}{c} A^{3y2} \\
A^{zr'3} \end{array} \right) = U_{r'r} \left( \begin{array}{c} A^{3y2} \\
A^{zr'3} \end{array} \right) \] (I-35)
and new RFs, \(K'_{t'}(\Gamma_4),\) obtained from their originals by the transformation (I-34). All other quantities are unaltered. With these changes our second set of RFs is:
The simplicity of the expressions (I-36) in comparison to those of (I-31) is obvious. Six of the RFs are now expressed in terms of six positive parameters and are independent of the remaining two factors. And although (I-36) and (I-31) are physically equivalent and the experimental problem of determining all RFs is not altered by our transformation, the form of (I-36) suggests that any attempt to find relations between them on a specific model will be made much easier by using the new set of 6js rather than the old set.

The last problem in this section which may be easily handled by our formalism is the equal linearly coupled system \( \Gamma_8 \times (\varepsilon = \Gamma_2) \) (Pooler and O'Brien (1977), Judd (1976)). The vibronic Hamiltonian is now invariant under the operations of the group \( \text{SO}_5 \) and the vibrational part under \( \text{U}_5 \supset \text{SO}_5 \). In the notation of Appendix IV where the necessary j symbols are listed, \( \lambda = \frac{1}{2}, \mu, \nu = 0,1,2 \). We find the RFs to be

\[
\begin{align*}
K(1) & = 1 - 8/5 \, b_1 - 4/5 \, b_2 \\
K(2) & = 1 - 4/5 \, b_1 - 6/5 \, b_2 \\
\text{or} & \quad K(2) = \frac{1}{4} \{ 1 + K(1) \} - 4/5 \, b_2
\end{align*}
\]

This result of the same form as (I-23). The compatability relations for \( \text{SO}_5 \supset 0 \) determine that,

\[
\begin{align*}
K(1) & = K(\Gamma_3) = K_{\infty}(\Gamma_5) \\
K(2) & = K(\Gamma_2) = K_{11}(\Gamma_5)
\end{align*}
\]
and \[ K(2) = K^{11}_{02}(\Gamma_4) = K^{11}_{11}(\Gamma_4) \]

The last two equalities must hold for either multiplicity separation in 0). (I-37) reduces to the results of HLK and Pooler and O'Brien only when \( b_2 = 0 \), which is a special case, by the argument in Appendix II.

4. EXTENDED MULTIPLETS

Section (I.3) dealt with the case of single electronic and vibronic multiplets, applicable to the study of the DJTE. For a better description of the JT systems excited vibronic levels must be included, certainly in the strong coupling limit (assuming that the interaction \( V \) is not only linear in the displacements of the lattice). In theory (I-17) allows all electronic and their derived vibronic states to be included in setting up an effective Hamiltonian (whose eigenstates will generally involve mixtures of the \( |z\kappa> \)) to describe the effect of (I-10) on the system. (Though in the systems of usual interest (orbital electronic states) the effects of excited electronic levels can be neglected in the formation of vibronic states, as the latter are typically separated by the order of phonon energies, much smaller than the electronic separations). We can extract all the symmetry information in these problems as well.

As an example, consider an electronic doublet \( x=x' \), \( \lambda=\lambda'=\Gamma_3 \). The possible vibronic irreps are \( \kappa,\kappa' = \{\Gamma_1', \Gamma_2', \Gamma_3'\} \) and there will be five RFs with fixed \( z,z' \) for \( \mu = \Gamma_2, \Gamma_3 \). Ham (1972) uses the RFs corresponding to the first excited singlet \( (\kappa'=\Gamma_1'/\Gamma_2') \) connected to the ground doublet \( (\kappa=\Gamma_3') \), \( r \) in his notation, to describe the transition to the static JTE. However, the only RFs that can be related have the \( \kappa,\kappa' \) labels in common, for all systems. Thus for \( \kappa=\kappa'=\Gamma_3' \) we find,

\[
K^{2'2}(\Gamma_3') = \delta_{2',2} + K^{2'2}_{12}(\Gamma_2') - 2 \sum_y \left[ A_{z4} \right]^{x4y7} \cdot A_{z4}^{x4y7}
\]

- a generalization of (I-23) to include all vibronic levels of \( \Gamma_3' \) symmetry and a result first given by Setser and Estle (1978). Clearly all the relations
of the previous section will generalize like this. Also there may exist additional relations for vibronic levels of other than ground state symmetry. The triplet \( \lambda = \lambda' = \Gamma_5 \) for example, gives,

\[
K^{\gamma'}(\Gamma_4) = K^{\gamma'}(\Gamma_5) \quad \gamma' = (z' \Gamma_3) \quad \gamma = (z \Gamma_4 / \Gamma_5)
\]

and

\[
K^{\gamma'}(\Gamma_3) + \frac{1}{4} \left( K^{\gamma'}(\Gamma_5) - K^{\gamma'}(\Gamma_4) \right) + \sqrt{3} \sum_y \left( A^{x5y4}_{\gamma'} \right)^* A^{x5y4}_\gamma = 0
\]

where \( \gamma' = (z' \Gamma_4) \quad \gamma = (z \Gamma_5) \).

A knowledge of the vibronic levels structure and the non-zero parameters for specific JT interactions would allow the above relations to be exploited in determining the effective Hamiltonian for any system, in the manner of Setser and Estle for the orbital doublet. We shall not pursue these problems, as our answer to an effective Hamiltonian description for the external perturbation will turn out to be quite different.

5. **SUMMARY**

The most general group-theoretic construction of the eigenstates of an arbitrary ion-lattice Hamiltonian, and a general definition for the RFs corresponding to an external perturbation, has led to an expression for these RFs, (I-17). The symmetry information inherent in their definition can now be simply extracted, given the 6j symbols of the invariance group. Unlike previous, and less general, formulations, our method emphasize the basis independence of the RFs. Also, it easily handles systems of any complexity: from a symmetry viewpoint, we have given the first complete treatment of the RFs for the \( \Gamma_6 \) states. Vibronic RFs will not be of specific interest to us in succeeding chapters. However, the relations between the ground state RFs will be, in particular, those for the \( \Gamma_3, \Gamma_5, \Gamma_8 \) systems listed in Section (I.3). (For the \( \Gamma_8 \) states there are a number of possibilities, depending upon which parameters \( b \) we choose to display). We shall refer to any special relation, appropriate to less than arbitrary coupling for example, or when one or more parameters are zero, as a sum rule.
CHAPTER II

REDUCTION FACTORS VIA GREEN FUNCTIONS

We review the formalism necessary for a quantum field-theoretic description of the interacting ion-phonon system which yields one-particle properties of the system, for example level shifts (eigenvalues) and widths (lifetimes). This description obviates prior knowledge of the eigenstates of the electron-phonon system. We then follow Gauthier and Walker (1976) and find the effect of the external perturbation on the eigenvalues of the system. However our analysis is quite general. We represent all the algebraic parts of the formalism by Feynman graphs and we show how the symmetry information in these graphs may be revealed. This allows the most general (electronic) reduction factor to be defined as the sum of a series of diagrams. We compare the Green function method with that of the previous chapter.

1. A PERTURBATIVE SOLUTION FOR THE ION-PHONON SYSTEM

1.1 The Green Function Formalism

As Thermal Green function and diagram techniques are discussed fully in the literature (Abrikosov et al. (1963), Fetter and Walecka (1971)), we only outline here those ideas necessary for an understanding of the formalism, as it applies to our problem.

Our electron-phonon system consists of an isolated impurity ion coupled to the continuum of lattice vibrations of a host paramagnetic crystal. In second quantized form the zero order Hamiltonian for the non-interacting system can be described by,

\[ H_0 = H_e + H_p \]

\[ = \sum_i \epsilon_i a_i^\dagger a_i + \sum_k \epsilon_k (b_k^\dagger b_k + \frac{1}{2}) \]  

(II-1)

The fermion operators \( a_i^\dagger (a_i) \) create (annihilate) the ionic level \(|i>\) of energy \( \epsilon_i \); \( |i> = a_i^\dagger |0> \). Similarly the boson operator \( b_k^\dagger \) creates a phonon
of energy $\varepsilon_k$ with wavevector $k$ in the Brillani zone and belonging to branch mode $s$, $k = (k_s)$ ($k \equiv (-k, s)$). The coupling $V$ of (I-2) is to be treated as a perturbation on the system of (II-1). It can take various forms but we restrict it to linear coupling in the meantime,

$$V = \sum_{ijk} V_{ijk} a_i^+ \phi_k$$

(II-2)

$\phi_k = b_k + b_k^\dagger$ is the phonon displacement operation and $V_{ijk}$ the coupling parameter.

Define a full one-particle electronic Green function $G_{ij}(\tau)$ by,

$$G_{ij}(\tau) = -<\tau a_1(\tau) a_j^+> \quad \tau = it/\hbar$$

(II-3)

where $\tau$ is the 'time' ordering operator, $a_1(\tau)$ is a Heisenberg operator

$$\hat{O}(\tau) = e^{H\tau} O e^{-H\tau}$$

(II-4)

and $<...>$ denotes a thermal average with respect to $H$,

$$<A> = Tr_\rho A \quad \rho = e^{-\beta H}/Tr e^{-\beta H}$$

The significance of (II-3) lies in the fact that it describes the propagation of excitations of the electronic subsystem in a 'time' interval $\tau$ allowing for all possible interactions with the phonon subsystem. Thus $G_{ij}(\tau)$ is proportional to the probability amplitude that the excitation $a_j^+ |\phi\rangle$ will not decay in a time $\tau$ and hence the state $|i\rangle$ acquires a finite lifetime as a result of interactions.

A consideration of the time development of the system in the interaction representation for the operators ($H \to H_o$ in (II-4)) yields,

$$G_{ij}(\tau) = <\tau S(\beta) a_1(\tau) a_j^+> / <S(\beta)>_o$$

Here

$$S(\beta) = T_\beta \exp \left\{ -\beta_o \int_\tau V(\tau) \right\}$$

is the $S$-matrix and $<...>_o$ denotes averaging with respect to $H_o$. (II-5) is a perturbative expansion to infinite order in $V$. At this stage in the usual theory of a many fermion system one proceeds by applying Wick's theorem to factorize the numerator and denominator of (II-5) into unperturbed propagators.
of the subsystems,

\[ g_i(\tau_2 - \tau_1) = - \langle T_\tau \{ a_i(\tau_2) a_i^+(\tau_1) \} \rangle \]  
\[ d_k(\tau_2 - \tau_1) = \langle T_\tau \{ \phi_k(\tau_2) \phi_k^+(\tau_1) \} \rangle \]  

(II-6)

If these propagators are represented by the diagrams in Fig. 2(a),(b) respectively, and the interaction by the vertex 2(c), then it can be shown the numerator and denominator of (II-5) have the respective diagrammatic expansions 2(d),(e), where, in order to reproduce all the terms in (II-5), all possible ways of connecting the propagators (II-6) are employed. For example, 2(d),(e) contain all diagrams to fourth order in \( V \). The advantage of the physical interpretation of each diagram in terms of the creation and annihilation of virtual phonons changing the character of the bare electronic levels, is obvious.

Rather than evaluating the contribution of each (Feynman) diagram to \( G_{ij}(\tau) \) (by integrating over \( \tau \) variables, summing vertices over state variables etc.) a simplification is made at this point. 2(d) consists of two classes of diagrams; connected (the first 12) and disconnected (the remainder). The \( \tau \)-integrations in the latter factorize. Cancellation of the diagrams common to 2(d) and (e) then occurs - this can be seen intuitively - and \( G_{ij}(\tau) \) can be rewritten as 2(f), the sum of all topologically distinct, connected diagrams - the linked cluster theorem.

Now we return to the one-particle system under consideration. The vacuum state \( |0\rangle \) and states occupied by more than one fermion e.g. \( a_i^+ a_j^+ |0\rangle \) (if\( j \)) are not physical states of the ion. To eliminate their contribution when evaluating quantities like \( \langle A \rangle \) in (II-5) Abrikosov (1965) added an extra energy \( \theta \) to each ionic level, \( E_i \rightarrow (E_i + \theta) \equiv \bar{E}_i \) in (II-1), and removed its effect for the one-fermion states (1) at the end of the calculation via the projection operator (Keiter (1971)),

\[ P = (\text{Tr}_1 e^{-\beta \bar{H}_0})^{-1} \lim_{\theta \to -\infty} e^{\beta \theta} \]

\[ P \langle A \rangle_o \text{ all states} \rightarrow \langle A \rangle_o \]

The effect of \( P \) on the numerator of (II-5) is to eliminate all those diagrams in 2(d) containing one or more fermion loops (e.g. 2(g)) and the linked cluster theorem breaks down. The uncancelled 'vacuum' contributions of the denominator
act essentially as a normalization factor and have no effect on the quantities we wish to calculate (McKenzie (1978)), so we ignore them. The resulting diagram expansion of \( G_{ij}(\tau) \) for the electron-phonon system reduces to 2(h).

The Fourier transformer of (II-3) is now taken:

\[
G_{ij}(z_v) = \int_{-\beta}^{\beta} d\tau e^{z_v \tau} G_{ij}(\tau), \quad z_v = (2\nu+1)\frac{i\pi}{\beta}
\]  

(II-7)

Corresponding definitions for (II-6) give,

\[
g_{\nu}(z_v) = \frac{1}{z_v - \theta_\nu}, \quad d_{\nu}(x_v) = \frac{1}{x_v - c_k} - \frac{1}{x_v + c_k}, \quad x_v = 2\nu\frac{i\pi}{\beta}
\]  

(II-8)

These functions are defined only at discrete 'energies' \( z_v, x_v \) (the subscript \( \nu \) will be dropped in the following). Now \( G_{ij}(z) \) is also represented by the series 2(h) but with \( \tau \) replaced by an 'energy' \( z \) which must flow through each diagram - Fig. 3(a). The advantage of working with the Fourier transform is that diagrams like Fig. 3(b) factorize in their contribution to \( G_{ij}(z) \). This results in the iterative Dyson equation. Defining \( G_{ij}(z) = \langle i | G(z) | j \rangle \), this equation is, in operator form,

\[
G(z) = g(z) + g(z) M(z) G(z)
\]  

(II-9)

where \( g(z) \) is diagonal in the basis \( \{ | i \rangle \} \). (II-9) has the diagrammatic representation of 3(c). \( M(z) \) is the self-energy operator consisting of the sum of all irreducible diagrams, 3(d), - those diagrams in \( G(z) \) which cannot be factorized - and can be written most compactly as 3(e). If the inverses of the operators \( g(z), \{ 1-g(z) M(z) \} \) are defined, (II-9) can be rearranged to,

\[
G(z) = \{ (g(z))^{-1} - M(z) \}^{-1}
\]

\[
= \{ z - H_{c} - M(z) \}^{-1}
\]  

(II-10)

Although the complex functions \( G(z), M(z) \) are defined only at discrete points along the imaginary axis, after evaluation (by rules to be given shortly) they can be analytically continued to the whole complex z-plane, in particular to the real axis, \( z \rightarrow E \pm i\sigma \) (Fetter and Walecka). Two Hermitian operators \( \Delta(E), \Gamma(E) \) may now be defined via,

\[
M(E \pm i\sigma) = \Delta(E) \mp i \Gamma(E)
\]  

(II-11)
a) \( \prod_{i}^{j} (z) \leftrightarrow \mathcal{G} \)

b) 

c) 

d) 

e) 

f) 

g) 

h) 

i) \( \prod_{k}^{\ell} (x) \leftrightarrow \mathcal{D} \)

j) 

FIGURE 3
Restricting \( G(z) \) to diagonal elements for simplicity \( G_{ii}(z) = G_i(z) \), then near the poles \((11-10)\) gives,

\[
G_i(E \mp i\epsilon) = (E - \theta_i - \Delta_i(E) \pm i \Gamma_i(E))^{-1}
\]  \hspace{1cm} (II-12)

The interpretation of \((II-12)\) is as follows: when \( V = 0 \), the state \(|i\rangle\) has an energy \( \theta_i \) (the pole of \( g_{ii}(z) \)); for \( V \neq 0 \), the energy is given by the solution of,

\[
E - \theta_i - \Delta_i(E) = 0
\]  \hspace{1cm} (II-13)

and defines a dressed excitation shifted in energy from the bare state. In the Lorentzian approximation in which the arguments of \( \Delta_i, \Gamma_i \) are made independent of \( E \) (in its simplest form \( E \to \theta_i \) in the argument, but see Stedman (1971), Hernandez and Walker (1972)), this 'quasiparticle' decays with an inverse lifetime \( \sim \Gamma_i(\theta_i) \) (Abrikosov et al). We refer to this as the width of the excitation since the spectral function describing the excitation is a Lorentzian of half-width \( \Gamma_i(\theta_i) \), peaked at \( \theta_i + \Delta_i(\theta_i) \), in this approximation (Stedman 1971).

Thus \( \Delta(E), \Gamma(E) \) are interpreted as shift and width operators respectively for the totality of ionic levels under consideration.

We now give the rules for calculating the contributions of diagrams in Fig. 3(d) to \( M(z) \) (and hence to \( \Delta, \Gamma \)). Firstly, \((II-2)\) is rewritten as

\[
V = \sum_k f_k \phi_k \quad V_{ijk} = \langle i|f_j|j\rangle
\]  \hspace{1cm} (II-14)

and since \( \sum_k \) is symmetrical about the origin, \( V = \sum_k f_k^\dagger \phi_k \) also. Hermiticity of \( V \) then implies \( f_k = f_k^\dagger \). The rules are:

1. Assign propagators \((II-8)\) to each internal line and factors \( f_k, f_k^\dagger \) to conjugate interaction vertices.
2. A net 'energy 'current' \( z \) must flow through the diagram. Assign an (arbitrary) direction to each phonon 'energy' \( x \) and conserve the sum of 'energies' at each vertex.
3. Sum over the \( x \)'s (with a factor \( \frac{1}{\beta} \) for each summation) and over phonon states \( k \), e.g.: the lowest order term in \( M(z) \) (Fig. 3(f)) is equivalent to,
- \frac{1}{\beta} \sum_{x,y,k} f_{x,y}^* g(z+x,y) f_{x,y} d_k(x,y)

(4) Convert the sum on \( x \) to a contour integral over the complex \( x \)-plane and evaluate by the method of residues (Fetter and Walecka, Schreiffer (1964)).

Since the residue of the pole of \( g(z+x) \) vanishes as \( \theta \to \pi \), the sum reduces to,

\[- \frac{1}{\beta} \int_{-\infty}^{\infty} dx \left\{ n_k \delta(x-\varepsilon_k) + (n_k+1) \delta(x+\varepsilon_k) \right\} \]

\( n_k = \left(e^{\beta\varepsilon_k} - 1\right)^{-1} \) is the Bose-Einstein population factor.

Although individual diagrams are most easily calculated by the above rules, a little thought shows that each diagram in Fig. 3(d) is reproduced by a term in the expansion of

\[ M(z) = \sum_{n=0}^{\infty} \left( \prod_{\mathbf{p}} \rho_{\mathbf{p}} \right) V_{\left( z+E_H^p - H_0^p \right)^n} \left| \mathbf{p} \right> \]  \hspace{1cm} (II-15)

Here \( \left| \mathbf{p} \right> \) is an eigenstate of \( H_0 \) and the thermal average is over all excited states of the lattice:

\[ H_0 \left| \mathbf{p} \right> = E_0 \left| \mathbf{p} \right> \quad \rho_{\mathbf{p}} = e^{-\beta E_0}/\text{Tr} e^{-\beta E_0} \]

Only irreducible diagrams are to be included in the summations.

Finally we note that interactions other than (II-2), hereafter denoted as \( V_1 \), are easily dealt with by the appropriate diagrams. For example the quadratic interaction,

\[ V_2 = \sum_{k\ell m} f_{k\ell}^* \phi_k^+ \phi_\ell \quad f_{k\ell} = \sum_{ij} V_{ij} k \ell a_i^* a_j \]  \hspace{1cm} (II-16)

contributes diagrams like Fig. 3(g) to \( M(z) \). (In future we shall not draw the mirror image of an asymmetric diagram as in 3(g) but it is understood to be included). And if we relax the approximation of a harmonic crystal the (lowest order) anharmonic phonon interaction,

\[ V^{(3)} = \frac{1}{3!} \sum_{k\ell m} V(k\ell m) \phi_k^+ \phi_\ell^+ \phi_m \]  \hspace{1cm} (II-17)
gives diagrams like 3(h). Strictly though, the last diagram in 3(h) will be included in a full phonon propagator \( D_k^\text{f}(x) \), also obeying a Dyson equation, 3(i),

\[
D(x) = d(x) + d(x) P(x) D(x).
\]

The phonon self-energy \( P(x) \), would then correspond to the series 3(j), where electronic loops are now eliminated by the Abrikosov procedure. The effect of the replacement of the unperturbed propagations \( d(x) \) in 3(d) by \( D(x) \) would be to change the value of \( P \) corresponding to \( H \) no longer being in the harmonic approximation. We ignore these corrections.

1.2 Comparison With the Standard Procedure

Much of the literature concerned with perturbative solutions to the electron-phonon problem uses the method of Section (I.1) - explicit construction of the vibronic eigenstates. We compare this method with the Green function approach. Firstly we note the effect of symmetry restrictions for the latter. We have in mind that the electronic Hamiltonian, \( H_e = \sum_i \hat{a}_i \hat{a}_i^\dagger \) will represent a sequence of multiplets, not degenerate with one another, each of which may be labelled by the irreps of the symmetry group of \( H_e \), \( |i> = |x_i \lambda_i \rangle \). The interaction \( V \) will modify the energies of these multiplets according to the solutions of,

\[
(E - H_e - \Delta(E)) |i> = 0
\]

where \(|i>\) is a vector constructed in the basis \(|i>\). This is just the generalization of (II-13) to include the off-diagonal elements. Since \( V \) and \( H_o \) are invariant with respect to the symmetry group so is (II-15), and therefore \( \Delta(E) \). By Schur's lemma (cf. (II-39)), its matrix elements have the form,

\[
<i | \Delta(E) | j> = f(E,x_i x_j ,\lambda_i \lambda_j ) \delta_{\lambda_i \lambda_j} \delta_{\lambda_i \lambda_j}\]

and the shifts in energies will be the same for all the components \( \lambda_i \) of a particular multiplet. Thus the electronic degeneracies are retained when the interaction is switched on.

Suppose we follow the usual procedure and construct exact eigenstates \(|\gamma> = |\gamma \psi \rangle\) of \( H = H_o + V \) from the product states \(|\alpha> |\beta> \equiv |x\lambda \psi > |\gamma \nu \psi \rangle\) of \( H_o \). We can use the results of Brillouin-Wigner perturbation theory (Ziman (1969)) adapted for this problem. For simplicity we consider a single electronic state, but many vibrational states \(|\beta_a>\), \( a = 1,2,\ldots \) Then for the zero-
order states \( |\alpha\rangle |\beta\rangle \), of energy \( E_{0a} \), the eigenstate \( |\gamma\rangle \) of \( H \) is given by,

\[
|\gamma\rangle = \sum_{n=0}^{\infty} \left( \frac{1}{E-H_{0}} \right)^{n} |\alpha\rangle |\beta\rangle \quad \text{(II-19)}
\]

\((P = P_{\alpha} + P_{\beta} - P_{\alpha}P_{\beta}^{\prime} \) is the complementary projection operator) with the corresponding eigenvalue,

\[
E_{a} = \langle \gamma_{a} | H |\gamma_{a}\rangle = E_{0a} + \langle \alpha | \left\{ \sum_{n=0}^{\infty} \left( \frac{1}{E-H_{0}} \right)^{n} |\beta\rangle \right\} |\alpha\rangle \quad \text{(II-20)}
\]

This also has the degeneracies of the symmetry group. We now construct the state \( |\gamma\rangle = \sum_{a} |\gamma_{a}\rangle \). It is not an eigenstate of \( H \) but we assume it to be approximately so with eigenvalue \( E_{a} \). This is allowable in the sense that one can never specify the eigenstates \( |\gamma_{a}\rangle \) precisely. Not only do they evolve in time as a result of interactions ((II-19) is the time independent solution), but the vibrational states \( |\beta_{a}\rangle \) can never be specified either—in reality they depend upon the temperature of the system. Measured quantities of the system are in fact (grand canonical) ensemble averages over the \( \{ |\beta_{a}\rangle \} \). Performing this for (II-20), we see that the change in the electronic energy, \( \Delta_{a} (E - E_{0a}) \), is just the energy shift \( \Delta_{a} (E) \) obtained from (II-18), (one can replace \( (E-H_{0})^{-1}P \) by \( (E-H_{0} + i\omega)^{-1} \))—Van Kranendonk and Walker (1968). Thus the two methods agree within our approximation.

Clearly the construction (II-19) makes it impossible to know the real matrix elements of operators. And even assuming that one could calculate the eigenstates of the time-dependent Schrödinger equation, (a very difficult task), it would be quite unnecessary: the one-particle thermal Green function determines all there is to know about the ensemble averages of observables corresponding to these operators (Ziman). The time evolution and temperature dependence of the system is fully incorporated in the Green function. In addition the coupling of the ion to the phonon continuum can be as complicated as one pleases. None of this information is so easily available using the standard procedure (for which reason many of the results have been simplistic).

Thus whenever a perturbative solution is possible, one can forget about constructing vibronic eigenstates altogether.
AN EFFECTIVE EXTERNAL PERTURBATION

The essence of Gauthier and Walker's (1976) approach to the calculation of RFs is to find how the eigenvalues of (II-18) are modified by the presence of an external electronic perturbation. This leads to an effective perturbation containing details of the ion-phonon interaction. We now set their analysis on a more general footing. We write (II-10) in second quantized form,

$$H_s = \sum_{ij} h_{ij} a_i^\dagger a_j$$

We restrict its magnitude to be much less than typical phonon energies - thus \(|H_s| < 1-2 \times 10^{14} \text{cm}^{-1}\). For Zeeman and strain interactions for example, this will certainly be satisfied and also for orbital systems where the spin-orbit interaction is not too large (if it is we incorporate it in \(H_e\)). Although we usually consider the case \(H_s < H_e\) only, we allow \(H_s\) to mix multiplets separated by small energies in our formalism, if only for completeness). Rather than treating (II-2) as a perturbation on the (solved) electron-phonon problem by finding the eigenvalue of \((H+H_s)\), a new zero-order 'spin' subsystem defined by,

$$\bar{H}_e = H_e + H_s$$

is allowed to couple with phonons via the interaction \(V\) (again restricted to \(V_\perp\) for the moment). This gives a new Hamiltonian

$$\bar{H} = (\bar{H}_e + H_p) + V = \bar{H}_o + V$$

whose eigenvalues may be found instead. This choice will allow \(H_s\) to be treated to first (or higher) order in perturbation, and to all orders in \(V\), giving first (or higher) order RFs.

We define a 'spin' zero-order matrix propagator analogous to (II-8), by,

$$\bar{g}_{ij}(z) = \text{F.T.} \left< T_a(T) a_i^\dagger a_j^\dagger \right>_o$$

$$\equiv \left\{ \frac{1}{z - \bar{H}_e} \right\}_{ij}$$

where the average is with respect to \(\bar{H}_o\). It will only be diagonal in some basis \(|i>\) a linear combination of the \(|i'>s\). The 'spin'-phonon system defined by (II-23) is now solved in an entirely analogous manner to the original
system \((H_0 + V)\). If \((II-24)\) is represented by Fig. 4(a) then a full 'spin' Green function, \(\tilde{G}_{ij}(z)\), can be defined which also obeys a Dyson equation, \(4(b)\), and produces a self-energy operator, \(\tilde{M}(z)\), with the expansion \(4(c)\).

The equation \((II-10)\), with barred operators, still stands, as does \((II-11)\), giving the shifts and widths of the states \(|\bar{i}\rangle\). In particular, corresponding to \((II-18)\) rewritten as,

\[
\{E - H - \Delta(E_i)\} |\bar{i}\rangle = 0 , \tag{II-25}
\]

we have,

\[
\{E - (H + H_S) - \tilde{\Delta}(E)\} |\bar{i}\rangle = 0 . \tag{II-26}
\]

\((II-26)\) will reduce to \((II-25)\) in the limit \(H_S \to 0\). The aim now is to express \(\tilde{\Delta}(E)\) in powers of \(H_S\) converting \((II-26)\) into an eigenvalue equation for an effective perturbation modified from the 'bare' form \((II-21)\). We can do this diagrammatically as follows. \(\tilde{M}(z)\) is given by \((II-15)\) with \(H_0\) replaced by \(H_0^\prime\). If \(|H_S| < |z + E_p - H_0^\prime|\) then

\[
(z + E_p - H_0^\prime)^{-1} = \left(1 - \frac{1}{z + E_p - H_0^\prime} \cdot H_S\right)^{-1} \cdot (z + E_p - H_0^\prime)^{-1} \tag{II-27}
\]

and a binomial expansion is possible, bringing powers of \(H_S\) to the numerator of \(\tilde{M}(z)\). Now the ordering of the operators in \((II-27)\) is such that if the external perturbation is represented by the vertex \(4(d)\) then all terms appearing in the expansion of \((II-15)\) for \(\tilde{M}(z)\) are exactly reproduced when \(4(a)\) is given the expansion \(4(e)\) and is substituted in \(4(c)\). This expansion is to be expected though, as \((II-24)\) has a self-energy operator \(H_S\) in its denominator with the corresponding Dyson equation \(4(f)\). Thus \(\tilde{M}(z)\) is given to all orders in \(H_S\) by the series \(4(g)\), equivalently,

\[
\tilde{M}(z) = \sum_{n=0}^{\infty} M_n(z), \tag{II-28}
\]

where \(M_n(z)\) is the series \(3(d)\) with \(n\) external vertices arranged in the internal electronic lines in all distinct ways. Some low order diagrams in \(M_1(z), M_2(z)\) are shown in \(4(h,i)\). These are to be evaluated by the usual rules, the only difference being the addition of an external vertex and an extra electronic propagator with it. Since we are concerned with first order reduction factors for the most part, we terminate the expansion \((II-28)\) at \(M_1(z)\). A similar expansion for the shift operators may be written,
\[ \Lambda(E) = \Lambda_0(E) + \Lambda_1(E) \]  

(II-29)

It is only valid for \(|H_S| < |E + E_p - H_o + i\alpha|\). Although the energy separation \((E - H_e)\) may be zero the remaining term is of order \(|E_p - H_p| \sim \epsilon_o\), a typical phonon energy. And since the phonon density of states typically peaks at energies \(\epsilon_o \sim \text{few} \times 100 \text{ cm}^{-1}\), \(|H_S| \ll \epsilon_o\) will be satisfied. \(\Lambda_0(E)\) is calculable from (II-15) and \(\Lambda_1(E)\) from the diagrams of 4(h). If we define an operator,

\[ T = (E + E_p - H_o + i\alpha)^{-1} \cdot V \]

(II-30)

with matrix elements represented by the diagram 4(j), and an operator \(\tilde{T}\) as the reverse ordering of \(T\), it is easy to see that each diagram in 4(h) must contribute a term in,

\[ \Lambda_1(E) = \text{Re} \left\{ \sum_{n,m=1}^{\infty} \sum_{p \neq p'} \langle T^n H_S T^m | p \rangle \right\} \]

(II-31)

Re denotes the 'real part of'.

We now insert (II-29) into (II-26). Since \(H_S\) is presumed small the eigenvalues of (II-26) should not differ greatly from those of (II-25). Setting \((E - E_o) = E_1 \ll E_o\) we perform a Taylor's expansion of \(\Lambda_0(E), \Lambda_1(E)\) about \(E_o\). To first order in \(E_1\) and \(H_S\),

\[ \Delta_o(E) = \Delta_o(E_o) + E_1 \cdot \frac{\partial \Delta_o(E)}{\partial E} \bigg|_{E_o} = \Delta_o(E_o) + E_1 \Delta_1^{(1)}(E_o) \]

(II-32)

\[ \Lambda_1(E) = \Lambda_1(E_o) \]

It is easy to show that \(\Delta_1^{(1)}(E_o)\) is just \((-1)\cdot \Lambda_1(E)\) with \(H_s \rightarrow I\), the identity operator. Substituting (II-32) into (II-26) and noting (II-25) we obtain,

\[ (E_1 \{I - \Delta_0^{(1)}(E_o)\} - \{H_S + \Delta_1(E_o)\}) \left| \tilde{\imath} \right\rangle = 0 \]

or

\[ (E_1 - H_{\text{eff}}) \left| \tilde{\imath} \right\rangle = 0 \]

(II-33)

This is an eigenvalue equation for the effective perturbation referred to earlier. It takes account of the fact that the electron-phonon coupling modifies the response of the electronic levels to the 'bare' perturbation \(H_S\).
It follows that a symmetry-adapted analysis of $\Delta_1(E_0)$ will yield the required reduction factors.

3. FEYNMAN TO GROUP-THEORETIC DIAGRAMS

We need a prescription for extracting the symmetry information about the ion-lattice (and the external) interactions from the Feynman diagrams and displaying it in graphical form. We give it below.

Consider first the interaction of the ion with the site-symmetry adapted linear displacements of the lattice. Its most general form is (cf. II-14),

$$V_1 = \sum_{c,v,n} f^c_{vn} \phi_{cv^*n'} (v)_{nn'}$$  \hspace{1cm} (II-34)

Here $c$ distinguishes different classes of lattice modes transforming as the irrep $v$ of the point group $G$. (II-34) is a generalization of the form of the interaction between an ion and the displacements of its nearest neighbours - the cluster model. In reality the ion is coupled to all neighbours, in a complicated manner which doesn't concern us. Stedman (1975) effectively rewrites (II-34) as,

$$i = (x, \lambda, \ell, \ell')$$

When the annihilation and creation operators are written as tensor operators and are coupled into the identity irrep (since $V_1$ is invariant) he gets diagrams corresponding to the coupling parameters. For example $V_{ijvn}^{C-}$ can be shown to correspond to Fig. 5(a), where the 3jm vertex is topologically identical to the Feynman vertex 5(b) if a 2jm stub is now associated with the creation of a state (electronic/phonon). Thus the Feynman diagram 5(c) has an isomorphic structure in the coupling of the 3jms as shown. It is an invariant diagram (stubs on all internal lines, reduced matrix elements etc.) as will be all the diagrams in $M(z)$ calculated using (II-34). This one example suffices to show that the symmetry information in a Feynman diagram can be made explicit and that this content at least can be handled by the usual manipulation of group-theoretic diagrams. However, the form of $V_1$, (II-14), is useful to us notationally, but then it does not display the point group symmetry. We get around this as follows. (II-14), (II-34) are equivalent descriptions of the interaction so there must be a unitary transformation between their
FIGURE 5

a) $\lambda_i^*\lambda_j$

b) $cvn$

c) $\lambda_i^*\lambda_j$

d) $cvn$

e) $k$

f) $\rightarrow$

g) $\rightarrow$

h) $\rightarrow$

i) $\rightarrow$

j) $\rightarrow$

k) $\rightarrow$

l) $\rightarrow$

m) $\rightarrow$

n) $\rightarrow$

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labels. We represent it by the invariant node $f_{k^*,avn} = 5(d)$. Here $k^*$ = (star $k$ $s$), where star $k$ is the set of distinct $k$ vectors under the operations of $G$ and $a$ is a repetition index. This follows the work of Stedman (1976) - the matrix representation of $G$ in the invariant basis $\{k^*\}$ can be block diagonalized into the matrix irreps $v_n$ of $G$, each occurring a times, by the matrix $f_{k^*,avn}$. Thus in (II-34) $c = (k^*s,a)$. We interpret this node as follows: when a propagating normal mode of the lattice, $k^*s$, excites linear combination of all symmetrized displacements of the neighbours of the ion, $f_{k^*,avn}$ will just pick out those transforming as $(vn)$. We now represent the electronic operator $f_k$ in (II-14) by the diagram 5(e) (note that the summations are $k, l, ...$ that occur in $M(z)$ can now be taken over $k^*, l^*...$, as the dispersion curves $\epsilon_k = \epsilon(k)$ have the point group symmetry. Accordingly we drop the asterisk in all future notation with this understanding). Since $5(d)$ is invertible we can expand the $k$ line as in 5(f) and thence redefine the interaction as 5(g) in terms of irreducible operators $U^\sigma_{sa}$, which act on the basis $\{|i\rangle, \}

$$f_k = \sum_{avn} U^{v*}_{n'a} (v*)^{n'n} f_{k^*,avn}.$$  

We construct $U^\sigma_{sa}$ similarly to Butler (1975),

$$U^\sigma_{sa} = \sum_{rij} <x_i\lambda_i^a |U^\sigma_{r^*} |x_j\lambda_j^r> (\lambda_i^s\lambda_j^r)^{s^r} i^s j^r |i\rangle \langle j| (II-36)$$

It is more convenient to factor out the reduced matrix element here and group it with the invariant node to form a new invariant. Taking the $ij$th matrix element of $f_k$ we perform these steps in 5(h,i). The new subdiagram in 5(i) is, in detail,

$$F_{kn,avn}^{ij} = \sum_n f_{k,avn}^{ij} <x_i|U^{v*}_{n'a}|x_j^*>$$  

We refer to it as a transformation factor for lattice to symmetry-adapted phonon and there will be one such factor for every vertex 5(j). The isomorphism of 5(i;j) is clear.

The conjugate operator to $f_k$ essentially gives the complex conjugate factor. We have,

$$f^+_k = f^+_{k} = \sum_{avn} (U^{v*}_{n'a})^{i^*} (v*)^{n'n} f^*_{k,avn}$$

$$= \sum_{avn} U^{v*}_{n'a} f^*_{k^*,avn}$$
where $\tilde{U}$ is the conjugate operator to $U$, (Stedman (1975)). The corresponding transformation factor is shown in 5(k). Via the reduced elements of $U$, $\tilde{U}$ it is related to (II-40) by,

$$F_{ijr}^{k,\nu n} = \left[ F_{ijr}^{k,\nu n} \right]^* \phi_{ijr}^* (\lambda^* \nu r)$$ (II-38)

For higher order electron-phonon interaction a similar construction is possible. For example the operator $f_{k\lambda}$ in the quadratic interaction (II-16) might be represented by 5(l) where the phonons $k$, $\lambda$ separately reduce to the irreps $\nu, \nu'$. However, only three-legged vertices exist so within the subdiagram $\Lambda, \nu, \nu'$ must couple to a third irrep $\sigma$. Thus with no loss of information we can represent $f_{k\lambda}$ by 5(m), where the new invariant mode, $f_{k\lambda, \alpha \sigma}$, defines a new factor $F'^{k,\nu n}$.

Thus all our Feynman diagrams can be redrawn: electronic propagators are stubbed and labelled by the group irreps, all interaction vertices become (coupled) $3jm\nu$ of the group summed with invariant subdiagrams which contain the physical details of the interaction. We can now apply the JL\nu theorems for our purposes. An important example is provided by 5(n), where $A, B$ are any invariant diagrams dependent upon a set of phonon and irrep labels, $K = \{k, \lambda\}$, $(x)\lambda\lambda$ respectively. For any function $f(K)$ we have the result, via JL\nu2, that

$$\sum_K f(K) A_{K, \lambda \lambda'} B_{K, \lambda' \lambda''} (\lambda)_{\lambda \lambda''}$$ (II-39)

reduces to an invariant, independent of the component labels $\lambda$ times a factor $\phi_\lambda \delta_{\lambda \lambda'} \delta_{\lambda' \lambda''}$, $(G(z)$ and $\Lambda(E)$ are examples of this - they are diagonal in the group labels but not the space labels, $x, x'$).

4. 'ELECTRONIC' REDUCTION FACTORS

As we can now display, without ambiguity, the symmetry information in our Feynman diagrams, we do so for $\Lambda_{\downarrow}(E)$. This leads to a definition of a RF.

We indicate all electronic operators explicitly in our diagrams. For example, $H_s$ is represented by Fig. 6(a) (cf. (I-10)) where $O^H_m$ is constructed as in (II-36) (but without the repetition label a). So for the purposes of symmetry calculations Fig. 4(h) becomes 6(b) with the shift operator shown explicitly ($\Sigma$ implied). We want to compare this series for some irrep $\mu$
with $O^\mu_m$ itself. We take the $ij$th matrix element of both sides. JLV3 for the left hand side gives 6(c) and defines a reduced matrix element for $(\Delta^\downarrow)_m^\mu$. For the right hand side we apply JLV3 twice, first to the external legs and then to the operator $O^\mu_m$ to obtain, symbolically, 6(d). Here the shaded box, $\text{dijab}_\mu(\mu) \equiv \text{dij}_\mu(\mu, x_i^\lambda, x_j^\lambda, (x_a^\lambda, x_b^\lambda))$, is defined by,

$$
\langle x_i^\lambda | (\Delta^\uparrow)^{\mu t}_m | x_j^\lambda \rangle = \sum_{ij}^{\text{dijab}_\mu(\mu)} \langle x_i^\lambda | O^\mu | x_j^\lambda \rangle (II-40)
$$

and every diagram in 6(b) will contribute to it. It is independent of the component labels of the basis $\{|i\rangle\}$ so the symmetry information in it must be the $j$ symbols of the group $G$. For example, its lowest order term, 6(e), has the form of a twisted $6j$. Besides, it contains all the dependence on the coupling $V$ and the phonon and electronic energies. We shall give the rules for evaluating $\text{dijab}_\mu(\mu)$ in the next chapter.

We proceed to define RFs. From (II-33) we have,

$$
H_{\text{eff}} = \{I - \Delta^\downarrow_o (E_o)\}^{-1} \{H_s + \Delta^\downarrow_o (E_o)\}
$$

$$
= \sum_{\mu m} h_{\mu m} Q^\mu_m (II-41)
$$

i.e.: $Q^\mu_m$ is the effective operator replacing $O^\mu_m$ when electron-phonon coupling is switched on. So the relation between the two operators in the basis $\{|i\rangle\}$ must give the required RFs. The $ij$th element of $Q^\mu_m$ is

$$
\langle i | Q^\mu_m | j \rangle = \sum_c \langle i | (I + \Delta^\downarrow_o (E_o)H_s = I)^{-1} | c \rangle \langle c | O^\mu_m + (\Delta^\downarrow_o (E_o))^\mu_o | j \rangle (II-42)
$$

The first operator is a group invariant so its matrix elements have the form

$$
D^i_c (\Gamma_i^\lambda)^{\delta_{iC}^\lambda}_{\delta_{iC}^\lambda} \delta_{ic} (II-43)
$$

In the event that $x_i = x_c$, for $\lambda_i = \lambda_i$, i.e.: there is at most one multiplet for each irrep of $G$, then this operator is diagonal and for $\mu = \Gamma_i^\lambda$ in (II-40),

$$
\langle i | \Delta^\downarrow_o (E_o) | c \rangle = |\lambda_i \rangle^{\mu} \sum_a d^{ia} (\Gamma_i^\lambda) |\lambda_a \rangle^{\mu}, \quad d^{ia} = d^{iiaa}
$$
where we have used the fact that the identity operator has a reduced matrix element $|\lambda_i^a|^2$. Thus,

$$D^{ic}(\Gamma_1) = [1 + \sum_a d^{ia}(\Gamma_1) |\lambda_i^a|^2]^{-1} \delta^{ic}$$

for this special case. For the general case, (II-43) ensures that the reduced matrix elements on both sides of (II-42) can be compared directly. Analogous to (I-15) we define a RF by,

$$<x_j^i\lambda_i^a|O^{\mu\nu}|x_j^i\lambda_i^b> = \sum_{p,a,b} K^{ijab}_{tp}(\mu) <x_a^i|O^{\mu\nu}|x_b^i>$$

(II-45) then give,

$$K^{ijab}_{tp}(\mu) = \sum_c D^{ic}(\Gamma_1) \left[ \delta_{tp} \delta^{ca} \delta_{jb} + d^{cjab}_{tp}(\mu) \right] \delta^{\lambda_i^a \lambda_i^b}$$

When (II-44) applies the RFs are normalized by,

$$\sum_a K^{ijaa}_{tp}(\Gamma_1) \frac{|\lambda_i^a|^2}{|\lambda_i^a|^2} = \delta_{ij}$$

- cf. (I-19). (There are no component labels in any of the above three formulae).

(II-45,46) give the most general definition of a RF for an electronic operator transforming as an irrep $\mu$ of $G$. Their respective interpretations are clear.

Firstly, the observable corresponding to the effective perturbation, measured in an experiment for the interaction of two multiplets $(i,j)$ via $H_S$, not only depends upon the matrix elements of $H_S$ between these two but between all other pairs $(a,b)$ as well. The inter-multiplet ion-phonon coupling ensures that multiplets do not necessarily respond in isolation to the external perturbation (though a consideration of their energy separations, amongst other factors, will enter here). Secondly, via the reduction Fig. 6(d), all the symmetry and the physical information contained in the RFs on a specific model is now available from a series of Feynman diagrams, e.g. 4(h). Of course this particular series is drawn for linear coupling only. We are free to put in all types of electron-phonon/phonon-phonon interactions and calculate their effect on the RFs merely by analysing the appropriate classes of diagrams (to any desired order) in the self-energy series. And herein lies the distinct advantage of the present method over that of Chapter I; we do not need to find the system eigenstates everytime we change the interaction in order to recalculate the RFs. In addition we can fully account for all interactions with temperature dependent phonon spectra, frequency dependent coupling parameters etc.
We now have two sets of definitions of RFs., the vibronic RFs (I-15, -17) and their many-body theory analogues (II-45, -46) which we loosely term electronic RFs. We now compare them. We follow the construction of Section (II-1.2) but form vibronic states \( |\gamma\rangle \) from all electronic states \( |a\rangle \equiv |j\rangle \) as

\[
|\gamma\rangle = N^{-1} \sum_{n=0}^{\infty} T^n |\beta_a\rangle |j\rangle , \quad \langle \gamma |\gamma\rangle = 1
\]  

(II-48)

Here \( T \) is the operator in (II-19) (cf. II-30) and a normalization \( N \) has been included in accordance with section (I.1). The irrep labels in the summations are such that \( \kappa \in j_a \times \lambda_j \). Consider the matrix element,

\[
\langle \gamma ' |O^\mu_m|\gamma\rangle = \sum_{n,m=0}^{\infty} N^{-2} \langle i|T^n|O^\mu_m|T^n|\beta_a\rangle |j\rangle
\]

If the \( T \) operator is replaced by (II-30) and the ensemble average performed, the effective electronic operator can be seen to have the form of \( Q^\mu_m \). So we expect,

\[
\langle \gamma ' |O^\mu_m|\gamma\rangle \rightarrow \langle \gamma ' |O^\mu_m|\gamma\rangle _{ave} \rightarrow \sum_{ij} \langle i|Q^\mu_m|j\rangle
\]  

(II-49)

to indicate how the vibronic matrix elements of \( H_s \) are to be replaced by the electronic elements of \( H_{eff} \). This is accurate to the extent that (II-48) is an eigenstate of \( (H_0 + V) \) and that one can average over the vibronic structure of the system. On this last point however, we note that the exact eigenstates (I-6) allow us to write,

\[
\langle \gamma ' |O^\mu_m|\gamma\rangle = \sum_{ij} \langle i|Q^\mu_m (\gamma ' \gamma) |j\rangle
\]

Quantum statistical mechanics claims that measurements of the response of the states \( |i\rangle \) to \( H_s \) only reveals the eigenvalues of \( \langle Q^\mu_m (\gamma ' \gamma) \rangle _{ave} \). Thus (II-49) can be the only correspondence between the two methods, but the absence of any vibronic labels in \( Q^\mu_m \) prevents any direct relation between the vibronic and electronic RFs. This is clear from a factorization of each side of (II-49) into \( 3jm \) symbols and reduced matrix elements giving, for the left hand side, with \( |\gamma\rangle = |zkk\rangle , \)

\[
\sum_{\kappa' \mu \kappa} (k'_{\mu \kappa})_{t' \nu \kappa} k'_{\gamma \nu}^{\gamma \mu} <x_{\lambda_a} |O^\mu P| |x_{\lambda_b} >
\]  

(II-50)

and for the right hand side,

\[
\sum_{\lambda_{i} \mu_{i} \lambda_{j}} (\lambda_{i} |O^\mu P| |\lambda_{j} >
\]  

(II-51)
However, there is one situation in which we might expect a correspondence between the RFs. We consider a single electronic multiplet but only its derived ground vibronic states following the usual practice for vibronic calculations when the coupling is weak enough. In the case \((x\lambda)_{i=j=a=b}, \gamma'=\gamma = (z\lambda^*)_{\text{zfixed}}\) and \((11-50,-51)\) imply,

\[
K_{\text{tp}}^{\gamma\gamma_{ii}}(\mu) \rightarrow K_{\text{tp}}^{\gamma^*\gamma_{ii}}(\mu) \tag{II-52}
\]

Now the left-hand side is equivalent to assuming that \(|\beta_{\text{a}}\rangle\) in (II-48) (with \(j\) fixed now) is the ground vibrational state, and that the lattice only enters excited states via the interaction \(V\). But in reality these states are thermally populated and the system can start in any one of a number of vibronic states and transfer to any other by emission and absorption of phonons. The right-hand side of (II-52) takes account of all this, whereas the vibronic model does so only by introducing different labels \(\gamma, \gamma'\) for the RFs. Clearly (II-52) is not the only correspondence that can be written down from (II-50,-51).

Nevertheless, it is unique because at zero temperature it becomes an equality for the ground vibronic labels but for no others. So from a symmetry point of view it will be possible to regard (II-52) as the many-body generalization of the RFs in Section (I.3) at least. (Gauthier and Walker presume the same for the electronic doublet).

For any other situation, for example a two multiplet system, \(|a\rangle \neq |b\rangle\), no simple replacement is possible. General relations between vibronic RFs determined from (I-17) will not carry over to the electronic RFs. The latter have their symmetry information inextricably tied up with the interaction. Overall though, we observe that our inability to relate the two sets of RFs is really of no consequence: experimentally it is only the electronic RFs which are measured and these contain all possible details of the ion-lattice interaction via (II-46).

5. SUMMARY

We have argued that the calculation of the exact eigenstates of an ion-lattice Hamiltonian, to obtain the RFs for the system, is unnecessary (and impossible). All vibronic RFs associated with a single electronic multiplet, effectively reduce to one ensemble averaged quantity for the purposes of measurements on a finite temperature system. (Excepting when an exact solution to \((H+V)\) is possible, this may not apply in the strong coupling limit). And this quantity can be calculated from the Green function.
On comparison with the formulation of Gauthier and Walker for the $\Gamma_3 \times e$ system, we note that:

(i) we have generalized their symmetry aspects to include multiplicity free/non-free JT systems of any symmetry. Any calculation is now basis independent;

(ii) we have not restricted an analysis to isolated electronic multiplets. Intermultiplet coupling, $H_e \neq 0$, is allowed. Likewise, we have allowed $H_s$ to mix multiplets (the magnitudes of the interactions will determine if this is an important consideration);

(iii) the analysis of $\Delta_1(E_0)$ for any system is completely diagrammatic, a logical extension, considering the advantages of the Feynman graphical method in enumerating all terms in a self-energy expression.
CHAPTER III

JAHN-TELLER SYSTEMS IN OCTAHEDRAL SYMMETRY - I

We briefly show how the formalism of the previous chapter can be used to calculate RFs in general, and then restrict the work to a consideration of isolated electronic multiplets in octahedral symmetry. In particular, we analyse the doublet state $\Gamma_3$ for linear and non-linear electron-phonon and anharmonic phonon-phonon interactions and study the resulting many-body expressions for the RFs $p,q$ with regard to dependence on phonon frequencies and temperature. Our analysis rests on the use of the $j$ symbols in their diagrammatic form and we look at the group-theoretic structure of Feynman diagrams in some detail. This not only simplifies the calculations for the $\Gamma_3$ system considerably, it also ensures that calculations and results for other JT systems carry over straightforwardly. Comparisons with other efforts at calculating $p,q$ are made.

1. METHOD OF CALCULATION

The calculation of RFs proceeds by a combination of the Feynman rules of Section (II.1.1) applied to the series of diagrams Figs. 4(h)/6(b), and the JLWn theorems applied to the group-theoretic content of these diagrams to factorize the matrix elements of the electronic operators involved. When (II-44) applies, and it usually does for orbital multiplets, the calculation of $\kappa_{ijab}^{\mu}(\mu)$ is equivalent to a knowledge of $d_{ijab}^{\mu}(\mu)$. We illustrate how to find the latter with a simple example.

Consider the diagram Fig. 7(a). From (II-31) its contribution to $\Delta_1(E_0)$ is,

$$\text{Re} \sum_k f_k \left\{ \frac{n_k}{E_0 - \epsilon_k + i\omega} \frac{1}{k e + i\omega} H_s \frac{1}{E_0 - \epsilon_k - i\omega} \right\} f_k \quad (III-1)$$
A matrix element of \((\Lambda_{1}(E_{o}))^{h}_{m}\) is then represented explicitly by 7(b) where the labelling is appropriate for finding \(d_{ijab}^{(ijab)}(u)\) (cf. Fig. 6) and the interaction vertices have been replaced according to the prescription of Section (II.3) (cf. Fig. 5(i,j,k)). We operate on 7(b) as follows:

(i) JLV2 is applied to the invariant diagram consisting of the connected transformation factors, \(F, \tilde{F} - 7(c)\), cf. 5(m);

(ii) JLV3 is applied twice, firstly, to obtain the reduced matrix element of \(o^{h}_{m}\), and secondly, to couple the external legs of the diagram - 7(d).

The diagram has been 'untwisted' with the aid of the permutation matrices. On comparison with 6(d) it can be seen that apart from energy and phonon population factors, the contribution of 7(a) to \(d_{ijab}^{(ijab)}(u)\) consists of a 6j symbol, with attached 3j phases, and a lattice/symmetry-adapted phonon transformation term. In detail these are,

\[
\sum_{\nu \in \Gamma} \frac{1}{\sqrt{\nu}} \tilde{F}_{i \nu \lambda}^{ar'} \tilde{F}_{b \nu \lambda}^{bjr'} \left\{ \begin{array}{ccc} \mu & \lambda & \lambda' \\ a & b & \nu \end{array} \right\} (\mu \lambda \lambda' \nu) (rr'p) = (ijab, \mu tp)_{k} \tag{III-2}
\]

For the energy factors the multiplier of \(n^{k}_{k}\), for example, is

\[
(E + \varepsilon_{o}^{k} - \theta + io)^{-1} (E - \varepsilon_{o}^{k} - \theta + io)^{-1}
\]

where \(E_{o}\) is the solution of (II-25). We cannot be more specific unless the labelling is restricted to \(i=j\) and \(a=b\), that is \(H_{s}\) acts within a multiplet (usually, realized experimentally), and off-diagonal elements of \(\Lambda_{1}(E_{o})\) are neglected (this is only justifiable if \(V_{iak} \gg V_{jak}\)). Now we are calculating \((\Lambda_{1}(E_{o}))_{ii}\) and \(E = \theta_{i}\) in a first approximation. For these restrictions then Fig. 6(e) gives,

\[
d_{ia}^{(ijab)}(u) = Re \sum_{k} (iiaa, \mu tp)_{k} \left[ \frac{n^{k}_{k}}{(E_{ia}^{k} + \varepsilon_{k}^{k} + io)^{2}} + \frac{(n^{k+1}_{k})}{(E_{ia}^{k} - \varepsilon_{k}^{k} + io)^{2}} \right] \tag{III-3}
\]

The point to note from this example is that (III-3) is factored into three parts: an energy/population sum which, apart from the state labels, is independent of symmetry; \(j\) symbols for the point group containing the dependence on \(u\); and phonon transformation factors.
FIGURE 7

a) 

b) 

c) 

d) 

e) 

f)
We now state the rules for writing the contribution of any Feynman diagram to \( d_{ijab}^{tp}(\mu) \):

1. Take the matrix element of a diagram in 6(b), labelling all internal and external lines. Evaluate the (labelled) energy denominators for all emission \( (n_k + 1) \) and absorption \( (n_k) \) processes, e.g. (III-3), and sum these.

2. Represent \( n \)th-order electron phonon vertices as \( 3j \)ms coupled to transformation factors, e.g. 7(e).

3. Operate on the diagram with JLVn as far as possible to produce:
   
   a. a reduced matrix element for the whole diagram and for the external interaction, to obtain the form of 6(d),
   b. diagrams for (coupled) transformation factors,
   c. \( 3j \), \( 6j \) and \( 9j \) symbols.

4. Compare with 6(d), and sum the quantities in the box with the energy term from (1) above, over all internal labels. Take the real part.

In Appendix V we give the details of applying Rule 3(c) to some of the low order Feynman diagrams that will be of interest to us in this chapter and the next. Regarding Rule 1, we note that the utility of (II-31) for obtaining energy factors easily is limited to diagrams that have, at most, pairs of electron-phonon vertices connected. Otherwise the operator \( V \) in (II-30) necessarily has a more complicated form than, say (II-14, -16). In such cases it is easier to follow the Feynman rules directly. We show in Appendix VI how these more complicated diagrams are best evaluated and introduce a contracted notation for the energy sums. We also indicate how the summation on \( k \) is to be performed. (Hereafter we remove the \( io \) term in all denominators with the understanding that it is to be included and the real part taken wherever phonon summations are required explicitly).

As nearly all of our work is concerned only with the effects of electron-phonon interactions within a single multiplet in octahedral symmetry we now simplify our notation as much as possible. We set \( i=j=a=b \) in (II-46) and replace \( d_{ijab}^{iii} (\mu) \) by \( d_{ijab}^{\lambda} (\mu) \) (we shall also drop these sub- and super- scripts wherever possible). For this multiplet, \( \lambda \), the phonon transformation terms can be rewritten, as only a few symmetry-adapted phonon irreps occur (v of Fig. 7(e). We shall refer to these as 'phonons', indicating that the details of formation of symmetrized phonons are last in the subdiagram F and that it is the lattice phonons labelled \( k \) that are of real interest). We employ the time reversal arguments of Abragram and Bleaney. For the interaction \( V_1 \) say, we
have that under time reversal $V$ is invariant and $\phi_k$ is a time even operator
i.e. $\phi_k + \phi_k = \phi_k$. So $f_k$ and hence $U^\nu$ are time even also, and within a
multiplet $\lambda$, we have,
$$\nu \in \{\lambda \times \lambda\}_{S/\lambda}$$
according to whether the ion has an even/odd number of electrons. Thus in
octahedral symmetry the only possible 'phonon' irreps are $\Gamma_1, \Gamma_3, \Gamma_5$. This
result applies for any interaction $V$. Now consider the transformation term
in (III-2). A check of the $lj,3j$ phases for the irreps $\lambda, \nu$ of interest shows
that $r=r'=0$ and that $\phi_r (\lambda \times \nu) = +1$. Using (II-38) this term is equivalent
to a factor,
$$f^\lambda_{kn} \equiv \sum_n \frac{1}{|\nu|} |F^\lambda_{kn}|^2$$  \hspace{1cm} (III-4)
and there will be one such term for every phonon line in a diagram corresponding
to linear coupling within the multiplet. Indeed, since each JT system we shall
study is well defined (fixed $\lambda$), it will be convenient to write,
$$f^\lambda_{kn} = |\lambda| (g_k (h_\lambda)) \text{ for } \nu = (\Gamma_3, \Gamma_5)$$  \hspace{1cm} (III-5)
($\nu = \Gamma_1$ need not be considered. The linear coupling (only) via the $\Gamma_1$ 'phonon'
can be transformed away within a multiplet. We leave the proof to Appendix
VII. For interactions other than linear similar factors to (III-4) can be
defined, although if the corresponding transformation diagram is asymmetric or
is produced by JLV($n>2$) then the factor will be complex.

It will also be convenient for our analysis to separate out the wholly
group-theoretic contribution, given by Rule (3(c)) above, of each Feynman
diagram in the series for $d^\lambda_{TP}(\mu)$. For each and every diagram we call this
quantity $\delta_{TP}(\mu)$. Structurally, it is just the closed diagram remaining after
Rules 3(a),(b) have been applied, so the 'phonon' irreps and their attached
multiplicites labels should also be specified. However the latter have only
one value and for our purposes the 'phonon' labels will be immaterial.
2. **LINEAR ION-PHONON INTERACTION** - $\Gamma_3 \times \epsilon$

2.1 Reduction Factors to Fourth Order

We restrict ourselves to the linear interaction and calculate the RFs to $O(V_1^4)$ for $\lambda = v = \Gamma_3 (\Gamma_3 x \epsilon)$ from the diagrams of Fig. 7(f). Now (II-46) is simply written as,

$$K(\mu) = [1 + d(\mu)] \left[ 1 + d(\Gamma_1) \right]^{-1}$$

A comment is needed here about its expansion in powers of $V_1$. Firstly, $d(\mu)$ itself is a series expansion in powers of a parameter $\nu = V_1^2 / \epsilon_0^2$ - indeed each diagram in 7(f) contains such an expansion if $E_o$ is written properly as the solution of (II-25). Convergence of this series is required. In addition, for a binomial expansion of the denominator we require $|d(\Gamma_1)| < 1$. We shall assume throughout our work that for the coupling of any type, both requirements are met. Thus,

$$K(\mu) = 1 + d(\mu) - d(\Gamma_1) - d(\Gamma_1) \cdot [d(\mu) - d(\Gamma_1)] + ... \quad (III-5a)$$

The contribution of each diagram in 7(f) to $d(\mu)$ is easily written down. There is a factor (III-5) for each phonon label, the numerical values of the $j$ symbols derived from these diagrams (see Appendix V) are obtained from Appendix IA, and the labels in 7(f) define the Feynman denominators given below. (The mirror images of $C_{kl}, D_{kl}$ are understood to be included. If the attached phonon labels are reflected along with the diagrams, the images produce the complex conjugate matrix elements. Thus the contributions of $C_{kl}, D_{kl}$ will appear multiplied by 2). As an example, we write $d(\Gamma_1)$ in similar form to (III-2, -3),

$$d(\Gamma_1) = \sum_{k} 2g_{k}^{2} X_{k} + \sum_{kl} 2g_{k}g_{l}^{2} \left( A_{kl} + 2C_{kl} \right).$$

In this manner,

$$K(\Gamma_2) = p = 1 - 2 \sum_{k} g_{k} X_{k} - 2 \sum_{kl} g_{k} g_{l} \left( 2C_{kl} - X_{k} X_{l} \right)$$

$$K(\Gamma_3) = q = \frac{1}{2} (1 + p) - \sum_{kl} g_{k} g_{l} \left( A_{kl} - B_{kl} \right) \quad (III-6)$$

Note that $D_{kl}$ does not appear in these formulae. In the contracted notation of Appendix VI the denominators are,
\[
X_k = \frac{\sigma_k n(k)}{(\Delta + k)^2}
\]

\[
A_{kl} = \frac{1}{(k+\xi)^2} \quad \begin{cases} \frac{1}{(k+\xi)^2} \\ \frac{1}{(k+\xi)^2} \end{cases}
\]

\[
B_{kl} = \frac{1}{(k+\xi)^2} \quad \begin{cases} \frac{1}{(k+\xi)^2} \\ \frac{1}{(k+\xi)^2} \end{cases}
\]

\[
C_{kl} = \frac{1}{(k+\xi)^2} \quad \begin{cases} \frac{1}{(k+\xi)^2} \\ \frac{1}{(k+\xi)^2} \end{cases}
\]

\[
\Delta \text{ in } X_k \text{ ensures that (III-6) will be correct to } O(V_{1/4}) - \text{ cf. (II-25).}
\]

To \( O(V_{1/2}) \),

\[
\Delta_0 = \sum_{\ell} g_\ell \sigma_\ell \frac{n(\ell)}{\ell}
\]

Substituting (III-7) into (III-6) and evaluating the sums \( \sigma_\ell \) last we find, with \( N_k = (2n_k + 1) \),

\[
p = 1 - 2 \sum_k g_k \frac{N_k}{e_k^2} + 4 \sum_{kl} g_k g_\ell \frac{N_k N_\ell}{e_k^2 e_\ell^2}
\]

(III-8)

\[
\text{and the difference between } p, q \text{ to be,}
\]

\[
\frac{1}{2} (1+p) - q = \sum_{k\ell} \left( A_{k\ell} - B_{k\ell} \right)
\]

(III-9)

\[
= 2 \sum_{k\ell} \frac{g_k g_\ell}{e_k^2 e_\ell^2} \left[ N_{k\ell}^+ (e_k - e_\ell)^2 + N_{k\ell}^- (e_k + e_\ell)^2 \right]
\]

(III-10)

where \( N_{k\ell}^\pm = (N_k N_\ell \pm 1)/(e_k \pm e_\ell)^2 \).

(III-8, 10) are the generalizations to all temperatures of the results first obtained by Gauthier and Walker (1973) and Halperin and Englman (1973), for if we set \( N_k = 1 \), corresponding to zero temperature where only spontaneous emission processes exist, we recover their formulae. Also in this limit, according to the arguments in Section (II.4), we must obtain the RFs of Section (I.3.1), in particular (III-9) must be (II-23). So we can make the identification,

\[
2b_7 = \sum_{k\ell} \left( A_{k\ell} - B_{k\ell} \right)
\]

(III-11)

for zero temperature. It is clearly convenient to parametrize (III-9) in this way for finite temperatures as well. As in the vibronic model we have the result that \( b_7 \geq 0 \), the equality only occurring if terms above second order are neglected altogether (an uninteresting possibility), or if all phonons are isoenergetic, \( e_k^+ = e_k^\ell \) (the iso factor in \( N_{k\ell}^- \) ensures this). In this single mode limit at zero temperature, we can recover the results of Ham's (1968) cluster model for a single \( \Gamma_3 \) phonon pair. (Such calculations can be obtained from
our results for a multiplet $\lambda$ in the limit that,

$$\sum_k f_k \phi_k \rightarrow \sum_{vn} v^\lambda_n U_{vn} Q_n$$

The coefficients and operators here are those used conventionally by Ham (1972) and Englman (1972). The only requirement is that the ligand mass be taken as unity (Ham et al. (1969)). Since $Q_{vn} = (\hbar/2\omega_v)^{1/2} \phi_{vn}$, the effect is to replace the matrix element,

$$F^\lambda_{kvn} (\lambda\nu\nu)_{ij}$$

by

$$(\hbar/2\omega_v)^{1/2} v^\lambda_v (U_{vn})_{ij}$$

A comparison of the 3jms (Griffith (1962)) and the matrices $U_{vn}$ gives the relation between $F^\lambda_{kvn}$ and $v^\lambda_v$. For $\Gamma_3 \times \epsilon$, $q_k \hbar v^{2\lambda}_v E_\omega E_k \delta_{k1}$ and Ham's exponential expressions are correct to $O(V^4)$. Although (III-8) has the first two terms of an exponential, the sixth order terms are not of this form and Ham's formulae are not justified, and certainly wrong for more than one mode at $T=0$. For the general case of finite temperature, we have instead $b_\gamma > 0$, whenever $\epsilon_k$ depends upon $k_s$ in any manner. And it always does in real crystals (Kittel (1971)). Note that the second term in (II-10) has its greatest contribution when the first term has its least, throughout the phonon spectrum; we expect it to be dominant except at very low temperatures. While we agree with Gauthier and Walker that such terms with 'vanishing' energy denominators require careful treatment, the techniques for evaluating the integrals exist and are identical to those required in, say, finding the effect of phonon Raman scattering on the shifting of zero-order electronic levels, (see Appendix VI). There is no reason to exclude terms with resonant denominators in reduction factor expressions as they have done.

So, realistically, for weak linear coupling to the whole lattice, $q$, $p < l$, and there are no conditions under which the relation $q = \frac{1}{2}(1+p)$ is obeyed.

It is of interest to find the temperature dependencies of the terms in (III-8,10), although simple results are possible only in the limiting cases of low and high temperatures. Consider the $V^2_1$ term in (III-8). For low temperature i.e. $\epsilon_o \gg KT$, the $n_k$ factor determines that the greatest contribution to $\Gamma_k$ comes from those phonons with energies $\leq KT$. So for sufficiently small $T$, only acoustic phonons need be considered and in this limit the long-wavelength approximation in the form (Stedman and Newman (1971)),

SEE ERRATA
\[ \varepsilon_k = h c \left( \hat{k} \cdot \mathbf{s} \right) |\hat{k}| \]  

(III-13)

is valid. Here \( \hat{k} = \frac{k}{|k|} \) and \( c(\hat{k}, s) \) is the velocity of sound in the host crystal. Also in this limit \( F_{k,vn} \propto (\varepsilon_k)^{1/2} \), so \( g_k \propto \varepsilon_k \). As (III-13) allows the \( \varepsilon_k \) to factorize we let,

\[
\sum_k \frac{g_k N_k}{\varepsilon_k^2} \rightarrow \frac{V}{8\pi^3} \sum_s \int d\Omega_k \int k^2 dk \cdot \frac{1}{\varepsilon_k} \cdot \coth \left( \frac{\beta \varepsilon_k}{2} \right)
\]

\( V \) is the crystal volume, \( \chi = |\hat{k}| \) and \( d\Omega_k \) is an element of solid angle centred on the Brillouin zone. For our purposes the integral over \( \Omega \) and the sum over \( s \) can be neglected. With \( x = \beta \varepsilon_k \) and (III-13) the remaining integral has the form,

\[
\beta^{-2} \int_0^\infty x \coth \left( \frac{\beta x}{2} \right) dx
\]

where the upper limit has been made temperature independent since the large \( k \) values make a negligible contribution to the integral. Thus for low \( T \), the second order terms have a \( T^2 \) dependence. By the same argument the fourth order terms, in particular \( b_7 \), vary as \( T^4 \). In the high temperature limit, we assume \( \varepsilon_k \ll KT \) for all \( k \). Then \( \coth x = x^{-1} = KT/\varepsilon_k \) and each phonon summation gives a term of the form \( KT \sum_k f(\varepsilon_k) \), that is a \( T, T^2 \) dependence for the order \( V_1^2, V_1^4 \) terms respectively in (III-8,-10).

### 2.2 Generalizations to Higher Orders

So far we have shown how the RFs may be calculated from diagrams to \( O(V_1^4) \) and have seen that particular diagrams will break the 'single mode' sum rule, \( q = 1/2(1+p) \). We now look at the linear diagrams occurring at an arbitrary order in some detail. Not only do patterns emerge simplifying the calculations but the diagrams breaking the above sum rule can be isolated and \( b_7 \) found immediately. A knowledge of this model-dependent parameter suffices as \( p, q \) can both be measured, in principle.

The simplification referred to depends in part upon the identity,

\[
\begin{pmatrix} 4 & 4 & 4 \end{pmatrix} = 0
\]

(III-14)
Consider the diagrams at $O(V_1^6)$ contributing to $p$, $q$ - Fig. 8(a,b,c). For clarity we have only labelled the possible positions of the external vertex (Fig. 6(a)) (image positions are marked). As the group-theoretic structures derived from these diagrams by application of Rule 3(a,b) are isomorphic to the Feynman diagrams, and the $2jms$, $(4)_i^j$, and the $ij$ phase, $\phi_4$, are both unity, we can apply JLV directly to $8(a,b,c)$ with quick results for some vertex positions. At a glance: JLV2 in 8(a) (the cutting positions are indicated by broken lines) shows that vertex $d$ has a zero contribution for all $\mu$, via (III-14); in 8(b) it reproduces the form of $D_{k\ell}$ for vertices $j, k, n, p$; and, JLV3 in 8(c) shows $s, t, w$ are zero. And by forming the reduced matrix elements for the remaining diagrams and using JLV to produce pairs of 'lower order' structures, some of which are mutually exclusive, one can show just as quickly that vertices $e, f, k, r, a, b, y$ vanish. Thus 27 of the 50 diagrams are trivially zero and of the remainder only those in 8(c) require any effort in their evaluation. We can approach the problem more generally. Let $8(d)$ represent the generic class of diagrams which includes in its three lowest orders $X_k$, $A_{k\ell}$, $C_{k\ell}$, and Figs. 8(a). Then it looks like either $8(d)$ or $8(dii)$, where the shaded region is a self-energy insert. Via JLV2, case (i) is zero only if the insert satisfies $8(e)$; otherwise it follows $X_k$ with $d(\Gamma_1) = -d(\Gamma_2)$, $d(\Gamma_3) = 0$. For case (ii) we apply JLV3 as in 8(f). It can only be non-zero when $8(g)$ is non-zero for $\mu = \Gamma_1 \Gamma_2$ (only). Thus we have the result that $8(d)$ contributes to $d(\Gamma_1), d(\Gamma_2)$ only. Similarly, for all orders, $8(h)$ can contribute to $d(\Gamma_3)$ only, whereas $8(i)$ is always zero. Thus the absence of contributions in $8(a,b)$ is explained. At each new order there exists diagrams creating a new generic class - at $O(V_1^6)$ these are in $8(c)$, and we find vertices $v + d(\Gamma_3), x, y, z + d(\Gamma_1), d(\Gamma_2)$ and we can generalize these results to higher orders also. An examination to $O(V_1^8)$ shows that the following rules apply:

I. The 'generic' diagrams contribute to (a) $d(\Gamma_1), d(\Gamma_2)$ or, (b) $d(\Gamma_3)$, for all orders.

(a) these are symmetric, e.g. $8(j,k)$ give the only possibilities at $O(V_1^8)$. Whether bare or containing inserts, e.g. $8(a)$, a diagram must contribute for each position of the vertex, or not at all. Thus vertices $a, b, c$ are all non-zero.

(b) these diagrams contribute for only one position of the vertex at the order in which they first appear. Furthermore, there must exist an even number of electron-phonon vertices to one side of the external interaction. Vertex $v$ in $8(c)$ illustrates both of these points.
II. The values of $\delta(\Gamma_1)$, $\delta(\Gamma_3)$ for any diagram are always $2^{-m}$ where $2^m$ is the number of electron-phonon vertices. And $\delta(\Gamma_2) = (-1)^n \delta(\Gamma_1)$ where $n$ is the number of these vertices to one side of the external vertex.

Considering the order of perturbation to which we have worked, we can expect these rules to apply for all orders. In Section (III.3.2) we shall justify this expectation.

In principle then, one can easily find formulae for $p,q$ to any desired order. Rule I, together with the methods used on Fig. 8(a,b,c), serves to eliminate many of the diagrams immediately and of the remainder only a (decreasing) fraction have an unfamiliar form, e.g. at $O(V_{\pi}^0)$ these include $8(k)$.

(While high order diagrams require extensive use of JLVn to obtain $6j$ and $9j$ symbols, I(a), (b) determine that only a few - usually two - vertex positions need be checked). Then Rule II and (III-5) allow $p,q$ to be written down at once as in (III-6). The only difficulty is in symmetrizing the formulae as in (III-10). Of particular interest is $b_7$. Using (I-23) we can express it as,

$$b_7 = \frac{1}{4} \left[ l + d(\Gamma_1) \right]^{-1} \cdot \left[ d(\Gamma_1) + d(\Gamma_2) - 2d(\Gamma_3) \right]$$

(III-15)

From Rule II the only diagrams that can possibly break the single mode sum rule are those that have $n$ even. For example, the contribution to $b_7$ at sixth order is,

$$\sum_{k\ell m} q_k q_{\ell} q_m (b + h + y - m - q - v)_{k\ell m}$$

(III-16)

from Fig. 8(a,b,c), as well as (III-11) corrected to this order by the denominator of (III-15) and $\Lambda_o$ in $A_{k\ell}, B_{k\ell}$. It is obviously quicker to check theory and experiment directly from (III-15). Because an odd number of phonons is involved in this example we cannot prove its contribution to be positive.

(Fletcher claims in private communication to Bates (1978) that the contributions to $b_7$ for $m$ even (Rule II) are positive and those for $m$ odd, zero. We do not agree with him for $m > 2$). However, in the single mode limit we still find $b_7 = 0$. This special result, which will generalize to all orders (our examinations reveal equal numbers of diagrams of type (a) (Rule I) with $\delta(\Gamma_2) = + \delta(\Gamma_1)$, as type (b)), was first obtained by Leung and Kleiner (1974) by considering the form of the vibronic ground state eigenfunctions.
We emphasize that the simplicity of the calculations for the linear \( \Gamma_3 \times \varepsilon \) system depends upon the identity (III-14). Although other JT systems may not imitate this, the method of analysing their diagrams will be essentially the same and one can expect similar expressions to (III-8) for their Rfs.

3. GROUP THEORETIC STRUCTURES OF FEYNMAN DIAGRAMS

3.1 Arbitrary Symmetry

The ease with which we have just inferred the patterns of Feynman diagrams contributing to \( p,q \) has also depended upon the recognition of the occurrence of 'low order' structures, for which \( \delta(\mu) \) is known, in all higher order diagrams. Before continuing with the calculation of the effects of non-linear and anharmonic interactions on \( p,q \) we take a general look at the group-theoretic structure of all possible Feynman diagrams, regardless of the point group symmetry.

It will suffice to consider the quadratic interaction \( V_2 \) and the cubic anharmonic interaction \( V^{(3)} \) in addition to \( V_1 \). This does not restrict our conclusions in any way. Figs. 9(a-f) show a few of the diagrams that can be drawn by combining these interactions at low orders. (We neglect the external interaction for the moment). Using the expansion Fig. 7(e) we proceed as in 7(c) to separate off the phonon transformation diagrams. The latter step will require \( JLV_n \) wherever \( n \) electron-phonon vertices are interconnected by phonons, e.g. the diagrams of 9(e) can all be put into the form of 9(g) where the shaded box consists of invariant diagrams (the labelling here is common to Figs. 12(j,k)).

The diagrams remaining after these operations have the basic structures shown in the corresponding Figs. 9(a'-f') (the 2jms which exist on all lines are omitted for simplicity). As the operation of \( JLV_2 \) only on pairs of electron-'phonon' vertices characterizes the linear interaction (to all orders), we see that diagrams like 9(a',b') are not qualitatively new. By defining appropriate symbols for the phonon-transformation diagrams and denominators and attaching the external vertex Fig. 6(a), we will obtain reduction factor expressions outwardly similar to those for the linear interaction.

For the remaining diagrams which involve \( JLV(n\geq 3) \) additional work is required, and the calculations will be more complicated in view of the multiplicity and irrep summations common to the structural and the transformation diagrams, e.g. 9(g). Nevertheless, from the few examples given in Fig. 9 it is clear that
FIGURE 9

a)

b)

c)

d)

e)

f)

g)

h)

a' )

b' )

c' )

d' )

e' )

f' )
many Feynman diagrams of differing complexity can reduce to a single structural diagram. If such a diagram is zero for a particular position of the external vertex then all such Feynman diagrams will not contribute to the reduction factors. Obviously it is the structural diagrams we should concentrate upon in our calculations.

To do this we need a systematic way of generating all those structures which can derive from all Feynman diagrams. There are enough examples in Fig. 9 to see that the following method works:

1. Draw all connected diagrams in the same manner as one draws Feynman diagrams restricted to linear interactions. E.g. 9(a',b') - we call these 'linear' structures.
2. In addition, to these diagrams add 'phonon' lines to connect existing 'phonon' lines to electronic lines in all distinct ways, e.g. 9(c'→f'). When m such additional lines connect to one existing 'phonon' line as in 9(e',f'), there are (m-1) irrep labels between 3-'phonon' vertices (which are to be summed with a coefficient as in 9(h)).
3. All vertices are 3jms, therefore they are 3-legged.

Figs. 10(a,b,d,e) show all the structures that can be drawn by adding one or two 'phonons' to 9(a',b'), 10(c) a few structures obtained by starting with 8(a,b,c), and 10(f,g) those by adding three and four 'phonons' to 9(a'). (The groupings in 10(e) and the markings of some vertex positions are for later reference). Note from what was said earlier, that these structures, including the 'linear' ones, are not necessarily ordered in the perturbative sense. Note also, that for diagrams derived using JLV(n>4) our generating method produces one of a number of apparently different structures, depending upon which 'phonon' lines are coupled together. As examples: in 9(g) the phonons could be regrouped as in 10(h) producing an 'incorrect' structure (with a different coefficient); and 10(i) appears to be distinct from 10(d). In both cases application of JLV4 to the structure and its associated coefficient corresponds to the simpler form of 10(d).

It only remains to add the external vertex to all electronic lines and reduce these structures to j-symbols (the details of this for 10(a) (d) can be found in Appendix V). Although such an analysis is fairly tedious we don't have to break all diagrams down to their component 6j, 9j symbols to observe the general features and compare JT systems. Often it suffices to factor a diagram into known structures times 6js, which are easily evaluated. For
FIGURE 10 contd.

h)

i)

j)

k)
example many of the diagrams like 10(a-c) will factor into 'linear' structures from which they were generated and those in 10(e) with a σ label will often reduce to 10(d). Fortunately, even for those diagrams for which this is not the case, simplifications exist for our problems: all the vertices shown in 10(a-f) are multiplicity free and the 3-'phonon' vertex places a major restriction on the 'phonons' that can be involved. This is most apparent for those structures which have been JLV3 produced and usually allows a quick check if the diagram is zero. As an example consider Fig. 10(j) (only the essentials are included in the diagram), with JLV3 applied as indicated. This produces the 6j,

\[
\left\{ \begin{array}{c}
\nu_1 \\
\nu_2 \\
\nu_3 \\
\lambda \\
\lambda \\
\lambda
\end{array} \right\}_{o o o o o o}
\]

summed with a 'linear' diagram whose result is already known provided \(x=0\) (the only system for which this is not the case is \(\Gamma_8 \times (c+r_2)\) where \(\frac{554}{333} \neq 0\) and the same applies to the remaining vertex positions on this structure.

A generalization of this example is provided by 10(k). A similar linear diagram is produced but the 6js now have the form,

\[
\left\{ \begin{array}{c}
\sigma \\
\nu_a \\
\nu_b \\
\lambda \\
\lambda \\
\lambda
\end{array} \right\}_{z o o o o}
\]

and it is the restrictions on \(\sigma\), which again require \(x=0\) for all systems but \(\Gamma_8 \times (c+r_2)\), that simplify the calculations.

3.2 Application to \(\Gamma_3 \times \varepsilon\)

We now consider the structures for the \(\Gamma_3 \times \varepsilon\) system. We begin by noting that the remarks made about the breakdown of the linear Feynman diagrams in Section (III.2.2) actually apply to all the 'linear' structures, as do the rules for the possible contributions. We need only look at the remaining structures of Fig.10. Again it is the fact that (III-17,-18) are zero for \(\sigma=\lambda=\nu_1=\Gamma_3\) that simplifies the reduction of the diagrams in Fig.10. We find that:

1. \(10(a,b,c,e(iii),f)\) are zero for all positions of the external vertex - for many this is trivial to show;
2. \(10(d,e(i,g)\) contribute to \(d(\Gamma_1), d(\Gamma_2)\) for all positions of the vertex with \(\delta(\Gamma_2) = (-1)^n \delta(\Gamma_1)\) again;
(3) \(10(d,e(i,ii),g)\) contribute to \(d(G_3)\) for the vertex position marked.

(4) \(\delta(G_1), \delta(G_3)\) for non-zero structures have the value \(2^{-m}\) where \(2m\) is the number of electron-'phonon' and 3-'phonon' vertices (this follows since the 6js are all \(\pm \frac{1}{2}\)). For structures with \(\sigma\) labels there is an additional sign determined by \(\sigma\) e.g. \(10(d)\) is better represented as \(9(h)\) and we find,

\[
d(G_1) \simeq \frac{1}{8} (V_o - V_\gamma), \quad d(G_3) \simeq \frac{1}{8} (V_o + V_\gamma)
\]

Clearly (2), (3), (4) do not exactly follow the Rules I, II found for the 'linear' structures. Those structures with \(\sigma\) labels above the vertex can contribute to \(d(\mu)\) for all \(\mu\) and the symmetry requirement of I(a) is now invalid. With these modifications and the broadening of the definition of \(m\) to (4) above however, we can use Rules I, II to eliminate much unnecessary work. However, (1) suggests a new rule - for two reasons. Firstly, from the results for \(10(a,b,c)\) we can expect all diagrams with only one 3-'phonon' vertex to be zero. And secondly, structures generated by adding \((2m+1)\) lines to \(9(a')\) are always zero. This is easy to see. For example \(10(f)\) produces, amongst other things, the form,

\[
\left\{ \begin{array}{c} p \\ 4 \\ 4 \\ 4 \end{array} \right\} \cdot \left\{ \begin{array}{c} \sigma \\ 4 \\ 4 \\ 4 \\ 4 \end{array} \right\} \cdot \left\{ \begin{array}{c} 4 \\ 4 \\ 4 \\ 4 \\ 4 \end{array} \right\}
\]

for all vertex positions. For a non-zero result we require \(p, \sigma \neq 4\), but then \(\left\{ \begin{array}{c} p \\ 0 \\ 4 \\ 4 \\ 4 \end{array} \right\} = 0\). This form of an odd number of 6js occurs for all structures generated via JLV\((2m+3)\). Thus we have the important simplification:

III. All structures with an odd number of electron-'phonon' vertices are zero for all positions of the external vertex.

With the exception of explaining why some structures contribute to \(d(G_1)\) and \(d(G_3)\) or both we now justify our rules with a general argument.

For an electronic multiplet \(\lambda\), an arbitrary structure to be reduced can be represented by the diagram 11(a), for some position of the external vertex. It has the value \(\delta_{\mathbf{tp}}(\mu)\). For any labelling of the 'phonons', \(\nu\), in this diagram we can transpose this vertex to one side as in 11(b). Successive transpositions eventually place the vertex at the extreme 11(a), labelled by \(\alpha\). The diagram is then equivalent to 11(c), for some different 'phonon' and electronic irreps \(\nu', \sigma\), and a 6j symbol can be separated off. It is the 6js in 11(b,c) that help determine any general results for \(\delta_{\mathbf{tp}}(\mu)\). Note that the
starting position in $l_1(a)$ determines the energy factors for the original \Feynman diagram from which $l_1(a)$ was derived, and therefore the contribution to $d_{tp}(\mu)$ for this diagram. This does not change. But any property of $\delta_{tp}(\mu)$ for some vertex position will also exist for $d_{tp}(\mu)$ there as well. We apply these ideas for $\lambda=v=\Gamma_3$, $r=p=0$. The results of one transposition are shown in $l_1(d)$ and of two, for $\mu=\Gamma_3$, in $l_1(e)$. For the 'end' structure $l_1(c)$, provided $x=0$, $\sigma=\lambda$, and the shaded diagram is non-zero, the complete diagram behaves as the simplest 'linear' structure (cf. Fig.7(d)). For $\Gamma_3 \times \varepsilon$ this gives $\delta(\Gamma_3) = -\delta(\Gamma_1)$, $\delta(\Gamma_3) = 0$ at each end, $\alpha$, $\beta$, of $l_1(a)$. Consider $\mu$, $\Gamma_1$, $\Gamma_2$ in $l_1(a)$. If $\delta(\Gamma_1) = k$ say (including $k=0$) for the vertex at $\alpha$, then by the transpositions in $l_1(d)$ each vertex position through to $\beta$ gives the value $k$; and the value of $(\Gamma_n)$ alternates as $(-1)^n k$. If there exists an odd number of electron-'phonon' vertices between $\alpha$, $\beta$, then at $\beta$, $\delta(\Gamma_2) = \delta(\Gamma_1)$, in contradiction to our statement about these 'end' diagrams. Now let $\mu=\Gamma_3$ and suppose $l_1(a)$ contributes to $\delta(\Gamma_3)$ for some $n$ odd - for example $l_1(f)$ with $n=3$. By pairs of transpositions $l_1(e)$, we can shift the vertex to the end position $l_1(g)$ where $\delta(\Gamma_3) = 0$. So $\mu=\Gamma_3$ contributes only for $n$ even. Suppose now that $n$ is even measured from one end of the structure, but there are an odd number of electron 'phonon' vertices altogether. By transferring to the opposite end of the diagram we again produce $l_1(g)$. Hence our rules follow.

An important consequence of any result proven by such a method, for some $\lambda$, is that it must be true independent of the type of electron-phonon coupling and its order of perturbation. In particular, it must hold to infinite order and hence for the range of coupling strengths for which this infinite series converges. It is not a strong assumption to state that it will hold for any other finite range where perturbation techniques are not applicable, that is, for arbitrary strengths of interaction.
FIGURE 11

a)

b)

c)

d)

e)
4. LINEAR, NON-LINEAR, ANHARMONIC INTERACTIONS

4.1 $\Gamma_3 \times \varepsilon$

Having completed our analysis of the structure for $\Gamma_3 \times \varepsilon$ we now evaluate some Feynman diagrams of low order in $V_1, V_2, V^{(3)}$ which will generate additional terms for $p, q$.

Fig. 12(a-g) shows all the diagrams that can be drawn correct to orders $V_2 V_1', V_2' V^{(3)} V_1$, having already excluded those at orders $V_2 V_1', V_1' V^{(3)}$ via Rule II. In 12(a) the two topologically distinct diagrams which arise from the different pairings of the phonon operators $\phi_k \phi_\ell$ in the quadratic interaction are shown. Their contributions are equal, so for 12(b-e)/12(f,g) it should be understood that a factor of $2/4$ is to be included in the calculation. The images of asymmetric diagrams should also be counted as in 12(b,c). Since 12(a-e) reduce to the linear structures of 9(a'b') we have labelled the vertex positions and their corresponding denominators to reflect their similarity to the diagrams of 7(f). We now proceed as in Sections (1.1) and (1.2.1).

Essentially, all we do is substitute the new denominators wherever their linear counterparts appear, and replace $f_{k\ell}^\lambda$ where necessary by (see 12(h)),

$$f_{k\ell}^\lambda = \frac{1}{n} \left| \frac{1}{V} \right|^2 |f_{k\ell}^\lambda_{k\ell\mu}|^2$$

or

$$f^{(3)}_{k\ell\mu\nu} = \frac{1}{n} \left| \frac{1}{V} \right|^2 F_{k\ell\mu\nu}^\lambda F_{\mu\nu\ell}^\lambda V(k\ell\mu)$$

or its complex conjugate. (Although (III-20) is always complex - $V(k\ell\mu)$ is pure imaginary - its conjugate exists for the imaged diagram e.g. 12(b,c)). We follow (III-5) and define for $\Gamma_1, \Gamma_3, \Gamma_5$ 'phonons' respectively,

$$f_{k\ell}^\lambda = \frac{1}{2} \lambda \left| (s_{k\ell}, g_{k\ell}, h_{k\ell}) \right|$$

and

$$(f^{(3)}_{k\ell\mu\nu} + c.c.) = \frac{1}{2} \lambda \left| (g_{k\ell\mu}, h^{(3)}_{k\ell\mu}) \right|$$

For $\Gamma_3 \times \varepsilon$ then, we simply replace $g_k$ whenever it occurs in $d(\mu)$ by $g_{k\ell}$ or $g^{(3)}_{k\ell\mu}$ and the contributions of 12(a-e) to $p, q$ will be the analogues of (III-6) provided we let $A_{k\ell} \rightarrow (A+A)_{k\ell\mu}$ and similarly for $B_{k\ell}$ ($B_{k\ell\mu} = B_{k\ell\mu}$) and $C_{k\ell}$. The expressions $X_k, X_{k\ell}, X^{(3)}_{k\ell}$ now include the multiplet shift $\Delta_0$ calculated from 12(i). If we further define...
\[ z = 1 - 4 g_p \frac{n(p)}{p^2} \]

these contributions to \( p \) are:

\[
- 2 \sum_{k \lambda m} g_{k \lambda} Z_m \cdot \frac{n(k)n(\xi)}{(k+\xi)^2} 
- 2 \sum_{k \lambda m} g_{k \lambda}(3) Z_p \cdot \frac{g_{k \lambda m}}{(k+\lambda-m)} \left\{ \frac{n(k)n(\xi)}{(k+\xi)^2} - \frac{n(m)}{m^2} \right\} - \frac{n(k)(n(\xi) + 1)}{(k+\xi)^2} \}
\]

And to \( 2 b_\gamma \):

\[
\frac{1}{2} \sum_{k \lambda m} g_{k \lambda} g_{m} g_{k \lambda m} \frac{n(k)n(\xi)n(m)}{(k+\lambda-m)^2} - \frac{2}{m^2} \frac{(k+\lambda)^2}{(k+\lambda + m)^2} 
+ \frac{1}{2} \sum_{k \lambda m} g_{k \lambda}(3) \frac{n(p)}{p^2} \frac{g_{k \lambda m}}{(k+\lambda-m)} \left\{ \frac{n(k)n(\xi)(k+\lambda-p)}{(k+\lambda)^2} - \frac{n(m)(n(k)+n(\xi)+1)(m-p)^2}{m^2(m+p)^2} \right\}
\]

To these terms we must now add the contributions of \( 12(f) \) and \( 12(g) \). As the calculations of both sets of diagrams are similar but each fairly lengthy, we shall only consider \( 12(f) \). The diagrams are labelled by \( i=1-8 \) and the denominators \( \frac{k}{i}, \frac{\lambda}{i}, \frac{m}{i} \) distinguish the vertex positions. All eight diagrams can be drawn as in \( 9(g,h) \) where the coefficients \( V_{\sigma}^i \) will depend on all labels e.g. following the labelling of \( 9(g) \), \( V_{\sigma}^1 \) is drawn in \( 12(j) \).

Clearly by twisting lines and applying JLV4, all \( V_{\sigma}^i (i \neq 1) \) can be related to \( V_{\sigma}^1 \) for some rearrangement of the irrep labels \( v_j \). Writing these as \( j \), for example, \( V_{\sigma}^5 (l*2*34 uv) \), Fig. 12(k), is related to \( V_{\sigma}^1 (41*32*wz) \) by,

\[
\left\{ \sigma \begin{array}{c} 3*4* \\ 1*2 \end{array} \right\} |\tau| \ (l*4\tau w) \ (34*\psi) \phi_1 
\]

This is particularly useful if all \( v_j \) are the same, for the coefficients of all diagrams are then simply related to one

\[
V_{\sigma}^i (k\lambda m) = \sum_{\tau} C_{\sigma \tau}^i (\psi) \cdot V_{\tau}^1 (k\lambda m) \quad \text{(III-24)}
\]

For such systems we give the C's (real irreps, multiplicity free)
FIGURE 12

d) $C_{k\ell m}$ $A_{k\ell m}$

e) $C^{(3)}_{k\ell m}$ $A^{(3)}_{k\ell m}$

f) (1) (2) (3) (4)

(5) (6) (7) (8)

g)
FIGURE 12 Contd.

h) k

j) k

k) m

l) m

m) n) \( t_{ij}^{k\ell} = \)

o) p) q)
\[ C_{\sigma \tau}^1 = C_{\sigma \tau}^2 = (\nu \nu \sigma) \quad C_{\sigma \tau}^7 = \delta_{\sigma \tau} \]
\[ C_{\sigma \tau}^3 = C_{\sigma \tau}^4 = (\nu \nu \sigma) \quad C_{\sigma \tau}^5 = (\nu \nu \sigma) (\nu \nu \tau) \quad C_{\sigma \tau}^6 = (\nu \nu \tau) \quad C_{\sigma \tau}^8 \]
\[ = |\tau| \left\{ \begin{array}{c}
\sigma \nu \nu \\
\tau \nu \nu
\end{array} \right\} (\nu \nu \tau) (\nu \nu \sigma) \quad (III-25) \]

Since the \( V^i_0 \) are complex in general, one must also count all the diagrams in \( 12(f) \) with \( k, m \) interchanged (and halve the sum). This produces the conjugate of \( 12(j) \) everywhere. Returning to the \( \Gamma_3 x \epsilon \) system, if we define,
\[ U^i_{\sigma} (k \lambda m) = \frac{1}{4} (V^i_{\sigma} (k \lambda m) + c.c.) \]
we can write the contributions of \( 12(g) \) to \( d(\mu) \) compactly as,
\[ d(\Gamma_1) = \sum_{ik\lambda m} (P^i + Q^i + R^i)_{k\lambda m} (U^i_{\sigma} - U^i_{\tau})_{k\lambda m} \]
\[ d(\Gamma_2) = \sum_{ik\lambda m} (-P^i + Q^i - R^i)_{k\lambda m} (U^i_{\sigma} - U^i_{\tau})_{k\lambda m} \quad (III-26) \]
\[ d(\Gamma_3) = \sum_{ik\lambda m} Q^i_{k\lambda m} (U^i_{\sigma} + U^i_{\tau})_{k\lambda m} \]

where, for \( i=5-9 \) the imaged diagram is to be included as well.

A calculation of the alteration to \( b_7 \) is sufficient for our purposes. So to (III-23) we must add,
\[ -2 \sum_{ik\lambda m} Q^i \omega_{k\lambda m} U^i (k \lambda m) \quad (III-27) \]

(III-24, -25) give,
\[ V^1_7 = V^2_7 = -V^7_7 \]
\[ -V^6_7 = V^8_7 = \frac{1}{2} (V^1_7 - V^1_7 - 2V^1_4) \quad (III-28) \]
\[ V^3_7 = V^4_7 = -V^5_7 = \frac{1}{2} (V^1_7 + V^1_7 - 2V^1_4) \]

Since \( 12(j) \) is equivalent to,
\[ V^1_\sigma = \sum_{abcd} F^4_{k4a} F^4_{k4b} F^4_{k4c} F^4_{k4d} \quad \left[ \begin{array}{ccc}
\sigma & 4 & 4 \\
4 & 4 & 0
\end{array} \right] \]
\[ \left( \begin{array}{ccc}
s & 4 & 0 \\
b & 4 & 0
\end{array} \right) \]
and if the 3jms in this equation are those for the tetragonal basis \((\theta, \varepsilon)\) of the doublet, then the three lines in (III-28) are respectively,

\[
\begin{align*}
\frac{1}{2} \sum_{ab} & \left( T_{ab} - T_{ab}^2 \right)_{k\ell m} \\
T_{ab} & = \frac{e}{k} a \frac{e}{k} a \frac{e}{k} m \frac{e}{k} m \\
T_{ab}^2 & = a b b a \\
T_{ab}^3 & = a b a b \\
T_{ab}^4 & = T_{ab}^4 \\
T_{ab}^5 & = T_{ab}^5
\end{align*}
\]

Finally, defining

\[
G_{ij}^{1/2} = \frac{1}{4} \sum_{ab} \left( T_{ab} - T_{ab}^2 \right)_{k\ell m} + c.c.
\]

we obtain for (III-27)

\[
\sum_{k\ell m} g_{k\ell m} n(k)n(\ell)n(m) \left\{ G_{12} \frac{(k-m)^2}{k\ell m (k+m)^2} + G_{31} \frac{(\ell-k-m)^2}{k\ell m (k+m)^2} - G_{23} \right\} \tag{III-29}
\]

This expression and the quadratic term in (III-23) give the contribution to \(2b_7\) correct to \(O(V_1^2 V_2^2)\). The anharmonic equivalent of (III-29) calculated from \(12(g)\) will be more complicated because of the energy factors, but otherwise the same - now factors like \(G_{ij}^{1/2}\) corresponding to linear combinations of coefficients like \(12(k)\) will replace the \(G_{ij}^{1/2}\).

We now compare these results for \(p, b_7\) with those for the linear interaction. Firstly, we note that apart from the terms of order \(g_{k\ell}^2\) and \(g_{k\ell}^2 g_{m}\), all others in (III-22,-23,-29) are indeterminate in sign. In particular, we don't necessarily have \(b_7 > 0\) for its first quadratic and anharmonic contributions. All we can be definite about is the effect of quadratic coupling on \(p\) - it reduces \(p\) (and \(q\)) by an amount,

\[
- \sum_{k\ell} g_{k\ell} \left( N_{k\ell}^+ + N_{k\ell}^- \right) \tag{III-30}
\]

analogous to the \(O(V_1^2)\) term in (III-8). (III-30) is the generalization of Gauthier and Walker's zero temperature calculation. For the anharmonic coupling the indeterminacy results both from the energy factors and the unknown sign of \(g_{k\ell m}^{(3)}\). However, at the next order of anharmonicty \((V_1 V_2^{(3)})^2\), Fig. 12(m), this is not the case. The diagram is symmetric and so gives a positive
definite contribution. We simply replace \( F_{k\ell \mu \nu}^\lambda \) in (III-19) by,

\[
F_{k\ell \mu \nu}^\lambda = \sum_m \frac{v(k\ell m)F_{m\mu \nu}^\lambda}{(k+\ell-m)}
\]

and for \( \Gamma_3 \times \varepsilon \) this produces the analogue of \( g_{k\ell} \), namely \( \bar{g}_{k\ell} \). Thus \( 12(m) \) reduces \( p \) as in (III-30). (At this stage we could extend the work of Stedman (1971) and Hernandez and Walker (1972) on the ordinary electron-phonon problem to our problem and define a two-phonon \( T \)-matrix, \( T_{ij}^{k\ell} \) as in \( 12(n) \). We would also need to define the square root of the external vertex as in \( 12(o) \). The idea is that when one calculates,

\[
\sum_{i,k\ell} |T_{ij}^{k\ell}|^2,
\]

all of \( 12(a,b,c,m) \) are reproduced exactly. The sum of the three amplitudes would then be equivalent to \( 12(p) \) where a new invariant, \( F_{k\ell \mu \nu}^\lambda \), is defined. Thus for \( \Gamma_3 \times \varepsilon \)

\[
F_{k\ell \mu \nu}^{4} = 2F_{k\ell \mu \nu}^{4} + F_{k\ell \mu \nu}^{4},
\]

and one would argue that \( 12(a,b,c,m) \), taken all together, reduce \( p \), whereas taken separately, one could not say. Unfortunately their method is incorrect. (III-31,-32) give twice the contribution of the diagrams in \( 12(a) \) (Stedman's method is correct in detail only because he neglects two-phonon absorption and emission terms. In contrast Hernandez and Walker's results are inconsistent with their definitions and the diagrams at \( O(v_2^2, v_2^3v_1^2) \)). Apart from this problem, one might still expect the idea to be useful for other diagrams. It is not. For example, if the amplitudes \( 12(q) \) are added to \( 12(n) \), (III-31) produces the combination \( (A_{k\ell} + B_{k\ell}) \) and the 3-vertex diagrams \( 9(c) \). The latter are zero and the former combination never occurs in \( p \) or \( q \).

The second point to be made in comparison with the linear results, is that the usual assumption for weak coupling, that the effect of linear coupling is greater than either quadratic or anharmonic coupling, at the equivalent order, may not be valid. (We follow Stedman (1971) and define order as \( 2(N-N_{a}) \) where \( N \) is the number of phonons in a diagram and \( N_{a} \) the number of anharmonic vertices - thus \( 12(a,b,c,m) \) and the \( v_1^4 \) diagrams in Fig. 7 are all of order four). Despite the lack of any information about the relative strengths of \( g_k, g_{k\ell}, g_{k\ell m}^{(3)} \), the contributions to \( p \) from \( 12(a,b,c) \) should be as
important as those at $O(V_1^4)$. We claim this by comparing, for example, 
$O(V_1^4)$ with the $V_1^4$ term in (III-8). The sum over $k, \lambda$ in the former is 
able to contribute to $p$ over a much greater range because of the difference 
of phonon energies in the denominator. So although only linear coupling 
has an effect at second order, it may not dominate at fourth order. For 
higher orders however, we cannot distinguish between the various contributions 
to $p$ and $b_7$ by this argument.

A third and related point is that whereas the presence of a non-zero 
$b_7$ in an experiment is evidence for a distribution of phonon energies, if the 
linear interaction only is presumed, this will not necessarily be the case if 
other interactions are important: (III-23,-29) are non-zero for isoenergetic 
phonons.

Finally we note that, in principle, it is possible to determine the 
significance of a particular type of interaction at any order by observing 
the temperature dependences of $p$ and $q$. The calculations of these proceed 
as in Section (III.2.1) but now, in the long wavelength limit (for the low 
temperature calculation), we have (Stedman (1971)),

$$F_{k \lambda m \ldots, \nu n} \propto \left(\frac{\varepsilon_k \varepsilon_\lambda \varepsilon_m \ldots}{\varepsilon_k \varepsilon_\lambda \varepsilon_m \ldots}\right)^b$$

$V(k \lambda m \ldots) \propto \left(\frac{\varepsilon_k \varepsilon_\lambda \varepsilon_m \ldots}{\varepsilon_k \varepsilon_\lambda \varepsilon_m \ldots}\right)^b \delta(k+\lambda+\mu+\ldots)$

In the table below we list the results to sixth order in combinations of $V_1$, 
$V_2$ and $V^{(3)}$ for both high and low temperature limits. The columns marked 
with an asterisk contribute to $b_7$.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Dependence of $p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order</td>
<td>2</td>
</tr>
<tr>
<td>$V_1^2$</td>
<td>$T^2$</td>
</tr>
<tr>
<td>$V_2^2$</td>
<td>$T^6$</td>
</tr>
<tr>
<td>$V_1^{(3)}$</td>
<td>$T^4$</td>
</tr>
<tr>
<td>$V_2^{(3)}$</td>
<td>$T^6$</td>
</tr>
<tr>
<td>$V_3^{(3)}$</td>
<td>$T^2$</td>
</tr>
</tbody>
</table>

High temperature

<table>
<thead>
<tr>
<th>Order</th>
<th>Dependence of $p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^2$</td>
<td>$T^2$</td>
</tr>
</tbody>
</table>

* * *
It can be seen that in the low temperature limit the linear interaction is the least temperature dependent at each order, by a factor of $T^2$ at least. The presence of a $T^n (n \geq 8)$ behaviour in $b_\lambda$ would thus be strong evidence for the importance of the quadratic and anharmonic couplings. To produce this behaviour using linear coupling alone would require a significant contribution from $V_1^8$ at least.

4.2 $\Gamma_3 \times (a_1 + \varepsilon)$

Implicit in the results of the above section is the complete ignorance of any ion-phonon coupling that takes place via the $\Gamma_1$ 'phonons'. The system Hamiltonian used above,

$$H = H_0 + V_1 + V_2 + V^{(3)} + H_s$$

contains terms transforming a $\Gamma_1$ from both of the coefficients $V_{ijk}$ and $V_{ijkl}$. (We call these $V^{(o)}_{ijk}$ and $V^{(o)}_{ijkl}$ respectively). For the linear $\Gamma_3 \times \varepsilon$ system we were able to neglect the first of these because it could be completely absorbed into a new zero-order Hamiltonian by a canonical transformation of $(H_0 + V_1)$. For $V_2$ or $V^{(3)}$ non-zero, this is not possible: under this transformation, $V^{(o)}_{ijk}$ remains in the interaction terms. And apart from this, no transformation exists to remove $V^{(o)}_{ijkl}$ from $V_2$. Thus (any) coupling via the $\Gamma_1$ 'phonons' cannot be removed once non-linear and anharmonic interactions are considered. In the past these 'phonons' have been neglected on the grounds that they are not 'JT active' (no splitting of the electronic energy levels on the vibronic model). Certainly, in the absence of any other 'phonon' symmetries they can have no effect on the RFs. Otherwise their presence is non-trivial as we now show for $\Gamma_3 \times (a_1 + \varepsilon)$.

In keeping with the approach to the linear system, we choose to use the canonical transform of (III-33), at the expense of slight complications. In Appendix VII we show that (III-33) becomes,

$$H'_{0} + (V'_{1} + V'_{2} + V^{(3)}_{3}) + H_s$$

where $V'_n$ is an effective interaction containing $n$ displacement operators, $\phi_k$. The respective coefficients $V'_{ijk}$, $V'_{ijkl}$, of (AVII-5,-6) can now be represented by new vertices, Figs. 13(a,b), and their construction from the original interactions made obvious. Here, with the exception of the first vertex in 13(a), which has no $\Gamma_1$ component, the linear vertices represent $V^{(o)}_{ijk}$. The internal electronic lines are summed trivially and make no contribution to the denomin-
ators of \(\Delta_1(\theta_1)\) (indicated by the absence of an arrow). The calculation of RFs using (III-34) now proceeds as usual. We simply attach 'blobs' to all electron-phonon vertices in all previous diagrams, and modify our calculations equivalently by replacing \(F_{kl}\ldots vn\) by \(\nu F_{kl}\ldots vn\) everywhere. Thus for \(\Gamma_3 \times (\alpha_1 + \epsilon)\) with \(\nu = \Gamma_3\), we can let \(g_k \rightarrow g'_k\), \(g_{kl} \rightarrow g'_{kl}\), etc., in all our previous formulae and, to lowest order in the expansions 13(a,b), those formulae will be reproduced. Any additional terms are entirely due to the presence of the component \(V^{(0)}\). For example, the \(O(V_1^2)\) term in (III-8) now reduces \(p\) with terms at \(O(V_1^1, V_1^2, V_2^1, V_2^2)\) by the expansion 13(c) (the anharmonic terms in 13(a,b) are diagonal only and transform as \(\nu = \Gamma_1\)). Our conclusions thus far can only change in the matter of the interpretation of the coupling parameters. However the contributions of diagrams for \(\nu = \Gamma_1\) must also be considered. Take the coupling \(V^{(1)}_{\Gamma_1}\), first, in particular the (modified) diagrams of Fig. 7. Setting \(j = \Gamma_1\) in 7(c) merely replaces the two 3jms of the electron-'phonon' vertices by 2jms, with a factor of \(|\lambda|^{-2}\) for each stub so produced. The external vertex is left isolated and multiplied by a factor independent of \(\mu\). In effect, we have detached the interaction vertices from the electronic lines in 7(a) and, for the purposes of group-theoretic calculations, this is the simplest way of observing the effect of coupling to \(\Gamma_1\) 'phonons' in any problem. (With this approach, the Rules I-III for \(\Gamma_3 \times \epsilon\) will still apply here). Thus the \(V^{(4)}_{\Gamma_1}\) diagrams of 7(f) all 'look' like 13(d) or 13(e) when the coupling is to \(\Gamma_1\) 'phonons' \((\xi)\) and \(\Gamma_3\) 'phonons' \((\kappa)\); 13(d) contributes to \(\delta(\mu)\) like 7(c) with \(\nu = \Gamma_3\) and 13(e) is independent of \(\mu\) and will not appear in the RFs at lowest order. Altogether, the \(\mu\)-dependent terms from 7(f) are (with \(d(\Gamma_3) = 0\) and \(d'^{(4)}_{\Gamma_0} = 2 S^4_{\Gamma_0}\))

\[
d(\mu) = (44\mu) \sum_{kkl} g'_k \, S'^{\prime}_{kkl} \left( 2C_{kkl} + 2D_{kkl} + A_{kkl} + B_{kkl} \right) + S'^{\prime}_{kkl} (A_{kkl} + B_{kkl}) + \sum_{k} g'_k \, X_{k}
\]

(The last term contains \(S'^{\prime}_{k}\) in \(\Delta_0\)). So \(p\) changes by an amount,

\[
- \sum_{kkl} \left( g'_k \, S'^{\prime}_{kkl} + S'_k \, g'_k \right) \frac{N_k N_k}{(\epsilon_k \epsilon_k)^2}
\]

which, apart from sign, is of the same form as the \(O(g'_k g'_k)\) term from (III-8). However the latter term should dominate, as \(g'_k\) contains second, fourth and sixth order terms in \(V_1, V_2\), whereas \(S'_k\) is sixth order only in \(V_1, V_2, V_3\). At \(O(V_6^1)\), the diagrams of 8(a-c) effectively reduce to those of 7(f) or 13(b) depending upon the products \(g'_k \, S'_k \, S'_k, g'_k \, g'_k \, S'_k\) considered. In particular, the first contribution to \(b_7\) comes from the latter product and then only for those diagrams which 'look' like \(A_{kkl}\) or \(B_{kkl}\) after the 'removal' of one lattice phonon.
FIGURE 13

a) \[ V_{ijk} \leftrightarrow \frac{1}{i j} \]

\[ = \frac{1}{i j} + \frac{1}{i j} + \frac{1}{i j} \]

b) \[ V_{ijkl} \leftrightarrow \frac{1}{i j k} \]

\[ = \frac{1}{i j k} + \frac{1}{i j k} \]

c) \[ \]

\[ = \frac{1}{i j k} + \frac{1}{i j k} + \frac{1}{i j k} + \frac{1}{i j k} \]

d) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

e) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

f) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

g) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

h) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

(i) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

j) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

k) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

l) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

m) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]

n) \[ k \]

\[ = \frac{1}{k} + \frac{1}{k} \]
Thus, following the form of $b_7$, at $O(g^3)$, $13(c)$ contributes,

$$\frac{1}{2} \sum_{k\text{lm}} (g_k^i g_k^j S_m^i + g_k^i g_k^j S_m^i - S_k^i g_k^j g_m^j) \cdot F_{k\text{lm}}$$

We can quickly express $b_7$ in this manner (there are also product terms following from the denominator of (III-15)) and we find that it is non-zero in the single mode limit, in contrast to the $O(g^3)$ term.

When $V_2^i, V^{(3)}$ are explicitly included in the diagrams, the same arguments apply. Figs. 12(a-c) do not contribute to $p$ at order $S_k^i$, $S^{(3)}$, but they and 12(d-g) do at $O(V_1^2 V_2^3, V^{(3)} V_2^i V^{(3)})$. For example, 12(a,d) reduce $p$ by,

$$\sum_{k\text{lm}} (S_k^i g_m^i + g_k^i S_m^i) \frac{1}{2} N_m (N_{k\text{lm}}^+ + N_{k\text{lm}}^-),$$

though, as in the previous section, the remaining contributions, 12(f), are of unknown sign (the structure 9(g) can only have pairs of irreps $v_1 - v_4$ set to $\Gamma_1$). Note that (III-36) is as important as the $g_{k\text{lm}} g_m$ terms of (III-22): at sixth order $S_k^i g_m^i + S_{k\text{lm}} g_m$ survives, and there is no reason to assume $S_{k\text{lm}}$ is not comparable to $g_{k\text{lm}}$. However we need not go to sixth order in $V_1, V_2$ to obtain terms in $p$. Unlike $\Gamma_3 \times \epsilon$, the non-linear structures of Fig. 10 with an odd number of 3-'phonon' vertices will not be zero, provided each such vertex has one of its 'phonons' labelled $\Gamma_1$, reducing the structure to a linear one. Thus the diagrams 13(g-i) must be considered, as well as the unusual diagram of 13(j). We show how their terms may be calculated, as odd-vertexed diagrams figure prominently in other JT systems. We first define factors which are again products of transformation factors. Thus corresponding to 13(g), redrawn as 13(k), there is a factor 13(l) (c.f. App. V) or,

$$\lambda^\star \left\{ k \ell m \atop v_1 v_2 v_3 \right\} = \left\{ v_3^\star v_2^\star v_1 \atop n_3^\star n_2^\star n_1 \right\} s^\star \left\{ k \ell \atop v_1 v_2 v_3 \right\} = \frac{1}{2} \sum_{k\text{lm}} \lambda^\star \left\{ k \ell m \atop v_1 v_2 v_3 \right\} \cdot F_{k\text{lm}}$$

which multiplies the $j$ symbols of the structure. The analogous factor for 13(i) is 13(m) or,

$$\lambda \left\{ k \ell m \atop v_1 v_2 v_3 \right\}$$

and those for 13(h) are equivalent, to within a $3j$ phase, to this or its complex conjugate. The images of 13(g-j) produce their conjugate factors and provided the phonon labels are imaged also,
For $\Gamma_3 \times (a_1 + \epsilon)$ we define

$$G_{a \beta \gamma}^{k k_l} = \frac{1}{2} \left( f_0^4 \left\{ k l m \right\} \left[ \gamma a \beta \right] + f_0^4 \left\{ k l m \right\} \left[ \gamma a \beta \right] \right) + c.c.,$$

an analogous equation for $G_{a \beta \gamma}^{k k_l}$ in terms of $f_0^4 \left\{ k l m \right\} \left[ \gamma a \beta \right]$ and for $13(j)$ a factor,

$$S_{k l} = \sqrt{2} \left( F_{k l}^4 + c.c. \right).$$

Then the contribution to $p$ at $O(V_2^2 V_1^2, V_1^{(3)} V_1^{(3)})$ is,

$$- \sum_k g_{k l}^2 \frac{n(k) n(k)}{k^2 l^2} \left\{ k(2k + l) G_{440}^{k l} + l(2l + k) G_{044}^{k l} + k l G_{404}^{k l} \right\}$$

where (see Appendix VI),

$$U_{k l m} = \frac{g_{k l}^2}{(m + k - k)} \left\{ \frac{n(m) n(k)}{m(m + k)} + \frac{n(k) n(-k)}{(k - k) k^2} - \frac{n(m) n(k)}{m k^2} \right\}$$

A contribution to $b_7$ will first appear in diagrams like $13(n)$ and it will also be non-zero for iso-energetic phonons. The lowest order terms in (III-38) are of interest. Only $13(i, j)$ and the second of $13(h)$ contribute when the bare vertices are substituted from $13(a, b)$. Thus $S_{k l}$ and $f_0^4 \left\{ k l m \right\}$ survive in (III-38) at $O(V_2^2 V_1^2)$, and we attach the same importance to their contribution to $p$ as we do to the fourth order terms in (III-22).

Clearly, unless non-linear and anharmonic interactions can be shown to be negligible altogether, it is unreasonable to omit the $\Gamma_1$ 'phonons' in a calculation of $p, q$, while including the effects of the $\Gamma_3$ 'phonons': the magnitudes of the $\Gamma_1^-$, $\Gamma_3^-$ symmetry adapted parts of $V_{ijk}$ and unlikely to be very dissimilar. And the same applies to $V_{ijkl}^{(3)}$. In principle the presence of both components can be detected, if the quadratic coupling is not too weak. The $O(V_2^2 V_1^2)$ terms from (III-38) and $O(V_1^2)$ have a $T$ behaviour in the low temperature limit, which is never produced for $\Gamma_3$-type coupling alone. Finally, we observe that as the effects of including the $\Gamma_1$ 'phonon' are largely independent of the multiplet $\lambda$, similar results will exist for other JT systems.
5.0 SUMMARY AND DISCUSSION

We have shown how to calculate RFs quite generally for the electronic doublet. Each Feynman diagram in the series Fig. 4(h) can be exploded to reveal the symmetry information in the vertices. By a combination of the Feynman rules and the manipulation of the group-theoretic parts, every diagram corresponds to a term in $d(\mu)$ of the form,

$$\sum \left[ \text{phonon transformation factors} \right] \cdot \left[ 3j, 6j/9j \right] \cdot \left[ \text{population and energy factors} \right]$$

In practice our analysis has been centred not on these diagrams but instead on their group-theoretic structures which give rise to the $j$ symbols. Indeed, we can take the view that the Feynman diagrams are immaterial now that we have a means of drawing all structures (Section (III.3)), as it is these that determine a contribution to $d(\mu)$. The effort of calculating the multitude of Feynman diagrams with the same structure is thereby reduced. We only need to change our definitions slightly corresponding to the first bracket above, and obtain the third bracket from the original diagrams. This is exemplified by the calculations of Figs. 7(f) and 12(a-e). Furthermore, we can expect the results obtained for the electronic doublet to appear in similar form for other JT systems: the values of the $6j$, $9j$ symbols are the only distinguishing features.

On comparison with the approach of Gauthier and Walker for the $\Gamma_3$ system, one might naturally enquire whether our method has any advantage over theirs, considering the dimensionality of the system and the initial effort that is required to learn the diagram technique for groups. Their approach consists of representing the electronic operators in (II-31) by two-dimensional matrices (effectively the $3jms$ of (II-36) in the $(\theta, \epsilon)$ basis), summed with basis dependent coefficients, multiplying these out explicitly, and then summing over components - which corresponds to our formation of the $j$ symbols. Quite apart from the fact that our notation is completely general and so applies for any other system, we would answer this question in the negative if results to $O(V_1^4)$ only were required, but in the affirmative otherwise. As evidence for the latter stand we refer to Sections (III.2.2) and (III.3.2). Most of the structures drawn there are easily reduced to simpler ones, many are trivially zero, and of the remainder their reduction is not too difficult because the non-zero $6j$ and $9js$ are few in number. In fact, we claim that the patterns of non-zero structures which have emerged and produced the Rules I-III, greatly simplifying the calculation at any order, are not obvious by matrix multiplication.
We now discuss our calculations of $p,q$. We group them as:

(A) $\Gamma_3 \times \epsilon$ - linear coupling only,
(B) $\Gamma_3 \times \epsilon$ - linear and non-linear anharmonic coupling,
(C) $\Gamma_3 \times (a_1 + \epsilon)$

Apart from the zero temperature results to $O(V_1^2,V_2^2)$ obtained by Gauthier and Walker, all our results are new. Not only do they include the significant interactions besides linear, and coupling via the $\Gamma_1$ 'phonons', but they are valid for all temperatures. The major effect of the latter is to be found in expressions which involve the difference of phonon energies in their denominators. These will resonate over the entire phonon spectrum for all but very low temperatures. In fact every equation bar (III-8, -35) falls into this category. For $p$, the effect at fourth order should be to make the contributions from $B, C$ comparable in magnitude to those from $A$. Certainly we know that the $O(V_2^2(V_1^{3})^2)$ terms from $B$ reduce $p$ below its value for linear coupling only. At higher orders any distinction between $A, B, C$, as far as resonating denominators goes, disappears. Overall, if the coupling of the doublet to the lattice is not so weak as to make all terms of order greater than $V_1^2$ insignificant, then $p$ should be calculated from $A + B + C$. In comparison, $b_7$ at fourth order in $A$ is not altered by the inclusion of $B, C$. These do not enter until sixth order where again $A, B, C$ are indistinguishable, both in the presence of resonating terms, and in the signs of their total contributions, which are undetermined.

Although at zero temperature we must have $b_7 > 0$, there is no proof that this is so at finite temperatures other than the fact that the leading term, (III-11), is always positive (as indeed are all terms from graphs which produce, by JLV2, the structures of $A_{k}, B_k$, and symmetric phonon transformation diagrams).

We now consider the conditions under which the single mode sum rule, $2q-p=1$, is disobeyed. In the zero-temperature calculations of Gauthier and Walker and Halperin and Englman, only the first term in (III-10) survives. As a result of their work, the standard interpretation (e.g. Abou-Chantous et al. (1974)) has been that a non-zero $b_7$ is evidence for coupling to a distribution of lattice states, $\epsilon_k \neq \epsilon_\ell$ for $k^* \neq \ell^*$. We have shown that for finite temperatures this is still correct to $O(V_1^0)$, and we assume it to be so to infinite order in $A$, and therefore for all strengths of linear coupling. However this interpretation requires support, as two objections to it can be raised. Firstly, terms in $b_7$ from $B, C$ are non-zero in the limit of isoenergetic phonons, and this is true to all orders for the multitude of
interactions in these systems. One way to resolve this conflict is to measure the temperature dependence of $b_7$ and determine the existence of terms from $B$, $C$ (though other experimental information may make this unnecessary. For example, Abou-Ghantous et al. are able to argue that anharmonicity is unimportant for the system they are considering). The second, and more important objection, exists when the temperature at which $b_7$ is measured is not small enough to make its resonant terms negligible. Consider (III-10). Even a doublet effectively coupled to phonons with only a very small range of energies, is able to make a sizeable contribution to $b_7$ through the denominator of the second term, while the first term is close to zero. And this argument applies to every term in $A + B + C$ to all orders. This example also serves to show that zero-temperature predictions of multi-mode effects will differ from the observed behaviour obtained when the system temperature is not very low. Muramatsu (1977) has followed the approach of Halperin and Englman, but has used numerical methods to examine the effects on the vibronic ground state values of $p, q$ of introducing linear coupling to phonons of two frequencies and variable coupling strengths. He finds that as long as the frequency ratio is smaller than about three, $b_7$ is very small and a single effective mode description is possible. Our results on the other hand, suggest that at finite temperatures a ratio close to unity becomes critical. And for a real crystal lattice, this will certainly occur for that part of the phonon spectrum with energies $\leq KT$.

Finally, our results show that a relation between the electronic RFs $p, q$, and $b_7$, determined by any class of Feynman graphs, is preserved independently of temperature. In particular, at zero temperature these three quantities reduce to their vibronic equivalents of Section (I.3.1), on a perturbative model. Obviously this feature will exist for any isolated electronic multiplet, by the factorization (III-39). So the form of the expansion of the vibronic RFs in the parameters $\lambda_\nu^A$ in Sections (I.3.1 - I.3.3), remains valid even at finite temperatures, provided each quantity is understood to be a many-body expression. This parameterization of many-body RFs will be convenient in describing later results.
The first three sections of this chapter present the results of our calculations of the RFs for isolated triplet \( \Gamma_5/\Gamma_4 \) and quartet \( \Gamma_8 \) electronic states. With the exception of the \( \Gamma_5 \times \epsilon \) system, these are obtained by following the methods of the previous chapter. For each multiplet we concentrate upon the linear coupling via \( \Gamma_3 \) and \( \Gamma_5 \) 'phonons', first separately, and then together, and find the many-body equivalents of the parameters in Sections (I.3.2) and (I.3.3). For the other interactions we do not give detailed results. Instead, we infer their effects directly using the approach of Section (III.3) and the results of (III.4) for the doublet. After comparing the \( \Gamma_5, \Gamma_8 \) JT systems, we look at the lattice model calculations of the Nottingham group (Bates (1978)) for the \( \Gamma_5 \) systems, and then finish off our discussion by considering isolated multiplets for any symmetry. In the last section we deal briefly with the extensions of our work to include intermultiplet coupling and higher order RFs.

1. TRIPLET STATES \(-\Gamma_5 \times \epsilon\)

The calculations for this system can be made particularly simple if we choose real tetragonal components for the basis \(\{ |i> = |x\lambda_i\lambda_i\rangle \}\). Then the electronic operators at all orders, \( f_k f_{kk'} \ldots \) only have diagonal elements \( V_{iik}, V_{iikk'}, \ldots \). This can be seen for the linear interaction for example, by comparing Figs. 5(h,i) directly to give,

\[
V_{ijk} = \sum_{r\nu n} P_{ijk}^{r\nu n} \langle \lambda_i \lambda_j \rangle (\lambda_i \nu \lambda_j)^{ln} (\lambda_i \nu \lambda_j^{*})^{r} \quad (IV-1)
\]

For \( \lambda_i, \lambda_j = \Gamma_5/\Gamma_4, \nu = \Gamma_3 \), the 3jms have the form \( \delta_{i j}^{l} \) for the basis chosen (Griffith (1962)).
1.1 Linear Interaction

With the above basis choice, it is possible to obtain the RFs exactly when there is linear coupling only. As our method is independent of symmetry considerations (i.e. number or type of multiplets coupled by (different) 'phonons') to the extent that the $3j$ms in (IV-1) are diagonal, we revert to the $V_{ijk}$ notation for this subsection. The Hamiltonian for the system is now,

$$H(a,b) = \sum_i E_i a_i^\dagger a_i + \sum_k \varepsilon_k (b_k^\dagger b_k + \frac{1}{2}) + \sum_{i,k} V_{iik} a_i^\dagger a_k \phi_k$$  \hspace{1cm} (II-2)

and we need not make any assumptions about the relative strengths of zero-order and interaction terms. It is well known that a canonical transportation of $H$ to $\tilde{H} = S H S^{-1}$, will remove the interaction term if the operator $S$ is chosen correctly (Duke and Soules (1969)). We take,

$$S = e^X, \quad X = \sum_k u_k \pi_k$$  \hspace{1cm} (IV-3)

with

$$u_k = \sum_i \frac{V_{iik}}{\varepsilon_k} a_i^\dagger a_i, \quad \pi_k = (b_k^\dagger b_k).$$

Here $\pi_k$ is the canonically conjugate operator to $\phi_k$. Since $u_k = (u_{-k})^\dagger$, and $\pi_k = (-\pi_{-k})^\dagger$, $S$ is unitary. We now transform each operator in (II-2) to $\tilde{O} = S O S^{-1}$ using the formula,

$$e^X O e^{-X} = X + [X, O] + \frac{1}{2!} [X, [X, O]] + ...$$

If for the $a$'s, $b$'s we denote $\tilde{O}$ by $A$'s, $B$'s then,

$$b_k \rightarrow B_k = b_k - u_k$$  \hspace{1cm} (IV-4)
$$a_i \rightarrow A_i = a_i e^{-z_i}$$

with

$$z_i = \sum_k \frac{V_{iik}}{\varepsilon_k} \pi_k.$$
Performing the transformation of (IV-2), \( \tilde{H}(A,B) \) has the same form as \( H(a,b) \). Upon substitution of (IV-4) however, the last two terms reduce to:

\[
\sum_k \epsilon_k \left( b^+_k b_k + u^+_k u_k \right)
\]

and so,

\[
\tilde{H}(a,b) \equiv \tilde{H} = \sum_k \left( E_k - \sum_i \left| V_{ik} \right|^2 / \epsilon_k \right) a^+_i a_i + \sum_k \epsilon_k \left( b^+_k b_k + z \right)
\]

(IV-5)

is diagonal as required. For a single multiplet this change in the electronic energy is the usual Jahn-Teller stabilization energy, \( E_{JT} \).

Any perturbation \( V \) on (IV-2) is transformed likewise to \( \tilde{V} \), a perturbation on \( \tilde{H}_0 \), and its effects on the ionic levels are now found by the methods of Section (II.1.1). One merely puts tildes on all operators wherever they appear, in particular (II-15) and II-18), the latter becoming:

\[
(E - \tilde{H}_0 - \tilde{\Delta}(E)) \cdot S \cdot i = 0
\]

(IV-6)

(the eigenvalues are unaltered of course). The external perturbation \( H_s \) is treated in this way. In the form (II-21), it transforms to

\[
\tilde{H}_s = \sum_{ij} h_{ij} a^+_i a_j e^{\tilde{z}_{ij}}, \tilde{z}_{ij} = z_i z_j
\]

(IV-7)

and to first order \( \tilde{\Delta}(E) \) becomes an effective electronic operator,

\[
\tilde{H}_{\text{eff}} = \sum_{ij} h_{ij} a^+_i a_j \langle \epsilon^{\tilde{z}_{ij}} \rangle
\]

(IV-8)

Obviously the thermally averaged quantity is the RF we are seeking. To evaluate it, we expand the exponential and average term by term:

\[
\langle \epsilon^{\tilde{z}_{ij}} \rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \langle \tilde{z}_{ij}^n \rangle
\]

(IV-9)

The \( \pi^k \) operators in (IV-9) must be paired, so the terms with \( n \) odd are zero.

For \( n=2 \) we have,

\[
\langle \tilde{z}_{ij}^2 \rangle = \sum_{k\ell} j^*_{k\ell} j^*_{\ell k} \langle \pi^k \pi^\ell \rangle \mathcal{O}, V^i_{j\ell} = V_{iik} - V_{j\ell k},
\]

and since

\[
\langle \pi^k \pi^\ell \rangle \mathcal{O} = -N_{k\ell} \delta_{k\ell},
\]

\[
\langle \tilde{z}_{ij}^2 \rangle = -\sum_k \frac{|V^i_{jk}|^2}{\epsilon_k^2} \cdot N_k = \langle -\tilde{x}_{ij} \rangle
\]

(IV-10)
More generally \( \langle \mathbf{x}_{ij}^{2n} \rangle \) will contain the term,

\[
\langle \prod_{k_1} \prod_{k_2} \ldots \prod_{k_{2n}} \rangle_0
\]

where each pairing of the \( \pi \)'s will produce the factor \((-x_{ij})\). So we need all possible pairings. This is just the number of distinct diagrams that occur in the full Green function \( G(z) \) at \( O(V_0^{2n}) \) or equivalently, the number of distinct ways of pairing \( 2n \) points on a line, \( (2n)!/2^n n! \). Combining these results we find,

\[
\langle e_i | e_j \rangle_0 = e^{-\Delta x_{ij}}
\]

Since \( x_{ij} \not\equiv 0 \), \( H_{\text{eff}} \) is generally smaller than, or at most equal in magnitude to \( H_s \), and this result is true for any system provided the linear ion-phonon coupling is diagonal.

To calculate the RFs for \( \Gamma_5 \mathbf{x}_s \), we compare (IV-8) to its symmetrical form (I-10) by expanding \( x_{ij} \) using (IV-1), and simultaneously expanding \( O_m^\mu \) in the one-particle basis (cf. (II-36)). Comparing their respective \( 3j \)m symbols, we find that only \( \mu = \Gamma_4, \Gamma_5 \) contribute for \( i \neq j \). Also \( |v_{jk}^i|^2 = f_{k4}^5 \), for all \( i,j \), by the result of (II-39). With \( f_{k4}^5 = 3g_{\kappa} \) (there can be no ambiguity with \( \Gamma_3 \mathbf{x}_e \)) we obtain,

\[
K(\Gamma_1) = K(\Gamma_3) = 1 \quad \text{(IV-11)}
\]

\[
K(\Gamma_4) = K(\Gamma_5) = \exp \left\{ -\frac{3}{2} \sum_k g_k N_k \frac{\varepsilon_k}{\varepsilon_k^2} \right\} \quad \text{(IV-12)}
\]

Since the energy shift in (IV-5) is,

\[
\Delta E_{JT} = \sum_k g_k / \varepsilon_k
\]

(IV-11,-12) are the generalizations to all temperatures and phonon energies of Ham's (1965) single mode results of 1 and \( \exp(-3E_{JT}/2k B \varepsilon) \) respectively. Although Ham did discuss the case for a continuous phonon spectrum, he only gave the result for zero temperature. Biernacki (1977) reproduced his result. Considering the amount of experimental work that has been done on supposed \( \Gamma_5 \mathbf{x}_s \) systems following Ham's original paper, we find it surprising that little attention has been paid to a finite temperature calculation. (The exception to this is the work of the Nottingham group – see Section (IV.4.2)). We can attribute this to the use, by the above authors (and others), of vibronic wavefunction constructions. In fact the temperature dependence of the RFs (IV-12) is very marked. By the argument of Section (III.2.1), they
behave as $e^{-T^2} / e^{-T}$ in the low/high temperature limits. Hence the reduction of operators transforming as $\Gamma_4$, $\Gamma_5$ is complete in the limit of high temperature, whereas those of $\Gamma_3$ symmetry are unaffected.

We emphasize that the above results are independent of the magnitudes of both the coupling parameter $V_{iik}$ and the external interaction, provided only that $|H_0| >> |H_S|$. 

1.2 Inclusion of Non-linear, Anharmonic Couplings

For interactions which involve more than one phonon operator $\phi_k$ it is not possible, by redefinitions of (II-3) or otherwise, to remove these interaction terms and make the Hamiltonian diagonal. Nor can we simultaneously diagonalize the linear and any other interaction. So we must return to the weak coupling model for any results. However the calculations are straightforward, as all electronic operators have diagonal matrix elements. We now indicate how these are best performed, but postpone comments on their effects to Section (IV.2.2).

In Fig. 14(a) is drawn some structure corresponding to any (number of) complicated Feynman diagrams in our perturbation series (again we neglect the $2j\pi$ stubs; they and $\phi_5$ are unity). Since each electron-'phonon' vertex is diagonal, it can be transposed with adjacent vertices (but not the external vertex), and 14(a) rearranged to 14(b). The only restriction is that those 'phonons' above the external vertex must remain there - all other vertices can be moved, in particular any complete sets of electron - 'phonon' and 'phonon-phonon' vertices can be factored right out, as shown. Thus, apart from such factors, every structure with $n$ lines over the extended vertex can be put into the form of 14(c), where the shaded vertices summarize the remaining features of the structure - 14(d). JLV3 can now be applied successively to the internal parts of 14(c), as indicated by the broken line. But this is equivalent to stringing together $n$ structures like 14(e). Hence to write down the contribution to $d(\mu)$ of any Feynman diagram at any order of interaction it is sufficient to know the values of all the structures in 14(f), summed with their respective coefficients. (In addition there will generally be a constant factor 14(g) corresponding to those structures separated out completely as in 14(b)). Although there is no simple pattern to the values of the $j$-symbols produced by 14(f), there are only a few distinct $6j$s involved in performing the summations over the irrep labels $p,\sigma...$

In principle then, the alterations to the linear results for the RFs of
\[ \Gamma_5 \times \epsilon \text{ are easily calculated to any order in } V_2, V_3^{(3)} \text{ etc.} \]

We can also demonstrate the RF equalities of (IV-11,-12) using these structures. Fig. 14(h) shows the essential features of any diagram in 14(f). Upon coupling the external legs of this diagram, its contribution to \( d(\mu) \) contains, apart from energy factors, the quantity,

\[
\sum_{\alpha} V_{\alpha} \ldots \omega \begin{bmatrix} \alpha 44 & \alpha 55 & \ldots \omega 55 \\ 555 & 555 & \ldots 555 \\ \alpha 55 & \omega 55 & \ldots 555 \end{bmatrix} (55\mu)
\]

(there are no multiplicities and all 3j phases multiply to unity). Since \( \alpha, \omega = (0,4) \) then \( \beta, \ldots, \rho, \sigma, \ldots = (0,4) \) also (though \( \alpha = \beta = 0 \) etc. gives zero). Consider,

\[
a_{\mu \sigma} = \begin{bmatrix} \mu 55 \\ \sigma 55 \end{bmatrix} (55\mu)
\]

Then,

\[
a_{\mu 0} = 1/3, \text{ all } \mu; \quad a_{\mu 4} = \begin{cases} 1/3 & \mu = \Gamma_1, \Gamma_3 \\ -1/6 & \mu = \Gamma_4, \Gamma_5 \end{cases}
\]

As

\[
d(\mu) - d(\Gamma_1) \geq \sum_{\sigma} (a_{\mu \sigma} - a_{0 \sigma})
\]

is non-zero only for \( \sigma = \Gamma_3, \mu = \Gamma_4, \Gamma_5 \), when the contributions are equal, we have, via (III-5a),

\[
K(\Gamma_3) = 1, \quad K(\Gamma_4) = K(\Gamma_5)
\]

The same result follows for \( \Gamma_4 \times \epsilon \). (IV-13) is a finite temperature result valid for all types of interaction to infinite order in perturbation and by assumption, for all their magnitudes. Leung and Kleiner first obtained the equalities (IV-13) for each vibronic RF, (I-17), for all vibronic states \( z = z', \kappa = \kappa' = \Gamma_4, \Gamma_5 \) derived from the electronic state \( \lambda = \lambda' = (\Gamma_4, \Gamma_5) \). Since, in reality, the vibronic states are thermally populated, their result is entirely equivalent to ours.

The inclusion of the \( \Gamma_1 \) 'phonons' in the calculations does not alter the result (IV-13). Each such 'phonon' merely reduces a structure like 14(n) to that immediately preceding it, i.e. with one less vertical line.
2. **TRIPLET STATES - OFF-DIAGONAL INTERACTIONS**

2.1 **Linear Interactions**

An obvious way to tackle the linear ion-phonon coupling for any system is to remove the diagonal part of the interaction by the transformation (IV-4), leaving an off-diagonal term,

$$
\tilde{V} = \sum_{i \neq j, k} V_{ijk} a_i^+ a_j e^{z_{ij}} (\phi_k - 2u_k)
$$

(IV-14)

as a perturbation on $H_o$. This is only of some use when intra-multiplet coupling alone is considered. For multiplying out the two terms in (IV-14), we find that the second contains a factor,

$$
\sum_{k} V_{ijk} V_{jkl} e^{-l}
$$

(IV-15)

which, in symmetrized form, can be represented by Fig. 14(i). JLV2 then fixes $V' = V^*$, and within a multiplet ($\lambda_i = \lambda_j$, but $l_i \neq l_j$) the 3jms of 14(i) are mutually exclusive. So only the first term of (IV-14) survives:

$$
\tilde{V}_{\text{multiplet}} = \sum_{i \neq j, k} V_{ijk} a_i^+ a_j e^{z_{ij}} \phi_k
$$

(IV-16)

The exponential phonon operator here, only complicates matters in the event that $V_{ijk}$ and $V_{iik}$ contain a common 'phonon' component. Not only will the pairing of $\phi_k$ and $e^{z_{ij}}$ be complex, but any perturbative expansion will simultaneously contain this component at infinite order, and at low order.

Little is achieved by the transformation. For the triplet states $\Gamma_4$, $\Gamma_5$ though, it is useful. $V_{iik}$ and $V_{iik}$ reduce to $\Gamma_3$ and $\Gamma_5$ 'phonons' respectively. So (IV-16) allows a perturbative solution for arbitrary coupling strength in the former and weak coupling in the latter.

We indicate the effects of the transformation on the RF calculations for $\Gamma_5 \times (e + \tau_2)$. The system Hamiltonian is,

$$
\tilde{H}_o + (\tilde{V} + \tilde{H}_s) = \tilde{H}_o + \tilde{W}
$$

(IV-17)

We have grouped the perturbations into one term here as they both involve phonon operators and the Green function for the system requires an average over these. $\tilde{W}$ is a weak perturbation provided $h_{ij}$ and $V_{ijk}$ are small enough,
(\langle e^{-ij} \rangle \leq 1), so it changes the \( \Gamma_5 \) states' energies according to (IV-6).

(An alternative scheme would be to group \( \tilde{H}_0 \) and \( \tilde{H}_5 \) as in (II-23) and follow the procedure of that section. However it will only approximate to (IV-17), as the Green function analogous to (II-24) averages over the phonon character of \( \tilde{H}_5 \) before the interaction \( \tilde{V} \) is switched on). We can draw the self-energy diagrams corresponding to \( \tilde{\Delta}(E) \) if we represent a matrix element \( \tilde{W}_{ij} \) by Fig. 14(j). Here the cross-hatched regions denote all the \( \pi_E \) operators in \( e^{Z_{ij}} \) which are paired, and the solid lines all those that are not (and these cannot pair with \( \phi_k \) in (IV-16) by the result of (IV-15)).

So, for example, the diagrams 14(k) will describe how the linear coupling, via \( \Gamma_5 \) 'phonons' to second order and \( \Gamma_3 \) 'phonons' to infinite order, modifies the external interaction for the triplet states (the first of 14(k) is just (IV-8)). Though the expansion of \( \tilde{\Delta}(E) \) can be continued to all even powers of \( \tilde{V} \) and first order in \( \tilde{H}_5 \), it is clear that even the formulae for the lowest order terms are complicated, as each solid line in 14(k) represents a sum over the excitation of all possible phonon numbers. Although such formulae are 'exact', we find it much easier to treat the coupling via both \( \Gamma_3 \) and \( \Gamma_5 \) 'phonons' as weak and proceed as in Chapter III. There will be no great loss of insight into the behaviour of the RFs if we do this.

We give the results for \( \Gamma_5 \)-type coupling first.

2.1(a) \( \frac{\Gamma_5 \times \Gamma_2}{k_5} \)

With \( f_{k_5}^5 = 3h_k \), Figs. 7(f) yield the RFs

\[
K(\Gamma_3) = 1 - \frac{3}{2} \sum_k h_k x_k - \frac{3}{4} \sum_{kl} h_k h_l (A_{kl} + 4C_{kl} + 2D_{kl} - 2X_{kl}^2)
\]

\[
K(\Gamma_4) = K(\Gamma_3) - \frac{1}{2} \sum_{kl} h_k h_l B_{kl}
\]

\[
K(\Gamma_5) = \frac{1}{3} \left[ 2 + K(\Gamma_3) \right] - \frac{1}{2} \sum_{kl} h_k h_l A_{kl}
\]

In fully expanded form these become,
\[ K(\Gamma_3) = 1 - \frac{3}{2} \sum_k \frac{h_k N_k}{\varepsilon_k^2} + \frac{3}{8} \sum_{kk'} \frac{h_k h_{k'}}{\varepsilon_k \varepsilon_{k'}} \left[ \frac{5N_k N_{k'}}{\varepsilon_k \varepsilon_{k'}} + N_k^+ - N_{k'}^- \right] \]

\[ K(\Gamma_4) = K(\Gamma_3) - \frac{1}{4} \sum_{kk'} \frac{h_k h_{k'}}{\varepsilon_k \varepsilon_{k'}} (N_k^+ - N_{k'}^-) \quad (IV-19) \]

\[ K(\Gamma_5) = \frac{1}{3} \left[ 2 + K(\Gamma_3) \right] - \frac{1}{8} \sum_{kk'} \frac{h_k h_{k'}}{\varepsilon_k \varepsilon_{k'}} \frac{(\varepsilon_k + \varepsilon_{k'})^2}{\varepsilon_k^2 \varepsilon_{k'}^2} (N_k^+ + N_{k'}^-) \]

In the cluster model limit of zero temperature and coupling to a single
triplet of phonons, \( h_k + \frac{\hbar^2}{2m} \frac{\omega_T^2}{\omega_T} \delta_{kk'} \), and we recover Ham's (1965) formulæ
and the single mode expressions,

\[ K(\Gamma_4) = K(\Gamma_3), \quad K(\Gamma_5) = \frac{1}{3} \left[ 2 + K(\Gamma_3) \right], \quad (IV-20) \]

but only if we ignore fourth order terms. If the latter are included and
the coupling is not too weak, the departures from (IV-20) may not be negligible.
In comparison with the general results of (IV-19) though, not only
is (IV-20) a bad approximation, but the magnitudes of all three RFs may be
significantly altered from their single mode values. One reason for this
is the presence of the resonant term, \( N_{kk'}^- \). However, as the signs of the
fourth order terms are unknown, their importance is best determined by
comparing the many-body equivalent of (I-24) with the single mode sum rule
obtained from (IV-20). The latter breaks down under exactly the same
conditions as we discussed for \( \Gamma_3 \times \varepsilon \) (cf. (III-11)) since,

\[ 3b_2 = \frac{3}{4} \sum_{kk'} \frac{h_k h_{k'}}{\varepsilon_k \varepsilon_{k'}} (A_{kk'} - B_{kk'}). \quad (IV-21) \]

This result contrasts with Leung and Kleiner's requirement of a tenth order
term to ensure \( b_2 \) non-zero on a zero-temperature, single mode model.
(Actually we disagree with their result. We have analysed the sixth order
diagrams Figs. 8(a-c) for \( \Gamma_5 \times \tau_2 \) in much the same way as we did for \( \Gamma_3 \times \varepsilon \).
Most of the diagrams reduce trivially to fourth order ones, and, so, there
are few zeroes, and certainly no simple patterns for the contributions to
\( d(\mu) \). And we find \( b_2 \neq 0 \).

2.1(b) \( \Gamma_5 \times (\varepsilon + \tau_2) \)

If the RFs for \( \Gamma_3^{-}/\Gamma_5^{-} \) type coupling are denoted as \( K_v^{(\mu)} \), \( v = 4/5 \),
then we find the RFs for \( \Gamma_5 \times (\varepsilon + \tau_2) \) correct to \( O(V_1^4) \) to be,
\[ K(\mu) = K_4^4(\mu) + K_5^5(\mu) - 1 \]

\[ + \frac{1}{8} \sum_k \frac{g_k h_k}{2} \left( N_{k,k}^+ H^+(\mu)_{k,k} + N_{k,k}^- H^-(\mu)_{k,k} \right) \tag{IV-22} \]

where \[ H^\pm(\mu)_{k,k} = a \varepsilon_k^2 + b \varepsilon_k^2 \pm c \varepsilon_k \varepsilon_k \tag{IV-23} \]

and the coefficients \(a, b, c\) for \(\mu\) are

<table>
<thead>
<tr>
<th>(\mu)</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_3)</td>
<td>12</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>(\Gamma_4)</td>
<td>27</td>
<td>27</td>
<td>60</td>
</tr>
<tr>
<td>(\Gamma_5)</td>
<td>13</td>
<td>17</td>
<td>48</td>
</tr>
</tbody>
</table>

Also there is an addition to (IV-21) of

\[ \frac{9}{4} \sum_{k,l} (g_k h_k + g_k h_k) \left( A_{k,k} - B_{k,k} \right) \tag{IV-24} \]

The result (IV-22) shows that for weak ion-lattice coupling calculations it is necessary to take both 'phonons' symmetries into account. Thus even if the coupling is mainly via \(\Gamma_3\) 'phonons', \(K(\Gamma_3)\) will no longer be unity.

It is of interest to compare the relative importance of the cross terms \(g_k h_k\) in (IV-22) in the two cases when the coupling of one 'phonon' symmetry may be dominant. Consider first the situation when the system is predominantly \(\Gamma_5 \times \tau_2\) and an admixture of \(\Gamma_3\) 'phonons' to order \(g_k\) is allowed. The greatest effect on \(K(\mu)\) will occur at second order. At fourth order, the denominators multiplying \(h_k h_k\) and \(g_k h_k\) are similar but we assume \(g_k < h_k\) and the changes will be small, and this applies to all orders in \(\Gamma_5 \times \tau_2\).

The converse situation, predominantly \(\Gamma_5 \times \varepsilon\), is quite different. There is a complete absence of resonant terms in the expansion of \(K_5^5(\mu)\), and so the crossterm in (IV-22) should have a comparable effect on \(K_4^4(\mu)\) to the \(g_k g_k\) terms, for the temperature range in which \(N_{k,k}^-\) is important, despite the assumption of \(h_k < g_k\). And this will apply to all orders in \(\Gamma_5 \times \varepsilon\). Indeed, the evidence for the significance of the \(\Gamma_5\) 'phonons' here is stronger than these observations suggest if we treat the system properly as (IV-17).

The denominators in \(\tilde{\Delta}(E)\) calculated from the diagrams of Fig. 14(k), give rise to factors (in contracted notation) like,
for \( p \) phonons excited. As \( p \) increases there will be an increasingly wider range of resonance contributions to the RF expressions. Thus the inclusion of a small \( \Gamma_5 \)-type coupling into an (arbitrarily coupled) \( \Gamma_5 \times \varepsilon \) system will have a greater effect on the RFs for the system than the changes at \( O(V_1^2) \) caused by \( h_k \) suggest, in contrast to the analogous case for \( \Gamma_5 \times \tau_2 \).

This is to be compared with the zero temperature and single \( \Gamma_3, \Gamma_5 \) modes work of Bersuker and Polinger (1973). For their case our cross terms will no longer be important. But we expect significant corrections to their calculations for coupling to the phonon continuum at finite temperature.

It is worth noting from (IV-21,-24), that although an experiment giving a non-zero \( b_2 \) may be taken to indicate linear coupling to the continuum, it can not determine which 'phonon' symmetry, if any, is dominant.

2.1(c) Equal Coupling - \( \Gamma_5 \times (\varepsilon=\tau_2) \)

The results (IV-22) give rise to the equally-coupled system as follows. We calculate,

\[
K(\Gamma_5) - K(\Gamma_3) = \sum_k \frac{N_k}{h_k^{3/2}} (h_k - \frac{3}{2} g_k) + O(V_1^4)
\]

Upon setting \( h_k = 3/2 g_k \) to remove the second order term, we find the right hand side vanishes to fourth order. By comparison with (I-27), we expect \( h_k = 3/2 g_k \) to be the condition for equal coupling to \( \Gamma_3 \) and \( \Gamma_5 \)'phonons'. Indeed in the cluster model limit it reduces to,

\[
\frac{V_T^2}{\omega_T} = 3 \frac{V_E^2}{\omega_E}
\]

which, apart from the effective ligand mass (=1 in the limit), is the condition for equal coupling provided \( \omega_E = \omega_T \) (O'Brien, 1969), i.e. a single quintet of phonons. For the lattice phonon condition, we note that via the transformation Fig. 5(d), any relation between \( f_{k\nu}^{\lambda} \) and \( f_{k\nu'}^{\lambda} \) \((\nu\neq\nu')\) requires the propagating mode \( k \), to reduce to 'phonons' \( \nu,\nu' \) simultaneously, so we can assume that \( h_k = 3/2 g_k \) characterizes the coupling via 'phonons' of \( S_0^3 \) symmetry, \( v=(J)=2 \). If we denote the RFs under this condition by \( K^m (\mu) \), we have to \( O(V_1^4) \),
\[
K^\infty (\Gamma_3) = K^\infty (\Gamma_5) = 1 - \frac{3}{2} \sum_k \frac{\sigma_k n(k)}{k^2} \\
+ \frac{3}{8} \sum_{k\ell} h_k h_{\ell} \sigma_{k\ell} n(k)n(\ell) \frac{(9(k+\ell)^2 + 10 k\ell)}{k^2 \ell^2 (k+\ell)^2}, \\
3K^\infty (\Gamma_4) - 5K^\infty (\Gamma_5) = \frac{15}{4} \sum_{k\ell} h_k h_{\ell} \sigma_{k\ell} n(k)n(\ell) \frac{(k-\ell)^2}{k^2 \ell^2 (k+\ell)^2} - 2
\]

This last equation is the many-body equivalent of (I-26), the parameter \( b_1 \) there being a linear combination of (IV-21,-24). The result of Appendix II is thus confirmed. Realistically, there are no grounds for ignoring either the temperature or the phonon frequency dependence of these RFs in theoretical calculations, as O'Brien (1971) has done. Of course, should \( \Gamma_5 \times (\varepsilon_1+\Gamma_2) \) prove to be a good approximation for some paramagnetic system, it is not necessary to calculate the RFs from (IV-22) for higher orders. One can use the SO_3 6js directly to evaluate the linear diagrams.

The relations between the factors \( f_{k\nu}^\lambda \) are:

\[
\begin{align*}
\text{SO}_3 \text{ labels} & & \text{O labels} \\
\text{S} \text{O}_3 \text{ labels} & & \text{O labels} \\
\frac{1}{f_{k2}^1} = & & \frac{5}{3} f_{k5}^5 = \frac{5}{2} f_{k4}^\lambda \\
& & \lambda = 5, 2
\end{align*}
\]

### 2.2 Linear, Non-linear, Anharmonic Interactions - \( \Gamma_5 \times (\alpha_1 + \varepsilon_1 + \Gamma_2) \)

The calculation of the effects of interactions besides linear, on the RFs for \( \Gamma_5 \times (\varepsilon_1+\Gamma_2) \), is more involved than for \( \Gamma_3 \times \varepsilon \). Not only are there now two 'phonon' symmetries to contend with (although the \( \Gamma_5 \times \varepsilon \) system is very simple as we have seen in Section (IV.1.2)), but the 6j symbols (III-17,-18) are always non-zero for \( \Gamma_3 \) and \( \Gamma_5 \) 'phonons', either separately or mixed. This results in all the structures of Fig. 10 contributing for each vertex position to each RF, in contrast to the \( \Gamma_3 \times \varepsilon \) system. Thus for example, the diagrams 13(g-i), with bare vertices, which were zero for \( \Gamma_3 \times \varepsilon \), must now be included with the other fourth order diagrams, 12(a-c). The factors

\[
\begin{align*}
f_{0}^{5}(\nu_{1} \nu_{2} \nu_{3}) & \text{ and } f_{0}^{5}(k \ell \mu)(w \mu') \text{ (with } F' \rightarrow F)
\end{align*}
\]

will now be labelled by the triples (555), (444) and (554) and the contributions of 13(g-i) will not be dissimilar to (III-38). Like 12(a-c), they
will not appear in \( b_2 \) simply because they produce the 'end' structure of \( 11(c) \) (with \( \lambda = 0 = \Gamma_5', x = 0 \)), and the \( \delta j \) is just that which gives rise to \( \text{O}(V^2) \) at \( \text{O}(V^2) \). It is not until the structures of \( 10(b) \) are included that one finds a non-zero \( b_2 \) (the vertex positions are marked). Apart from these new diagrams, the calculations proceed as in Section (III.4.1). The definitions (III-21) ensure that the contributions of \( 12(a-e) \) can be found from the \( \text{O}(V^4) \) expressions (IV-18), in exactly the same manner as for \( \Gamma_3 \times \epsilon \). Numerical coefficients aside, they will be similar to (III-22,-23) provided we make the replacements,

\[
\begin{align*}
g_k & \rightarrow g_k + h_k \\
g_{kl} & \rightarrow g_{kl} + h_{kl} \\
g_{k\ell m}^{(3)} & \rightarrow g_{k\ell m}^{(3)} + h_{k\ell m}^{(3)}
\end{align*}
\]

although the equivalent of (III-23), \( 3b_2 \), will not contain terms for \( \Gamma_3 \) 'phonons' alone. Similarly \( 12(f,g) \) will contribute, but with many more coefficients \( V^i_0 \), as \( V_j \) (Fig. 12(j)), takes its two symmetry values. Nevertheless for each coefficient, it will only be the central vertex position - \( Q \) of \( 12(f) \) - that contributes to \( b_2 \), as the remaining positions \( (P,R) \) again reduce to the end structure of \( 11(c) \).

The major difference between the \( \Gamma_3 \) and \( \Gamma_5 \) JT systems lies in the significance of the above contributions. Firstly, there are many more Feynman diagrams to be considered at each equivalent order of interaction. For example, at sixth order in \( V_2, V_1 \) we have, in addition to Figs. 12(a,d,f) \( \text{O}(V^2 V_1) \), all those diagrams at \( \text{O}(V^2 V_1^5) \) corresponding to the structures of \( 10(a,b) \). Secondly, the resonant denominators, which are always present for non-linearity and anharmonicity, affect the 'linear' RFs differently for the two systems. For \( \Gamma_5 \times T_2 \) for example, we do not expect the fourth order diagrams of \( 12(a-c) \) to have the effect on (IV-19) that they will have on (III-8), although we cannot disregard them either. For \( \Gamma_5 \times \epsilon \) on the other hand, unless there is evidence that interactions other than linear are negligible, the exponential expression (III-12) will only be an approximation to the real situation. The argument for this is the same as that in subsection 2.1(b) above: at each order of linearity \( (>V^2_2) \), there will be an equivalent order containing (at least) one power of \( V^2_2/V^{(3)} \) multiplying a resonant term, and, unless the system temperature is very low, these couplings
will manifest themselves in the measured RFs, \( K(\Gamma_4), K(\Gamma_5) \). The comments of that subsection about the relative importance of cross terms in \( \Gamma_5 \times (\varepsilon + \tau_2) \), also apply here whenever linear coupling terms appear. In particular, the inclusion of terms of order \( g_k h_{km}, g_k h_{mp}^{(3)} \) and higher, can only add to the departure from (IV-12).

The effects of the participation of the symmetric 'phonon' \( \Gamma_5 \times (\alpha_1 + \varepsilon + \tau_2) \), can be found as in Section (IV.4.2). Formulae similar to those of that section will be obtained. The conclusions of the above paragraph can only be reinforced (particularly for \( \Gamma_5 \times (\alpha_1 + \varepsilon) \)), and there can be no justification for excluding the \( \Gamma_1 \) 'phonons' a priori.

3. QUARTET STATES

In obtaining the results for this section we have used the 6j symbols of Appendix IA exclusively. Our RFs must therefore be the many-body generalizations of the set (I-36), and without ambiguity we can drop the primed notation used there.

3.1 Linear Interaction

3.1(a) \( \Gamma_8 \times \varepsilon \)

Using (III-5) for \( \lambda = \Gamma_8 \), we find to \( O(V^2) \) that \( K(\Gamma_2), K(\Gamma_3) \) are given precisely by the same expressions as they were for \( \Gamma_3 \times \varepsilon \), namely (III-8,-10), and the remaining RFs to be

\[
K_{00}(\Gamma_5) = K(\Gamma_2), K_{11}(\Gamma_4) = K_{11}(\Gamma_5) = K(\Gamma_3)
\]

\[
K_{10}(\Gamma_4) = K_{01}(\Gamma_4) = 0
\]

(IV-26)

Indeed, the \( \Gamma_3, \Gamma_8 \) systems must produce the same formulae for \( K(\Gamma_2 / \Gamma_3) \) for all orders of linearity, since the 6js occurring in the linear structures for each system are simply related by

\[
\begin{bmatrix}
\sigma & 44 \\
\tau & 44
\end{bmatrix}_{0000} = -\frac{1}{2} \begin{bmatrix}
\sigma & 33 \\
\tau & 33
\end{bmatrix}_{0000}
\]

and there is a phase \( (\lambda \lambda_\sigma 0) \) to take care of the sign difference, and a factor of 2 from (III-5) for \( |\lambda| \). We can also prove, using the transposition method.
of Section (III,3.2), that the relations (IV-26) must hold for quite general electron-phonon coupling. Any such proof consists of showing an equality of $\delta_{tp}(\mu)$ and $\delta_{tp'}(\mu')$ for an arbitrary structure, Fig. 11(a), in two steps. Successive (or pairs of) transpositions, 11(b), must be the same for $(\mu p)$, $(\mu' p')$; and upon reaching the end structure of 11(c), the 6j symbol and its attached phases must be equal for $(\mu tp)$ and $(\mu'tp')$. The results for $\Gamma_8 \times \varepsilon$ are similar to those of 11(d-g) as expected. Of particular note is the transposition of $(\mu p) = (5 0)$ which follows that of $(7 0)$ in 11(d). It shows that the vertices labelled by $(5 0)$ and $(4 0)$ anticommute.

As additional confirmation that the $\Gamma_3 / \Gamma_8 \times \varepsilon$ systems are equivalent in general, we can use the relations (IV-26) to determine that the only non-zero parameters in (I-36) are $b_4^3$, $b_7^3$, to be compared with $b_4^4$, $b_7^4$ in Section (I.3.1). And for linear coupling anyway, the many-body expressions for the former may be obtained directly from the latter by a simple change of labelling everywhere.

3.1(b) $\Gamma_8 \times \varepsilon$

To fourth order in the coupling of the ion to the $\Gamma_5$ 'phonons', expressions similar in form to those of $\Gamma_8 \times \varepsilon$ are obtained:

$$K(\Gamma_2) = 1, \quad K_{10}(\Gamma_4) = K_{01}(\Gamma_4) = 0$$

$$K(\Gamma_3) = 1 - 2 \sum_k \frac{h N_k}{2} + \frac{1}{3} \sum_{k\ell} h_k h_\ell \frac{N_k N_\ell}{2 \varepsilon_k \varepsilon_\ell}$$

$$K_{00}(\Gamma_4) = K_{00}(\Gamma_5) = 1 - \frac{2}{3} \left[ 1 - K(\Gamma_3) \right] - \frac{8}{9} \sum_{k\ell} h_k h_\ell \left( A_{k\ell} - B_{k\ell} \right)$$

$$K_{11}(\Gamma_4) = K_{11}(\Gamma_5) = K_{01}(\Gamma_4) + \frac{1}{3} \left[ 1 - K(\Gamma_3) \right]$$

Clearly, in any experiment, the $K_{tt}(\mu)$, $\mu = \Gamma_4, \Gamma_5$, will always be smaller in magnitude than the assumption of a single mode equivalent for a measured value of $K(\Gamma_3)$ would suggest. Like $\Gamma_8 \times \varepsilon$, the simplifications above do not finish at $O(V_1^4)$. The transposition method again shows for an arbitrary structure diagram, that

$$\delta_{tt}(\Gamma_4) = \delta_{tt}(\Gamma_5)$$

(IV-28a)
\[ \delta(\Gamma_2) = \delta(\Gamma_1) = (-1)^n \delta(\Gamma_3) \]

(\text{n defined as in Rule II Section (III.2.2)}). Hence for arbitrary coupling,

\[ K(\Gamma_2) = 1, \quad K_{tt}(\Gamma_4) = K_{tt}(\Gamma_5) \]

And while (IV-28b) implies that one should approach the calculation of \( K(\Gamma_3) \)
in the same manner as for \( K(\Gamma_2) \) in \( \Gamma_8 \times \epsilon \), it should not be presumed that
the resulting expressions will have the same form above \( O(V_1^4) \). For example,\(^\text{45}\)
all of the vertex positions for \( n \) odd in Fig. 8(a-c) contribute to \( K(\Gamma_3) \).
We also suggest further simplifications to the calculations for \( \Gamma_8 \times \tau_2 \).
An examination of all the diagrams at \( O(V_1^6) \) shows that,

\[ \delta_{10}(\Gamma_4) = \delta_{01}(\Gamma_4) = 0 \]  
\[ \delta_{11}(\Gamma_4) = (-1)^n \delta_{00}(\Gamma_4) \]

And although we have not yet proven these equalities generally, (successive
transpositions, Fig. 11(b) for \( \nu = 5, \mu = 2,5 \), attach a complex set of irrep
and multiplicity labels to the base of any structure 11(a)), if they are true
to \( O(V_1^6) \), we cannot see why this should not be so to all orders of linearity.
We assume this to be the case. Now, we can use (IV-29) to obtain \( b_4 = b_{21} = b_{51} = 0 \) in (I-36), and provided (IV-30a) is always correct, \( B_2 = B_5 = 0 \) also.
Thus three parameters should suffice to describe the RFs for the linear
coupling (of any strength) of the lattice to the \( \Gamma_8 \) states via the \( \Gamma_5 \) 'phonons'.
(\text{The last equation in (IV-27) suggests that only two parameters are necessary,}
but this is a special consequence of (IV-28a) and (IV-30a), valid to \( O(V_1^4) \)
only. In general it has the form,

\[ K_{11}(\Gamma_4) = K_{00}(\Gamma_4) + \frac{1}{3} \left[ 1 - K(\Gamma_3) \right] - \frac{8}{3} b_7, \]

where the contributions to the last term can only come from those diagrams
with \( n \) odd at \( O(V_1^6) \) and higher).

Another example of the similarity between the results for the linear
\( \Gamma_8 \times \epsilon/\tau_2 \) systems is provided by the sum rule,

\[ K_{11}(\Gamma_5) + K_{00}(\Gamma_4) - K(\Gamma_3) = 1 - 8/3 b_{20} \]
As these equations are the analogues of (III-9,11), and both systems exhibit an $(\pm 1)^n$ relation between the $\delta_{tt}$ ($\mu$) involved in their respective sum rules, we expect the results of Section (III.2.2) - that only diagrams with $n$ even contribute to $b_7$, and only in the single mode limit in $b_7$ zero, for all strengths of linear coupling - to apply to $b_{20}$ also. To $O(V_1^6)$ this is the case, and it may safely be assumed to be so to infinite order. Thus $b_7$, $b_{20}$ perform identical roles in checking the validity of the single mode sum rules for the two systems.

3.1(c) $\Gamma_8 \times (\epsilon + \tau_2)$

Considering the number of multiplicity summations that must be performed to evaluate any structure for a $\Gamma_8$ multiplet, it is fortunate that the calculation for coupling via both $\Gamma_3$ and $\Gamma_5$ 'phonons' effectively separates into the calculation for each. We show this with the aid of Figs. 15(a-c). 15(a) is taken to represent any linear structure where the internal 'phonon' lines have a definite labelling of $\nu = 4, 5$. As the electron-'phonon' vertices labelled by these two irreps anticommute, 15(a) becomes 15(b) generally (to within a sign), where the hatched regions (4), (5), separately maintain the structure they had in 15(a). Repeated JLV3 gives 15(c) and the useful result for $\delta_{tp} (\mu)$ corresponding to 15(a),

$$\delta_{tp} (\mu) = (-1)^a \sum_r \delta^5_{tr} (\mu) \delta^4_{rp} (\mu)$$

(IV-34)

where $a$ is the number of anticommutations required to form 15(b). So one only needs to know the values of the lower order linear structures for $\Gamma_8 \times \epsilon/\tau_2$ to obtain those for the combined coupling. (Despite the summation in (IV-34), no extra work is required for $\mu = \Gamma_5$ as the 6j symbols ensure $\delta^4_{rp} (\Gamma_5) = 0$, $r \neq p$. Thus $t=p=r$ when $\mu = \Gamma_5$). In particular, the 6js at $O(V_1^4)$ in the two previous subsections give the cross terms in the RFs to $O(V_1^4)$:

$$K_{tp} (\mu) = K_{tp}^4 (\mu) + K_{tp}^5 (\mu) - 1$$

(IV-35)
FIGURE 15

a) 

b) 

(+) 

c)
where the coefficients $a, b, c$ of (IV-23) for $t_p(\mu)$ are,

<table>
<thead>
<tr>
<th>$t_p(\mu)$</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_2$</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>2</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>$00\Gamma_4$</td>
<td>= $2/3 (\Gamma_2)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$11\Gamma_4$</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>$00\Gamma_5$</td>
<td>$7/3$</td>
<td>$7/3$</td>
<td>$16/3$</td>
</tr>
<tr>
<td>$11\Gamma_5$</td>
<td>$= 11(\Gamma_4)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$01\Gamma_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

An important result follows from (IV-35). The equalities,

\[ K_{11}(\Gamma_4) = K_{11}(\Gamma_5) \]  \(\text{(IV-36)}\)

\[ K_{10}(\Gamma_4) = K_{01}(\Gamma_4) = 0 \]

are seen to remain valid in the combined system. This is a simple consequence of (IV-26,-28a,-30a) and (IV-34). But significantly, provided (IV-30a) is valid to all orders, (IV-36) characterizes linear coupling to all orders.

We shall have more to say on this later. Note that the fourth order behaviour of $K(\mu)$, $\mu = \Gamma_2, \Gamma_3$, is altered from that for $\Gamma_8 \times \varepsilon/\tau_2$, respectively, by the addition of $N_{k\lambda}$ terms at $O(q_k h_k)$. Now resonant terms have the same significance for all RFs. To describe other results following from (IV-35), it will be convenient to obtain many-body expressions for the parameters in (I-30), by forming linear combinations of the RFs in (IV-35). The relations (IV-36), assumed valid to infinite order and hence all strengths of linear coupling, give the simplifying conditions,

\[ b_{21} = b_{51}, \quad B_2 = B_5 = 0 \]  \(\text{(IV-37)}\)

and the eight parameters otherwise required for arbitrary electron-phonon interaction are reduced to five in number. To $O(V_4)$ they are given by,

\[ b_7 - \text{as in (III-11) with } q_k \text{ appropriate to } \Gamma_8 \]

\[ b_{20} - \text{as in (IV-33)} \]
Firstly, we note that provided terms at $O(V_l^1)$ and above can be neglected, it is possible in principle to measure each of $b_7$ and $b_{20}$, by measuring the appropriate combinations of RFs, and so compare the extent to which an energy spectrum exists for the $\Gamma_3$ and $\Gamma_5$ 'phonons' separately. But all five RFs will need to be determined to do this. Our second result, on the other hand, distinguishes between the single mode assumption and the phonon energy spectrum quite generally. From (I-36) we have,

$$2K_{11}(\Gamma_5) - K_{00}(\Gamma_5) = 1 - 4b_7 - \frac{4}{3}b_{20} - \frac{8}{3}b_{21}$$  \hspace{1cm} (IV-39)

Upon substitution of the formulae in (IV-38), it can be seen that the accuracy of any assumptions made about the phonon spectrum may still be determined merely by measuring two RFs, although at the loss of any information about the relative importance of the couplings of the 'phonon' types. (This result is remarkable when compared with the $\Gamma_5 \times (\epsilon + T_2)$ system—for the latter three RFs must be determined for the equivalent information).

Above $O(V_1^4)$, each parameter in expressions like (IV-39) will contain $g_k$ and $h_k$ factors, though within the restrictions imposed by the $\Gamma_8 \times \epsilon/\tau_2$ systems. For example, only $b_7$ obtains terms from $\Gamma_3$ or $\Gamma_5$ 'phonons' separately whereas $b_{21}$ can have neither of these. Such conditions may be useful for an elementary determination of the dominance (if any) of either 'phonon' symmetry. Thus $b_{21}$, evaluated from

$$K_{00}(\Gamma_4) - K_{00}(\Gamma_4) + K(\Gamma_2) = 1 - 16/3b_{21},$$ \hspace{1cm} (IV-40)

will be close to zero (along with one of $b_4$ or $b_{50}$) if one 'phonon' is effectively absent. Otherwise, the effects of both symmetries cannot be disentangled. Note, that despite the similarity of $b_7$, $b_{20}$, $b_{21}$ at $O(V_1^4)$, and the identical behaviour of $b_7/b_{20}$ in the single mode limit for $\Gamma_8 \times \epsilon/\tau_2$, $b_{21}$ is non-zero in this limit at $O(V_1^6)$ and above, and the existence of a
phonon spectrum is not guaranteed if a measurement determines the right-hand side of (IV-39) to be less than unity.

Finally, we complete the relating of Ham et al.'s (HLK) RF expressions to ours, begun in Section (I.3.1), and so present the finite-temperature, many-body formulae for their (undetermined) parameters. To do this we temporarily restore the primed (the above results) and unprimed (cf. (I-31) notation of that section. The conditions (IV-37) are now

$$b_{51} = b_{21}', \quad B_5 = B_2' = 0,$$

and via the transformation (I-35) they become

$$b_{51} = \frac{1}{5} (4b_{21} + b_{20} - 2B_2),$$
$$B_5 = \frac{1}{5} (4b_{21} - 4b_{20} + 3B_2) = 0.$$

Substitution of these into (I-31) yields three sum rules characterizing general linear coupling:

$$K_{10}(\Gamma_4') = K_{01}(\Gamma_4') = \frac{1}{2} \left[ K_{00}(\Gamma_4') - K_{11}(\Gamma_5') \right]$$
$$= 2 \left[ K_{11}(\Gamma_4') - K_{11}(\Gamma_5') \right]$$
$$= \frac{2}{3} \left[ K_{00}(\Gamma_4') - K_{11}(\Gamma_4') \right]$$

(IV-41)

With the correction (I-33), HLK's RFs are found to obey (IV-41) also. So the only difference between the (restricted) set (I-31) and their expressions, are the parameters used. (I-32) gives two of the relations between the parameters. By direct comparison of the RFs the others are,

$$q' = 1 - 2b_{50}, \quad a^2 = \frac{4}{3} b_{51},$$
$$\delta^2 = \frac{4}{15} (4b_{20} + b_{21} + 2B_2) = \frac{4}{3} b_2'.$$

(IV-42)

Thus $p', q', a^2, b^2$ and $\delta^2$ may be calculated quite generally by our methods for weak coupling. And while we agree with HLK's assignments to these parameters in the special cases of $\Gamma_8 \times \varepsilon, \Gamma_8 \times \tau_2$ and/or single modes, we disagree with their speculations concerning them: it is not necessary to have strong coupling to phonons of very different frequencies for $a^2, \delta^2, b^2$ to become significant in comparison with $p', q'$, as the presence of resonant terms in (IV-38) shows.
3.1(d) Equal Coupling - $\Gamma_8 \times (\varepsilon_{\tau_2})$

The RFs for the equally-coupled system are obtained as for $\Gamma_5 \times (\varepsilon_{\tau_2})$. Using (IV-35) we set $K_{00}(\Gamma_5) - K(\Gamma_3) = 0$ and find $h_k = 3/2 g_k$. This in turn makes the remaining RFs satisfy the equalities (I-38). Thus setting $h_k = 3/2 g_k$ is equivalent to making the linear electron-phonon interaction an $SO_5$ invariant and the calculation of the two RFs for this system can now proceed by using the $SO_5$ $j$ symbols to evaluate all linear structures. (Unlike the other $\Gamma_8$ systems there is no relation between the $\delta(\mu)$ to reduce the computations). The factors $f^\lambda_{k\nu}$ for the two symmetries $SO_5$, 0, obey the analogous relation to (IV-25), and to $O(V_1^4)$, the parameter $b_2$ in (I-37) has the usual $(A_{kk} - B_{kk})$ form via (IV-38,-39).

3.2 Linear, Non-linear, Anharmonic Interactions - $\Gamma_8 \times (\varepsilon_1 + \varepsilon_2)$

We subdivide this discussion into the three 'phonon' couplings $\Gamma_3$, $\Gamma_5$, $\Gamma_3 + \Gamma_5$, and consider the addition of the $\Gamma_1$ 'phonon' last.

(a) $\Gamma_8 \times \varepsilon_1$

For the reasons stated in Subsection 3.1(a) above, all the results of Sections (III.3.2) and (III.4.1) will apply to $\Gamma_8 \times \varepsilon$ generally, independently of the electron-phonon coupling. The only differences occur in the values of the structures and the labelling of the phonon transformation factors. The former are now $4^{-m} 2^{-m'}$, where $2m/2m'$ is the number of electron-'phonon'/3-'phonon' vertices, but if this change is compensated by requiring $F^4_{k\ell} \ldots \nu n + \sqrt{2}^3_{k\ell} \ldots \nu n$, the formulae for $\lambda = \Gamma_3/\Gamma_8$ become identical.

(b) $\Gamma_8 \times \varepsilon_2$

The similarity of results for the linearly coupled $\Gamma_8 \times \varepsilon_{\tau_2}$ systems, is found to extend to other coupling mechanisms as well. For those non-linear Feynman diagrams reducing to linear structures this is a foregone conclusion - one proceeds immediately as in Section (III.4.1) to obtain the analogues of the linear RF expressions. For the non-linear structures however, it is a comparison of the $6js$ (III-17,-18), commonly occurring for the two systems, that suggests patterns of contributions to $\delta_{tt}(\mu)$ for $\Gamma_8 \times \varepsilon_{\tau_2}$, similar to those of Section (III.3.2). Thus

$$\begin{pmatrix} 4 & 4 & 4 \end{pmatrix}_{0000}^{(4,4,4)} = \begin{pmatrix} 5 & 5 & 5 \end{pmatrix}_{0000}^{(5,5,5)} = 0,$$
and (III-18) is non-zero only for \( \sigma = \Gamma_1 \) or \( \{ \nu \times \nu \}_A \). And we now find that: Figs. 10(a, b, e(iii), f) are zero - as should be all structures with an odd number of 3-'phonon' vertices; 10(d, e(i), g) contribute for all positions of the external vertex according to (IV-28, -30) - as do the last two diagrams in 10(e(iii)), in contrast to \( \Gamma_8 \times \nu \); the first of 10(e(ii)) however, behaves analogously to \( \Gamma_8 \times \nu \) - only \( \delta_{tt}(\Gamma_{4/5}) \) are non-zero for the vertex marked. So (IV-30) appears to be obeyed by all non-linear structures as well and, in conjunction with (IV-29), implies that the most arbitrary \( \Gamma_8 \times \tau_2 \) system is completely described by only three parameters, \( b_7, b_{20}, b_{50} \).

The effects of the diagrams Figs. 12(a-g) on the \( O(\nu^4) \) RFs, will follow those of \( \Gamma_8 \times \nu \) - for example 12(f, g) give \( b_7 = 0 \), and \( b_{20} \) non-zero only for the central vertex position - and the conclusions of Section (III.4.1) will apply here.

\[ (c) \quad \Gamma_8 \times (\nu + \tau_2) \]

The calculation of the RFs for general coupling to \( \Gamma_3 \) and \( \Gamma_5 \) 'phonons' is considerably more complex wherever non-linear structures are involved, mainly because the separations of Fig. 15 cannot be made when 3-'phonon' vertices exist labelled by both \( \Gamma_3 \) and \( \Gamma_5 \) - although one may still usefully rearrange a structure to reduce the computation. Now the equalities (IV-36) cannot be proven, and all eight parameters in (I-36) will be required to describe the behaviour of a \( \Gamma_8 \) multiplet under a perturbation. This is borne out for even the simplest of non-linear structures. For example, Figs. 10(a, b, d) now give,

\[ \delta_{10}(\Gamma_4) = \pm \delta_{01}(\Gamma_4), \quad \delta_{tt}(\mu) = 0 \text{ for all } \mu, \]

for all vertex positions for several combinations of the \( \Gamma_3, \Gamma_5 \) labels. Of course 10(d) also contributes to \( \delta_{tt}(\mu) \) in the main, but always for a different labelling of the 'phonons': the 6js responsible for \( \delta_{10}(\Gamma_4) \neq 0 \) are such that there is never a simultaneous contribution to \( \delta_{tt}(\mu) \), for any structure. And we find \( \delta_{11}(\Gamma_4) \neq \delta_{11}(\Gamma_5) \) for some of these labellings. Considering the number of terms that result from 10(a, b) alone, and that only the lowest order in \( \nu^2 \) or \( \nu^{(3)} \) is required to form these (and indeed every other structure with only one 3-'phonon' vertex), \( K_{\Gamma \Gamma}(\Gamma) \) should be an excellent indicator as to whether or not linear coupling is the only mechanism at work. The difference, \( K_{11}(\Gamma_5) - K_{11}(\Gamma_4) \), will also serve
this purpose but probably not as well, as the diagrams contributing to it involve an extra power of $V_2^2/V^{(3)}$. As to the actual calculations for linear structures produced, (IV-34) remains true and the non-linear/anharmonic analogues of (IV-38) can be obtained without too much effort from diagrams like Figs. 12(a-e). For the likes of 12(f,g) there are no shortcuts, excepting that the end vertex positions on any non-linear structure will still require $\delta_{tt}(\mu)$ to behave as the $O(V_1^2)$ result (cf. Fig.11(c)), and $b_7, b_{20}, b_{21}, b_{51}$ will be zero for these. The contributions at sixth order to $B_2, B_5$ however, are more difficult, requiring all the structures in 10(a,b,d) to be evaluated.

The linear and non-linear coupling via the $\Gamma_1$ 'phonons' can now be included in the above three systems as they were for $\Gamma_3 \times (\alpha_1 + \epsilon)$. Since the result of setting any 'phonon' line in a structure to be $\Gamma_1$ is to reduce that structure to a simpler one, our conclusions based on the analysis of these are unchanged. For example, a three parameter description of $\Gamma_8 \times (\alpha_1 + \tau_2)$ remains. As for the electronic doublet, one of the major effects of the $\Gamma_1$-type coupling is to make all structures with an odd number of 3-'phonon' vertices non-zero for all RFs for the above systems. Since these (and $O(V_1^2)$) provide corrections from lowest order upwards in $V_1$ and $V_2$, the $\Gamma_1$-component must be included alongside the $\Gamma_3/\Gamma_5$-components of the couplings.

We conclude our discussion of the $\Gamma_8$ JT systems, by reaffirming the role of the multiplicity choice for the triple (332r) in obtaining the above results. From the point of view of detailed calculations, the 6js of Appendix IA are much preferred over those of Appendix IB. The former give fewer multiplicity summations when structures are reduced to 6j and 9j symbols. This is especially true for $\Gamma_8 \times (\epsilon + \tau_2)$, and even the simple non-linear structures. As an example, the 6j (III-18) has two values of $z$ for $\sigma = \Gamma_4$ using Appendix IB, but only one for Appendix IA. The results of the transposition method are correspondingly simpler for our multiplicity choice. It is the natural scheme to use to demonstrate the equivalence of the $\Gamma_3/\Gamma_8 \times \epsilon$ systems, and the similarity of these to $\Gamma_8 \times \tau_2$, for general coupling, is most obvious. Likewise the results (IV-36), although equivalent to (IV-41), clearly distinguish between arbitrary linear coupling and other mechanisms.
4.0 DISCUSSION

4.1 Features of the $\Gamma_5/\Gamma_8$ Systems

We review here the main features to emerge from our studies of the various $\Gamma_5/\Gamma_8$ JT systems.

Essentially our results reinforce the early comments of Section (III.5). Considering the complexity of the systems though, we feel that some of the advantages of calculating RFs via our method can stand repeating here. In the first place, we have avoided the matrix multiplication which would normally be associated with (any) perturbative calculation for degenerate systems. For our problem each Feynman diagram with $n$ electron-'phonon' vertices would require the multiplication of $(2n+1)$ matrices of rank $|\lambda|, |\nu|^{n}$ times, and summed in the appropriate manner, to obtain the same information available from our broken down structures. Even for $|\lambda| = 3$, this becomes very tedious. The existence of multiplicity and/or more than one 'phonon' symmetry only complicates the computation more so. In contrast, the arbitrary labelling of our structures has allowed us to handle the $\lambda = \Gamma_5, \Gamma_8$ systems with comparative ease. Secondly, a general analysis of the structure diagrams, as for the electronic doublet, has proved beneficial, particularly for some systems. Thus for $\Gamma_5 \times \epsilon$ the calculation of all structures reduces to that of a well defined set, and equalities for the RFs follow, independent of coupling strength and type. And the proof only requires a knowledge of a few $6j$ symbols. The same applies, via the transposition method, to the $\Gamma_8 \times \epsilon/\tau_2$ systems. For the latter, in addition, we have been able to prove or assume simple relations for the $\delta_{\mu}$, simplifying computations in $\Gamma_8 \times \{\epsilon + \tau_2\}$, and placing restrictions on its RFs in linear coupling. And again, these results are not apparent if one follows Gauthier and Walker's prescription. A third, and important, advantage of our method, is that it predicts that the RF expressions will be much the same for all JT systems for all interaction types. With the exception of the linear $\Gamma_5 \times \epsilon$ system, where there is a complete absence of resonating denominators, we find this to be the case. In particular, (and here we include the $\Gamma_3$ systems), the sum rules of Section (I.3) enlarged to include Eqns. (IV-32,-39,-40), all have the property that their free parameters, $b_{\nu r}^\lambda$, obtain their contributions at the earliest, at fourth order in $V_1$, and then at sixth order when $V_2$ or $V^{(3)}$ are added. Furthermore, their terms at $O(V_1^4)$ have exactly the same form, namely,
At sixth order and above in $v_1, v_2, v^{(3)}$, they are different in form for the various systems, though not in effect. The sum rules valid for cluster model type calculations are recovered when these parameters are zero. With the exception of the continuous symmetry systems (see below) this can not occur above $O(V^{4c})$. The classes of diagrams responsible for these $b_{v_r}^\lambda$ are easily recognised: the external interaction vertex has at least two electron-'phonon' vertices to either side of it in any structure. This property is readily explained. We first note that the labels of $b_{v_r}^\lambda$ are such that $v_r \in \{\lambda x \lambda\}_S/A$ for even/odd electron systems. We then observe that the structure of Fig. 11(c) (for $\Delta$) never contributes to these $b_{v_r}^\lambda$, because on the vibronic model it must correspond to the creation of a one-'phonon' state, $|v'n\rangle$, where, via time reversal, $v'r' \in \{\lambda x \lambda\}_S/A$. So only the $b_{v'r'}^\lambda$ derive terms from 11(c) (of course these parameters reproduce the single mode sum rules without restrictions). We shall return to these results later.

The information that is available directly by measurements of the RFs is the prime reason for their study. We now compare the $\Gamma_5$ and $\Gamma_8$ systems on this point. Take linear coupling to $\Gamma_3, \Gamma_5$ 'phonons' first. For the $\Gamma_8$ system a measurement of the RFs and a check of any equalities will determine whether or not both 'phonons' are involved in the coupling. One may estimate which symmetry is dominant, and to $O(V^{4c})$ (only) measure this relative coupling. However, similar measurements cannot distinguish between $\Gamma_5 \times \tau_2$ and $\Gamma_5 \times (\epsilon + \tau_2)$ or determine the relative coupling in the latter, excepting the equal coupling case. (A possible source of information here might be the temperature dependences of the RFs. For dominant $\Gamma_3$-type coupling the solution of (IV-17) will ensure that the RFs have an $\exp(-f(T))$-like dependence even at lowest order in the $\Gamma_5$-coupling. Of the three RFs though, we expect $K(\Gamma_5)$ to show the least dependence, as it must do in the limit that the $\Gamma_5$-type coupling disappears altogether. We have yet to check this conjecture. For dominant $\Gamma_5$-type coupling ($O(g_k)$ only, for example), the three RFs will behave in the low temperature limit as $T^{2n}$ at $O(V^{2n}_1)$. When non-linear and anharmonic couplings of the two 'phonons' are added in the calculations of the RFs, the difference remains, because in this case $\Gamma_8 \times \epsilon/\tau_2$ and $\Gamma_8 \times (\epsilon + \tau_2)$ are distinguishable by $K_{\pi \pi'}(\Gamma_4)$, but no such distinction exists between $\Gamma_5 \times \epsilon/\tau_2$ and $\Gamma_5 \times (\epsilon + \tau_2)$. Also, the relations (IV-36) for
\( \Gamma_8 \times (\varepsilon + \tau_2) \) determine the existence of (any) interactions other than linear - but there is no such easy check for the \( \Gamma_5 \) systems (or for that matter \( \Gamma_8 \times \varepsilon/\tau_2 \)). And yet such interactions should be much more important for the \( \Gamma_5 \) systems, simply because all the non-linear structures are non-zero, in contrast to the \( \Gamma_8 \) systems where the majority of these are zero at any order (with the exception of \( K_{\text{LRP}}(\Gamma_4) \)). Thus if the lowest order terms, \( V_2 V_1^2, V_1^{(3)} \), which appear in the RFs of \( \Gamma_5 \times \varepsilon, - \tau_2 - (\varepsilon + \tau_2) \), are significant, this can only be determined by temperature measurements alone (for example \( V_2 V_1^2 \sim T^5 \) in the low temperature limit). The addition of the \( \Gamma_1 \) 'phonons' in the coupling mechanisms is important to note: they remain undetectable for an isolated triplet, but for the non-linear \( \Gamma_8 \) systems temperature dependences such as that above should appear.

One feature that the most arbitrary \( \Gamma_5/\Gamma_8 \times (\varepsilon_1 + \varepsilon + \tau_2) \) systems have in common, is that an experiment showing the breakdown of the single mode sum rules does not definitely prove that the ion is coupled to the phonon continuum. Even if other experimental data excludes electron-phonon interactions other than linear, the two 'phonon' symmetries ensure that the \( b^{\lambda}_{ur} \) discussed above are non-zero in the single mode limit. (This is still true even if the single \( \Gamma_3 \) and \( \Gamma_5 \) modes have the same frequency). The only systems which do give unambiguous proof in this limit are the special symmetry systems in linear coupling: \( \Gamma_3 \times \varepsilon; \Gamma_8 \times \varepsilon/\tau_2; \Gamma_5 \times (\varepsilon = \tau_2); \Gamma_8 \times (\varepsilon = \tau_2) \) - invariant under the \( S_02; S_03; S_05 \) groups respectively. We note that the RFs for \( \Gamma_5 \times (\varepsilon_1 + \varepsilon) \) are unique in that no information about the frequency dependence of the coupling is directly available from measurements.

4.2 Other Lattice Models

Other workers have considered the coupling of a JT ion to the phonon continuum and the effects on the RFs, but in some approximation. The only other general approach to RF calculations on a lattice model has been that of the Nottingham group, whose results are collated by Bates (1978). We compare our results with theirs first.

We briefly survey their method. They take a JT ion in a cubic environment to be linearly coupled to the symmetrized displacements constructed from the motions of the star of nearest neighbours. The latter are in turn coupled via a lattice potential to stars of the next nearest neighbours and so on. Assuming a particular form for the potential, they try to find a transformation of the system Hamiltonian which will remove the ion-lattice
interaction, V. The external perturbation is simultaneously transformed - as in Section (IV.1.1). Clearly, the motivation for their approach is that the method is exact for electronic triplets coupled via \( \Gamma_3 \) 'phonons' (Stevens (1969)). But although their transformation applies for all strengths of V it has limitations: for other JT systems analytical results will only appear in some approximation (weak or strong coupling); the coupling must be linear; and the lattice must be cubic or trigonal. Now to specific comparisons for triplets and doublets in octahedral symmetry. For \( \Gamma_5 \times \varepsilon \), their \( K(\Gamma_4/\Gamma_5) \) are effectively the same as ours as required, - \( \exp(-2sC_s^2N_s) \), \( s \) the wave vector for their lattice modes. For the assumed lattice potential, the sum is evaluated at zero temperature, both approximately (Debye model), and numerically (Steggles (1977)). For the latter it is found that a wide range of mode frequencies is important in the sum. The same will be true for our more general result (IV-12) where, in reality, \( V_{\text{ik}} \) is a complicated function of \( \omega_k \). (A method is described by Bates for coupling the ion to the whole lattice, but results are not given). However, we object to their omission of the population factor, unless the system temperature is very low. (Stevens rejected the temperature dependent part of \( N_k \) in comparison with its constant part (unity) for temperatures \( T \ll 1/2\theta_D \), the Debye temperature. But frequency sums using the Debye model are only a good approximation for \( T<<\theta_D \) and long-wavelength acoustic modes. In any case, the effects of population factors are still observable in principle, even at helium temperatures. We discuss this further in the next subsection). Our formulae predict that the combined effects of finite temperatures and non-linear and anharmonic coupling of both \( \Gamma_1 \) and \( \Gamma_3 \) 'phonons', should also be considered for these RFs when a wide range of frequencies is present. For \( \Gamma_5 \times \tau_2 \) they derive formulae in weak coupling to \( O(V_1^2) \), which will be equivalent to ours, (after their assumptions) to this order. The relations (IV-20) are thus reproduced. Rather than calculate their lattice sums however, it seems easier to go to \( O(V_1^4) \) and distinguish between the cluster and lattice models directly, as in (IV-21). Likewise for \( \Gamma_5 \times (\varepsilon+\tau_2) \). Here two successive transformations are performed, one for the \( \Gamma_3 \) 'phonons', which have arbitrary coupling strength, and a second for weakly coupled \( \Gamma_5 \) 'phonons'. Thermal averages are taken after each transformation. The RFs so obtained by Bates (see his Equn. (9.8)) have lead him to argue that the \( \Gamma_5 \) 'phonons' can usually be ignored in the coupling because their effect is quenched by the \( \Gamma_3 \) 'phonons' anyway. We can obtain equivalent forms to his RFs by calculating the contributions of the diagrams Fig. 14(k), but with the solid lines connecting the hatched vertices removed (only the first two graphs will survive).
However, at finite temperatures (the case considered by Bates) this is not a good approximation and the results and comments of Section (IV.2.1(b)) disagree with his findings. For $\Gamma_3 \times \varepsilon$, no new detailed results are presented, only sufficient to conclude that $2q-p<1$ on a multimode model. We note that they have not yet examined the RFs for the $\Gamma_8$ systems. Overall, apart from the absence of any strong coupling solutions outside $\Gamma_5 \times \varepsilon$, our method has the following advantages over theirs: (i) it is not restricted to linear coupling or to any lattice symmetry; (ii) the temperature and frequency dependence of the RFs as a result of phonon excitations are always explicit.

With the exception of the linear $\Gamma_5 \times \varepsilon$ system, two consequences of this are, that lattice sums need not be performed to decide in favour of multimode or single mode coupling (to $O(V^{-1}_1)$ certainly), and that resonant terms can be much more important for all JT systems than the formulae of Bates et al. suggest; (iii) no particular form of the ion-lattice coupling or lattice potential is presumed, which is convenient as any representative form can be inserted in our sums. For example, Halperin and Englman (1975) and Ham et al. ((1969), Appendix A) together present methods for expressing the dependence of our $f_{k\nu}^A$ on $k$ and $\omega_k$ when the coupling is to an octahedron of nearest neighbours.

Other continuum models advanced warrant a mention. Ray et al. (1975) expose the inadequacy of single frequency model, by calculating the JT energy and the RFs for $\Gamma_5 \times \varepsilon$ using the (zero temperature) classical Green function for the lattice, evaluated on a model of the MgO lattice designed to fit measured dispersion curves. The effective cluster model frequency, $\omega_{E'}$, appearing in $E_{JT}$ and $K(\Gamma_4)$, is required to alter by 200 cm$^{-1}$ to reproduce these two quantities. Biernacki's (1977) model for the zero temperature $\Gamma_5 \times \varepsilon$ system, involves nearest neighbour coupling and displacements, and the use of combined Einstein and Debye models (suitably averaged) for the phonon spectrum. $E_{JT}$ and $K(\Gamma_4)$ then depend upon two frequency parameters. He argues (1978a,b) in favour of an effective frequency interpretation for some impurity/host systems and considers his method applicable to $\Gamma_3 \times \varepsilon$ as well, a view we do not share for lattice sums over more than one phonon variable (see the following subsection). Halperin (1976) also considers an effective frequency description for $\Gamma_5 \times \varepsilon$, $\Gamma_3 \times \varepsilon$. Via a thermodynamic variational calculation a cluster-like Hamiltonian is derived from the coupling of the ion to the lattice phonons. However the model presumes in the first place that this coupling is predominantly within a narrow frequency range, a condition which may well be satisfied for strong coupling but which is unnecessarily restrictive for the opposite limit. Finally, Ham et al.'s
(1969) original indication of how one might calculate RFs for \( \Gamma_5 \times (\epsilon + \tau_2) \) for nearest neighbour coupling is also approximate. Their frequency integrals are for \( O(\epsilon_1^2) \), zero temperature, and a Debye spectrum.

4.3 \textbf{Predictions for Any Symmetry}

We conclude our examination of first-order RFs within a multiplet, by reviewing the limitations of our model, and outlining its consequences for the interpretation of RFs for multiplets in any symmetry. We mention the experimental conditions likely to produce temperature and multimode effects, and the evidence that has been advanced for the latter.

Our method is applicable to any system, for which (as magnitudes),

\[
H_o = (H_e + H_p) \gg V, H_S
\]

The states of \( H_e \) can be orbital or spin-orbital in high or low static crystal field symmetries, and \( H_S \), though referred to as an external perturbation, can represent the spin-orbit interaction, and/or lower symmetry distortions of the site group of the ion, as well as Zeeman, strain, and hyperfine interactions. Within a multiplet this condition becomes

\[
V, H_S \ll \epsilon_0, \quad (IV-44)
\]

for some representative phonon energy of the host crystal. More precisely, we only require \( V, H_S \) small enough that our perturbation expansions converge. So \( V \ll \epsilon_0 \) may be allowable. (Since the JT energy, the multiplet shift, is to lowest order

\[
E_{JT} = |\Delta (E_0)| \sim \sum_k |V_{ijk}|^2/\epsilon_k, \quad (IV-44a)
\]

the condition for weak coupling on the cluster model, \( E_{JT} \ll \epsilon_0 \), is roughly recovered). Nor are any assumptions made about the relative magnitudes of \( V, H_S \) in our initial expansion of \( M(z) \). Thus it is immaterial whether

\[
E_{JT} \gg H_S \quad (IV-45a)
\]

or

\[
E_{JT} \ll H_S \quad (IV-45b)
\]

for our calculations to apply, as long as (IV-44) is satisfied. However as long as one takes \( H_S \) to find order only but \( V \) to any order, (IV-45a) is implicit. In the case of the reduction of spin-orbit coupling within an orbital triplet, (IV-45a) is the condition required by Ham (1965, 1972) for the validity of his RF description. But we see no objection to the use of perturbation theory in the case \( E_{JT} \sim |\lambda| \), provided one calculates higher
order RFs as well. (IV-45b) is the limiting case of this. Now though it is certainly easier to treat $V$ as a perturbation on the eigenstates of $(H_e + H_s)$. For the spin-orbit coupling this can lead to Van Vleck stabilization: the spin-phonon interaction within spin-orbit multiplets can be so weak that the RFs are very close to unity (Ham (1965)). Nevertheless, the quenching of external perturbations in $\Gamma^3_8$ (Kramer's ions) and $\Gamma^4_3, \Gamma^5_4, \Gamma^6_5$ (non-Kramer's) states will still occur. Obviously, the limitation to weak coupling is a major restriction on the application of our model to many experimental situations. (The exception to this is the linear $\Gamma^5_5 \times \varepsilon$ system. Here again we disagree with Ham (and Bates): we do not have to invoke (IV-45a) for the system to ensure that the reduction of $H_s$ at first order is given by (IV-12). Contrary to Bates, the thermal averaging of $H_s$ is allowed independently of the relative sizes of $V, H_s$).

As we have considered the more complicated JT systems in our work, the application of our calculated method to ions which do not have octahedral site symmetry should be relatively straightforward. There are no problems in handling non-degenerate 'phonons' and multiplicity only reappears for the tetrahedral group T (the triplet $\Gamma^4_4$ of T can couple to two $\Gamma^4_4$ phonons, - but these will be distinguished by different phonon transformation factors). Ions in trigonal and tetragonal symmetry should be easily treated as the 6js and 9js are much fewer in number. And for all systems the transposition method should be used first to see if any simple patterns exist for the contributions of structures. The formulae for the RFs for any systems will obviously be very similar to those we have already produced, e.g. to within numerical values we have their form exactly at lowest orders $V_{11}^2, V_{22}^2, V_{12}^2 V_{12}^2 V_{12}^2 (3)$. Bearing in mind that measurements of perturbations on any multiplet must give RFs corresponding to these formulae, we now consider how much can be simply inferred about the ion-lattice coupling from these measurements. The three areas of interest are: multimode or single mode coupling; the coupling mechanisms; determination of coupling parameters. The first two areas have been mentioned in part before so we shall be brief with these.

(1) Multimode coupling. In principle this information is easily available for any system. In practice it is probably not, as it requires that all RFs can be measured simultaneously, and this is known to be difficult (see the references at the end of this section). Following the comments of Section (IV.4.1) one can expect to obtain this information as follows: the RFs (I-20) for various $\mu$ are combined such that
the only free parameters are the $b_{\nu r}^\lambda$, $v_r \in \{\lambda x \lambda \} A/S$. At fourth order these should have the form of (IV-43), by our experience with all the octahedral systems (the proof only depends upon the signs of the two 6js and the 9j relevant to $A_k^x$ and $B_k^y$) and, to this order, one can decide in favour of multimode coupling. If one admits sixth order and above in $V_1$, $V_2$, $V^{(3)}$, the $b_{\nu r}^\lambda$ will always be non-zero for single mode coupling. The only solution, in principle, is to perform the lattice sums and find the relative contribution of the iso-energetic part at some effective frequency. However, if the coupling parameters have a broad frequency dependence this contribution will be very small and the $b_{\nu r}^\lambda$ significant. On the other hand, for a narrow frequency dependence, and at low enough temperatures, the $V_1^4$ term will be negligible and the $b_{\nu r}^\lambda$ small also. So it is still sensible to gauge the extent of multimode coupling by this measurement. We remark that the true extent of multimode coupling is only determined near zero temperature, where resonant terms will be unimportant.

(2) Coupling mechanisms. The relative effects of the couplings $V_1$, $V_2$, $V^{(3)}$ on the RFs for any multiplet will not be easily disentangled, even if the lattice sums can be performed exactly. The usual approximation is to neglect the quadratic and anharmonic effects for weak and intermediate coupling strengths, but we see no reason to do so unless they can be shown to be absent altogether. For the $\Gamma_8 \times (\alpha_1 + \epsilon + \tau_2)$ system this can be checked directly, but not so for all the remaining octahedral systems nor, we expect, for any other systems. While the presence of anharmonicity can be detected by other experimental means, (thermal conductivity data for example), linear and non-linear interactions can only be distinguished by their characteristic low temperature dependences. The difficulty here is that powers of $V_1$, $V_2$... produce a $T^n$ behaviour for $n=2$ upwards - thus the $T^5$ character at $O(V_2^2 V_1^2)$ is sandwiched between the $T^4/T^6$ behaviour at $O(V_1^4V_2^2/V_1^6)$ and may not be distinguishable (if the temperature variation of RFs is not observable at low temperatures that of the spin-lattice relaxation time for the multiplet will be, but the problem will remain).

(3) Coupling parameters. Typically a linearly-coupled cluster model has been used for the purpose of interpreting RFs, by assuming the coupling to be to a phonon of one symmetry type having some (pronounced) frequency of the host crystal (e.g. Ray and Regnard (1974)). Our
model restricts the accuracy that can be attached to the coupling parameter $V_v$ in this approach. Suppose the coupling is sufficiently weak that only $O(V_1^2)$ sums are important (the arbitrary strength $\Gamma_x \times \epsilon$ is included here. We assume that $F^\lambda_{kvn} \sim V_v \cdot f(\omega)$. Equating the measured RF to our lattice sum, will produce a $V_v$ different from that of the cluster model. However, the form of the sum does admit the use of a single effective frequency, (or maybe two e.g. Ham and Slack (1971)) and an effective $V_v$, provided these are treated as temperature dependent parameters. Otherwise, this assignment is inaccurate. For all terms above $O(V_1^2)$, the combined effects of the phonon spectrum and finite temperature are more complicated (exceptions to this can occur at $O(V_1^4)$, e.g. p of $\Gamma_3 \times \epsilon$). The effect of the population factors is to enhance the sign of a contribution at any order, and is important for those phonons with energies $\epsilon_k \leq KT$. At $O(V_1^4)$ and above, this is especially so for the resonant terms. Thus the magnitude of the coupling parameter is effectively magnified by the combination of its frequency dependence and the system temperature. The presence of additional (weaker) coupling to another phonon symmetry $v'$ also highlights the assumptions in the cluster model - the effects of $v$ and $v'$ are not simply additive above $O(V_1^2)$. The $\Gamma_5 \times (\epsilon + T_2)$ system is a good example, and relevant to the many calculations of $V_E$ on the cluster model: although $V_{T_2} < V_E$ often (e.g. Ray and Regnard), the neglect of $\Gamma_5$-type coupling at non-zero temperatures will certainly enlarge $V_E$ above its true value. In general, the RFs will be of little direct help in determining the relative importance of different 'phonon' couplings (assuming they are not very different in magnitude). The exception is $\Gamma_8 \times (\epsilon + T_2)$, because the number of parameters, $b_{v'r'}$, exceeds those of the type $b_{v'r'}$, (Section (IV.4.1)), allowing direct measurement at $O(V_1^4)$. This is not repeated for any other system). One should also admit the possibility of non-linear and anharmonic couplings contributing to the 'apparent' linear parameter, $V_v$, of the cluster model. Likewise, their presence is magnified by coupling to the phonon spectrum. In addition, one must now include the $\Gamma_1$-parts of $V_1, V_2$ etc., as these can be comparable in magnitude to the 'JT active' 'phonons'. (As examples of the importance of the $\Gamma_1$ component for triplets in cubic symmetry, we refer to the moments analyses of absorption spectra by Ham and Slack and Koidl et al. (1973). For most systems this will be the only method of detecting this 'phonon'). Taking all the above
into account therefore, it can be seen that a cluster model determination of \( V \) is, at best, an approximation. However, this model has had success, for which there is some justification. Firstly, RFs are usually measured at a very low temperature, \( T_0 \) say, so that population factors are negligible for phonons of energy \( > KT_0 \). Secondly, many of the calculations are of the \( O(V^2) \) type, either for weak coupling, e.g. Ham et al. (1969), Ham and Slack, or for \( T_5 \propto \exp \left( O(V_1^2) \right) \). The effective frequencies used here are around peaks in the phonon density of states, which will act like localized modes; these points should also be significant for our lattice sums. Also, Ham et al. argue, on their lattice model, as to why the coupling appears to be predominantly with the optical phonons. They find the low frequency acoustic modes to be relatively unimportant in their lattice sum, a result we might agree with to \( O(V_1^2) \), but not above for finite temperatures.

Thus the only information that is simply available from RF measurements with any degree of accuracy, is the existence of multimode coupling. If this is observed, then our lattice sums should be evaluated to determine the magnitudes of coupling parameters. This will be extremely difficult for a real lattice. In practice one must assume same frequency dependence for the couplings, and use a density of states, \( D(\omega) \) for the host lattice (see Appendix VI). For the former one might begin with Halperin and Englman's (1975) nearest-neighbour model (a knowledge of dispersion relations is also required). But a calculation with a realistic \( D(\omega) \) will probably require numerical methods. We see little point in using the theoretician's standby of the Debye spectrum to estimate multimode and temperature effects at second and fourth order: not only is it limited to low temperatures but it overestimates the high frequency contributions to the integral. These problems prevent a reasonably accurate prediction of the relative size of the resonant and non-resonant terms at \( O(V_1^4) \) for any temperature. In the absence of such calculations though, we can at least suggest the experimental conditions that will almost certainly require the use of our model.

Multimode effects. These should be most pronounced for systems satisfying the following:

(a) The ion lattice coupling is not so weak that \( O(V_1^4) \) terms are negligible.

(b) \( D(\omega) \) for the host lattice is such that a localized frequency description is not possible (Rozenfel'd and Polinger (1976) give criteria for this).
(c) Alternatively, for those systems where representative acoustic and optical frequencies are required on a cluster-type model for the explanation of experimental data. This implies a frequency dependence of the coupling over a wide range, e.g. Ham and Slack, Koidl et al.

Temperature effects. Provided the system is at helium temperatures, these should be small. The population factors, \( n_k \), are then appreciable only for very long wavelength phonons, but their presence is diminished by \( D(\omega) \), which is proportional to \( \omega^2 \) at low frequencies. So spontaneous emission processes will dominate. As the temperature rises, its effects will appear in the \( O(\nu^2) \) term initially. At some temperature though, the resonant terms at fourth order (all combinations of \( V_1, V_2, V^{(3)} \)) will begin to contribute significantly to the RFs. This point may be anticipated: in the theory of ion-lattice relaxation rates (Hernandez and Walker, Stedman (1970)), resonant terms and their associated population factors, at fourth order in the expansion of \( M_0(\omega) \), are responsible for the Raman processes. These compete with direct process relaxation \( O(\nu^2) \), except at very low temperatures (the Orbach process will not occur for an isolated multiplet - but this is on idealization). So around and above the temperature at which the Raman processes dominate (identifiable by their characteristic dependences), our fourth order (and higher) terms should not be neglected. For some impurity-host systems this temperature can be quite low, \( \sim 10K \). These relaxation rates also suggest a method of checking for the temperature variation of the RFs, which may be easier than the direct measurement of the latter. For the \( T_3 \times \varepsilon \) system for example, the Raman process (for \( V_1 \) coupling) gives rise to a rate for the strain - split doublet, of the form

\[
\tau^{-1} \sim c. (q \nu_1)^4 \cdot T^5
\]

at sufficiently low temperatures (Ham (1968), Gauthier and Walker (1976)). Any significant variation of \( q \) with temperature would then show up as a departure from the \( T^5 \) law. (Of course, for small \( T \) one does not expect \( q \) to vary much but then for larger \( T \), where it may, the \( T^5 \) law may not be accurate (Gauthier and Walker)). For other systems similar measurements will be possible for some RFs.
The evidence that has so far been presented for the existence of multimode coupling, has been for systems in which the ion-lattice coupling is strong. Abou-Ghantous et al. (1974, 1975), Bates (1978a), and Bates et al. (1976, 1979) have all performed calculations for $I_3 \times \epsilon$ systems. In none of these works are both $p, q$, measured: in some cases $p$ is unobtainable. Typically, $q \leq \frac{1}{2}$, and the presence of the first excited vibronic singlet is included, via the RF $r$, to fit the experimental data. Either the cluster model ratio of $q/r$ is not observed or, when $p$ is calculated, $2q-p<1$ is found. While these experiments clearly indicate the inadequacy of a cluster model description, our weak coupling formulae are hardly appropriate for the interpretation of these experiments - the RF $r$, does not exist in our theory. The other JT systems examined, have been interpreted as $I_5 \times \epsilon$ - Bates and Steggles (1975), Abou-Ghantous and Bates (1980). Here, the cluster model is most simply tested by trying to fit the observed first- and second-order RFs with functions of a single parameter (see Section IV.5.2 following). These authors find this to be impossible. Although the observations to date have been of strongly coupled systems, this does not imply that a similar search for multimode effects in more weakly coupled systems will be fruitless. We see no reason for drastically altering our conclusions about the possible interpretation of RFs for these strongly coupled systems. The demonstration of the inaccuracy of the single mode sum rules will have similar implications for the estimation of coupling parameters here as it has in our perturbative solution.

5. OTHER ASPECTS OF THE FORMALISM

The use of our formalism for calculation of RFs extends beyond the simple cases we have considered so far. We briefly show how intermultiplet coupling effects and higher order RFs can be incorporated in a fuller analysis.

5.1 Intermultiplet Coupling

To this point, we have interpreted RFs based on intramultiplet coupling alone. In reality, a multiplet is never isolated, though the effects of coupling between multiplets will obviously depend upon their energy separation, as well as the coupling strength. We demonstrate what this coupling implies for the effective external perturbation. We start with (II-26) and (II-29),

$$
\{ E - (H + \Delta_0 (E)) - (H + \Delta_1 (E)) \} \mid i\rangle \rangle = 0, \quad (IV-46)
$$
i.e. we assume $H_s < V << (H_H + H_P)$. For definiteness, we consider two multiplets, say a triplet $(\lambda_1^1, \text{energy } \theta_1^1)$ and a doublet $(\lambda_2^2, \theta_2^2)$, with $\theta_{21} = E_{21} > 0$. As we wish our perturbation expansion to be valid for coupling within either multiplet, we take $V << \epsilon_o$. The case $E_{21} >> \epsilon_o$ is then of little interest, as intermultiplet effects, involving factors of $V/E_{21}$, will certainly be negligible. In simplifying (IV-46) to the effective perturbation, (II-33), we assumed only that the splittings of the multiplets by $H_s, E_1$, were small compared with the multiplet shifts resulting from the interaction $V$. The Taylor's expansion of the shift operators in (IV-46) about $E = E_o$ could then be performed, giving

$$\{E - E_o - E_1, \Delta_{o}^{(1)}(E_o) - (H_s + \Delta_{1}(E_o))\} |1>> = 0$$ (IV-47)

with $E_o$ given by (II-25). In hindsight though, it appears that we should distinguish between two cases in the transition from (IV-46) to (IV-47), even if our assumptions are satisfied. The first case is when the separation of our two multiplets is of the same order as their ion-phonon shifts, $E_{21} \sim \Delta_{o}(E_o)$. This is usually termed the pseudo-JTE. We can envisage two situations here. The two values of $E_o$ may be very close, i.e. the multiplets shifted towards one another. If $H_s$ is of the order of their separation, its effects should then be similar to intramultiplet coupling for a five-fold degenerate level. Alternatively, the values of $E_o$ may be separated $\gtrsim E_{21}$. The determinant of (IV-47) then gives then distinct eigenvalues, $E_1 = f(E_o)$, corresponding to the two values of $E_o$, and it is not clear which splittings should be associated with the two multiplets. Although we have not examined this problem in detail, it can be overcome by solving (IV-46) self-consistently. The second case is when the zero-order multiplets are sufficiently well separated so that $E_{21} >> \Delta_{o}(E_o)$ is satisfied. They will then tend to act like isolated multiplets and we can set $E_o = \theta_1^1, \theta_2^2$ in a first approximation. Ten values for $E_1$ will still be obtained, but the three values describing the splittings of the triplet for example, will be identifiable by the fact that the intramultiplet coupling terms in $E_1 = f(\theta_1^1)$ contain no $\theta_{12}$ factors in their denominators. Similarly for the doublet. The remaining five eigenvalues will decrease with increasing $\theta_{12}$ and we may neglect them. With these limitations then, we can safely use (II-33) and avoid the diagonalization of (IV-46). (In the event that two multiplets have the same irreps, $\lambda_1 = \lambda_2$, we certainly require $E_{21} >> \Delta_{o}(E_o)$ in order to write (IV-47). This condition will correct an oversight in Section (II.2), where we set

$$\{E_o - H_e - \Delta_{o}(E_o)\} |1>> = 0$$
in deriving (II-33). This is only true if $|_{1}\rangle\rangle$ is a proper linear combination of the states $|_{i}\rangle\rangle$, which will only occur (generally) when $|_{i}\rangle\rangle = |_{i}\rangle$, i.e. when $\Delta_{o}$ has no off-diagonal elements. This is not so for $\lambda_{1} = \lambda_{2}$ but, if $\Delta_{o}$ is sufficiently small, it is approximately. The values of $E_{o}$ to first order are

$$E_{o} = \theta_{i} + (\Delta_{o}(\theta_{i}))_{i} \equiv \theta_{i}'$$

and the off-diagonal elements only give small corrections at second order,

$$\sum_{j} |(\Delta)_{ij}|^2/(\theta_{i}' - \theta_{j}')$$

We now examine the matrix elements of $H_{eff}$, (II-41), in our five-state basis. According to our RF definition, (II-45), the matrix elements ($O_{m}^{\mu}$)$_{ij}$ have the form

$$\sum_{a} K^{i j a a}(\mu) \langle \theta_{a} | O_{m}^{\mu} | \lambda_{a} \rangle , \quad (IV-49)$$

where $i, j, a = 1, 2$, and we have used the fact that $H_{s}$ acts within a multiplet (we assume no multiplicity). Thus each matrix element depends upon two reduced matrix elements of $O_{m}^{\mu}$. While the $5 \times 5$ matrix should be diagonalized to yield the splittings, in the manner described above, we shall simplify matters, further by neglecting the matrix elements outside the $3 \times 3$ and $2 \times 2$ block diagonals. This is in keeping with our perturbative approach and is justifiable, as the $K^{i j a a}(\mu) = d^{i j a a}(\mu)$. $d^{i i (\Gamma_{1} \mu)}$, $i, j \neq a$,

are already smaller than $K^{i i i i}(\mu) = K^{i}(\mu)$: the former go to zero as the coupling strength does, whereas the latter tends to unity. We now have two RFs for the two multiplets $\lambda_{1}^{i}, K^{i}(\mu)$ and $K^{i a a}(\mu) \equiv K^{i a}(\mu), i \neq a$. Despite this approximation, and the fact that the $K^{i}(\mu)$ should produce the major reduction of an operator $O_{m}^{\mu}$, it is clear that the idea of an effective operator, $K^{i}(\mu) O_{m}^{\mu}$, acting alone within the manifold $\lambda_{1}^{i}$, should be discarded. Via the intermultiplet coupling, the external interaction operating in the triplet states appears as an effective interaction in the doublet states and vice versa, but only for those irreps $\mu$ common to $\lambda_{1}^{i} \times \lambda_{1}^{i}$ and $\lambda_{2}^{i} \times \lambda_{2}^{i}$. Consider the RFs for the triplet,

$$K^{i a}(\mu) = (\delta_{i a} + d^{i a}(\mu)).(1 + d^{1 i}(\Gamma_{1}^{i}) + \frac{2}{3} d^{12}(\Gamma_{1}^{i}))^{-1} , \ a = 1, 2$$

with $K^{i i}(\Gamma_{1}^{i}) = 2/3, K^{i 2}(\Gamma_{1}^{i}) = 1.$
\(d^{11}(\mu)\) will now obtain contributions additional to those we have already calculated, as a result of the intermultiplet coupling (via 'phonons' \(\nu \in \lambda_1 \times \lambda_2\)). In Figs. 16(a,b), we show two low order diagrams. \(d^{11}(\mu)\) will only be altered by diagrams like 16(b), for \(a=1, i,j=2\), which have four or more coupling vertices. \(d^{12}(\mu)\) on the other hand, has contributions from \(O(V_1^2)\) upwards - 16(a) for \(a=2\). Thus \(d^{11}(\mu)\) may or may not be reduced below the value it has in the absence of intermultiplet coupling, depending upon the sign of \(d^{12}(\Gamma_1)\) (which, unlike \(d^{11}(\Gamma_1)\) need not be positive at \(O(V_1^2)\)). And the change in \(d^{11}(\mu)\) may or may not be offset by \(k^{12}(\mu)\). Both reduced matrix elements in (IV-49) must be calculated in deciding how much an operator \(O_m^\mu\) is quenched within the triplet states. However, the magnitude of the corrections to \(d^{11}(\mu)\) and \(d^{12}(\mu)\) can still be guessed at given the multiplet separation \(E_{21}\). All the diagrams in their expansions will produce factors in their denominators of the form \((E_{12} + \epsilon_k + \epsilon_{\ell} + \ldots)\), their number depending upon the particular diagram and its labels. The importance of the corrections will depend upon the size of \(E_{21}\) relative to typical phonon energies, the number of intermultiplet vertices and the temperature of the system (we shall assume here that \(V_{iak} \approx V_{iak}\) for \(i \in \lambda_1, a \in \lambda_2\)). For example, at \(O(V_1^2)\) \(d^{12}(\mu)\) is given by (III-3). If \(E_{21} \approx O\), then both terms in (III-3) will be fairly small (since \(V < O\)). For smaller \(E_{21}\), the first term will be the larger of the two, but only appreciably so at those temperatures which allow it to resonate significantly, (but we are limited to \(E_{21} \gg \Delta_o (\theta_1)\)). As the temperature tends to zero, \(n_k \to O\) and only the second term survives. This contrasts with \(d^{21}(\mu)\) for the doublet, which derives its main contribution from the \((n_k + 1)\) term for all temperatures. (In the zero temperature limit then, the corrections to the RFs are preferentially for those belonging to excited multiplets, at this order). At \(O(V_1^4)\) similar considerations will apply to \(d^{11}(\mu)\), but the details will depend upon the individual diagrams. Expressions as simple as those as we have found for intramultiplet coupling will not occur, but our diagram notation will be to advantage in keeping track of all terms and calculating the contributions of the participating 'phonons'.

Although the above example is a limiting treatment, it does indicate the effects that must be considered irrespective of the values of \(E_{21}\). When \(E_{21}\) is sufficiently small, \(E_{21} \approx \Delta_o (E)\) for example, and (IV-46) is to be solved, resonant terms will be significant, from lowest order upwards. Intermultiplet coupling corrections will be far from negligible. At the other extreme, \(E_{21} \gg \Delta_o (E)\), their importance will more likely depend upon the magnitude of \(V_{iak}\) and may only be sizeable for those terms at lowest
FIGURE 16

a) 

b) 

c) $\Delta_2$ 

d) 

e) 

f)  

g)  

h)  

$\leftrightarrow d_{\sigma tt'pp'}(\mu_1\mu_2)$
order in this coupling. (For $d_{i j a}^{a} (\mu)$, $i \neq j$, for example, this occurs at first order, and may overshadow the corrections given by $d_{i i}^{a} (\mu)$ and $d_{i a}^{a} (\mu)$). We expect intermultiplet effects to be most pronounced at low temperatures on our weak coupling model, for systems where spin-orbit or small crystal field components leave multiplets separated by energies $\ll \hbar \omega$. In principle, their presence is detectable when a calculation of RFs is compared with experiment: those for irreps $\mu$ not common to the products $\lambda \times \lambda$ will be interpretable via an intramultiplet coupling parameter alone (assuming $V_{\lambda}$ only, say), whereas the remaining RFs will not. For examples of the necessity of introducing intermultiplet coupling to fit measured RFs, we refer to the discussion of Ham et al. (1969) and references therein.

5.2 Higher-Order Reduction Factors

When the external perturbation is not small, higher powers of $H_{S}$ must be included in the perturbation expansion in $V$. It is trivial to do this for the Feynman diagrams as we indicated in Section (II.2): for $n$-th order in $H_{S}$, we expand $\tilde{M} (z)$, as in (II-28), up to and including $M_{n} (z)$, with a corresponding extension for (II-29),

$$\tilde{\Delta} (E) = \Delta_{0} (E) + \Delta_{1} (E) + ... + \Delta_{n} (E).$$

Substitution of this equation into (II-26) then gives the splittings of the multiplets correct to $O(H_{S}^{n})$. $\Delta_{i} (E)$ may be calculated directly from the diagrams in $M_{i} (z)$, but it can be written in closed form, as $\Delta_{1} (E)$ was in (II-31): the operator in (II-31) is replaced by

$$\tilde{\Delta} (E) = \Delta_{0} (E) + \Delta_{1} (E) + ... + \Delta_{n} (E).$$

Again, it is convenient to perform a Taylor's expansion of $\tilde{\Delta} (E)$ about $E = E_{0}$ in (II-26). The $m$-th derivative of $\Delta_{i} (E)$ is simply

$$\Delta_{i}^{(m)} (E) = (-1)^{m} \Delta_{i+m} (E),$$

where it is understood that $\Delta_{i+m} (E)$ has $m$ external vertices set to the identity operator in all distinct ways. An effective perturbation can thus be written in the same manner as (II-33). At $O(H_{S}^{n})$ it will involve the calculation of diagrams in $M_{n} (z)$ alone, with $n,n-1,n-2 ... 0$, vertices $H_{S} / 0, 1, 2 ... n$ identity operators. The group-theoretic analysis of these diagrams will, of course, become more difficult with increasing $n - JLV(n+2)$
will be required to couple the external legs of the diagram, in order that
a comparison with the 'bare' interaction diagram can be made to derive the
RFs (this step will introduce the basis-dependence of the higher-order RFs).
However, there is no obstacle, in principle, to carrying out the calculations
for any n. It will certainly be the most efficient method - barring a
direct diagonalization of (II-26).

Second-order RFs are usually the only ones of interest. We have
performed computations for some systems, but, as they are incomplete, we
shall only sketch them. With the definitions
\[ N = H_s + \Delta_1(E_o) , \quad D = \{ 1 - \Delta_1^{(1)}(E_o) \}^{-1} , \]
the second order corrections to (II-33) can be shown to be
\[ D.\Delta_2(E_o) + D.\Delta_1^{(1)}(E_o) , \quad DN + \frac{1}{2} DND^2 . \Delta_1^{(2)}(E_o) , \quad N \]  
(IV-50)
For a single multiplet, \( \lambda, D \) and \( \Delta_1^{(2)} \) commute with the remaining operators, and (IV-50) is simply
\[ H_2 = D.\Delta_2(E_o) + D.\Delta_1^{(1)}(E_o) , \quad H_1 + \frac{1}{2} D.\Delta_1^{(2)}(E_o) , \quad H_1^2 , \]
where \( H_1 = ND \) is the first order perturbation, (II-33). A matrix element
of \( H_2 \), which contains operators transforming as \( \mu_1, \mu_2 \), now reduces to known
first order RFs, times reduced matrix elements, and new factors depending
upon the matrix elements of \( \Delta_2 \). The latter can be reduced within the multi-
plet as in Fig. 16(c). We write this diagram as
\[ \sum_{\sigma} \sigma_{tt'}pp' \cdot \chi^{12ij}_{\lambda \sigma \lambda'} \cdot d_{\sigma \sigma_{tt'}pp'}(\mu_1 \mu_2) . \quad \lambda\lambda' \mu_1 \mu_2 \]
(IV-51)
with \( i = (\lambda \lambda'), \lambda = (\mu_1 m_1) \). It is to be compared with
\[ \chi^{12ij}_{\lambda \lambda'} \quad \lambda\lambda' \mu_1 \mu_2 \]
the bare second order interaction. For multiplicity free systems, this is
most simply done by expressing \( X^{2ij}_{\sigma} \) and the reduced matrix elements as second
order operators, whose symmetry depends upon \( \sigma, \mu_1, \mu_2 \). These will have the
form of the equivalent operators given by Bates (1978), for example. The
\( d_{\sigma}(\mu_1 \mu_2) \) can then be computed by the same rules that apply to the \( d(\mu) \) at first
order. In this way we have obtained second-order RFs for \( \Gamma_3 \times \varepsilon \), which
agree with Ham's (1968) at \( O(V_1^2) \) in the single mode limit. (At this order,
there is no temperature dependence of these RFs for any system - \( \Delta_2 \) produces
a factor \( \kappa_n(k/k^3) \). At the same order, the RFs for \( \Gamma_5 \times \tau_2 \) are related
by simple numbers, depending upon the symmetry of the equivalent operators. With one exception, these numbers agree with those given by Bates (we reserve judgement on the discrepancy). We have not yet considered the multiplicity non-free cases and we shall leave further details of this and the above to a later publication.

The linearly-coupled $I_5 \times \varepsilon$ system is the one case for which it is relatively straightforward to calculate the RFs, to any order in $H_s$, and any for any strength of $V_l$. We shall give the (exact) result to $O(H^2)$ as, in combination with the first order result, (IV-11,-12), it allows a direct check of the validity of the cluster model, by-passing the problem of performing the lattice sums. The starting point is (IV-6), with the shift, $\Delta(E)$, resulting from the external perturbation, (IV-7). With $H_s$ represented by the first vertex in Fig. 14(j), the diagram expansion for $\Delta(E)$ can be written down as usual: all vertices $H_s$ are connected by the solid lines (representing the unpaired operators in $e^{zij}$) in all possible ways. Thus, to third order in $H_s$, $\Delta(E)$ can be calculated from Fig. 16(d), if the solid line is expanded as all numbers of phonon excitations, (16(e)). The calculation of $\Delta(E)$ now reduces to a combinatoric problem, of increasing complexity with the order of perturbation. At second order, we require the thermal average

$$\sum_{p} \rho_p \langle \tilde{H}_s (E + E_p - \tilde{H}_o + io) \cdot \tilde{H}_s | p \rangle.$$  \hspace{1cm} (IV-52)

We indicate the steps in this calculation. Consider the term with $p$ phonons excited. $(H_s)_{ik}$ contains a term

$$\sum_{s \geq 0} \frac{1}{(s+p)!} z^{s+p}_{ik}$$  \hspace{1cm} (IV-53)

represented by 16(f). $z^{s+p}$ consists of $p$ operators $\pi_k$, $n=1,..,p$, distributed amongst $s$ such operators, already paired. When these equivalent distributions are counted, (IV-53) factors into

$$\left( \sum_s \frac{1}{s!} z^s_{ik} \right) \cdot \frac{1}{p!} z^p_{ik}.$$  \hspace{1cm} (IV-53)

or 16(g). Upon averaging, the term in brackets becomes $e^{-\frac{1}{2} x_{ik}}$ (s is even). The adjoining vertex, $(H_s)_{kj}$, factors as in 16(h). When connecting 16(g,h), there are $p!$ pairings of the $\pi$ operators, each producing a term (after averaging),
\[ (-1) \, X_{i,kj}^n(k_n) = (-1) \cdot \nu_{i,k}^n \cdot \nu_{j,k}^n \cdot q_{k_n} \cdot n(k_n) \cdot (k_n)^{-2} \]

(in the contracted notation for energy and population factors). Finally, after summing over all phonon excitations \( p \), (IV-52) is equivalent to the operator

\[ \sum_{ij} a_{ij}^+ \cdot h_{ik} \cdot h_{kj} \cdot e^{-\frac{1}{k}(x_{ik} + x_{kj})} \cdot F(i\bar{k}j), \]

with

\[ F(i\bar{k}j) = \sum_{p=1}^{\infty} \frac{(-1)^p}{p!} \cdot \sum_{k_n}^{P} \prod_{n=1}^{P} X_{i,kj}^n(k_n) \cdot (E_{i,k} + \sum_{m=1}^{P} x_m)^{-1} \quad \text{(IV-54)} \]

(Here, \( E_i \) is the electronic energy given in (IV-5)). All higher order calculations can be handled in the same manner. Within a \( \Gamma_5 \) triplet, (IV-54) produces two second-order RFs, one for the diagonal elements, \( i=j \), and the other for \( i \neq j \). For a single phonon excitation for example, these are respectively

\[ K^{(2)} = (K(\Gamma_4))^2 \cdot -3 \sum_k g_k / \epsilon_k^3, \quad \text{(IV-55)} \]

and \( \frac{1}{2} K^{(2)} \). But no simple relation exists between the two in general.

On the other hand, in the single-mode, zero-temperature limit, \( x_{i,k} \rightarrow x \) say, and the two RFs are

\[ e^{-X} F(i\bar{i}) = -\frac{1}{\epsilon} e^{-X} \cdot \sum_p x_p / p! \cdot P, \quad \epsilon = \hbar \omega_E \]

\[ \equiv -\frac{1}{\epsilon} e^{-X} G(x) \]

and

\[ e^{-X} F(i\bar{j}) = -\frac{1}{\epsilon} e^{-X} G(\frac{1}{2}x) \cdot \]

These are the expressions originally obtained by Ham (1965) in his treatment of the linear coupling. On this simple model, the first and second-order RFs are all determined by a single parameter, \( x \). For full lattice coupling and finite temperatures, this is never the case. Even for weak coupling, where (IV-55) would be a first approximation, the argument of \( K(\Gamma_4) \) is not simply a phonon energy \( \epsilon \), times the lattice sum shown. As noted already by Bates and co-workers, this fact has an immediate use in distinguishing between the cluster and lattice models. (Unlike Bates' (1978) formulae, (IV-54) contains the temperature dependence, and does not rely on an asymptotic expansion for large 'x'.).
CONCLUSIONS

The preceding analysis of reduction factors for JT systems in octahedral symmetry, in the weak coupling limit, has several features which make it the most complete to date:

(i) The effects of finite temperature and of coupling to the phonon continuum are fully accounted for;

(ii) The combined effects of linear and non-linear ion-lattice interactions, and lattice anharmonicity are fully included;

(iii) The dependence of RFs on these has been shown explicitly, to sixth order for $\Gamma_3 \times (\alpha_1 + \varepsilon)$, and to fourth order (linear) for all the $\Gamma_5$, $\Gamma_8$ systems, (though the effects of extending the calculations here as for $\Gamma_3$, have been indicated).

The only comparable calculations, are those of Gauthier and Walker, who considered the zero temperature $\Gamma_3 \times \varepsilon$ system, calculating to fourth order in $V_1$ and $V_2$, and of Bates and co-workers. They treated linear coupling in $\Gamma_5 \times \varepsilon$ exactly (as we do), but only to second order for weak coupling via the $\Gamma_5$ 'phonons'. Both of these groups of authors were restricted by their methods to essentially their applications. The unified formalism we have developed, on the other hand, does not have this limitation.

The basis of our analysis has been our prescription (Sections II.3, II.4, III.1) for extracting the symmetry constraints on the Feynman diagrams in the expansion for the effective perturbation: the calculation of RFs (for any JT system) reduces to the consideration of an economic number of group-theoretic structures (Section III.3). Only the $j$ symbols of the group of the JT system are required to evaluate these, a distinct advantage for the more complex systems. Moreover, for a number of systems, we have deduced much from the knowledge of a few 6j symbols, simplifying computations of their RFs generally, and proving results valid to arbitrary order (and hence coupling strength) in linear, and/or non-linear, and anharmonic couplings: our group-theoretic technique is not merely an aid for specific computations.

The formal dependence of the RFs on the lattice temperature and the couplings of the ion to the lattice modes, prohibits an accurate inference of the magnitudes of ion-lattice coupling parameters for any 'phonon' symmetry, in the manner of the cluster model, for any JT system. Of these, the neces-
ity for consideration of multimode coupling may be determined experimentally, by the detection of one or more parameters, \( b_\nu \) (Section IV.4.1), whose presence denotes the breakdown of a simple sum rule for the RFs, above second order. Temperature dependences will be more difficult to establish, but there exists a simple criterion to minimize their effect: experiments should be performed at temperatures below those at which Raman relaxation processes dominate in a system. Even granting the evaluation of lattice sums, it will still be difficult to differentiate linear, non-linear and anharmonic contributions to the RFs, for systems for which multimode coupling is observed. In the absence of precise calculations, such measurements must remain as being useful only for order-of-magnitude estimates of coupling strengths, at best. Though these conclusions follow from our analysis in the weak coupling regime, similar reasoning should apply in the intermediate and strong coupling regions. The cluster model should not be presumed to be applicable to any system: it is testable.

The Green function solution to RFs in JT systems has little in common with the traditional vibronic approach. The latter is inadequate even for the usual single multiplet calculations: vibronic RFs are not 'observables' in an experiment. We only need retain their construction, from symmetry arguments, for the ground state labels, for notational convenience: for an isolated multiplet, their form generalizes to the observable RFs at finite temperatures. The concept of 'JT active phonons' is irrelevant in the formalism - the symmetric 'phonon' is only 'inactive' for an isolated multiplet in linear coupling. Indeed, there is no 'JT effect': the formalism treats degenerate and non-degenerate states in the same manner. RF calculations are easily extended to a consideration of interactions between separated multiplets, for which our notation and diagram method is most efficient. Similarly, higher order RFs may be calculated in a systematic manner, for any system.

There are two important areas for future study. One is an estimation of temperature and phonon spectrum effects on RFs, using realistic models for density of phonon states and ion-lattice coupling. Variations on the latter should help define limits for the extent of these effects. A second, and major problem, is the removal of the restriction to weak coupling. In the strong coupling limit, a coherent state type solution, in the manner of \( \Gamma_5 \times \varepsilon \), with a variational approach (generator coordinate method) is a possibility.
The inclusion of Butler's (1981) tables of \( j \) and \( jm \) symbols for
crystallographic point groups into the literature, introduces another
(systematic) labelling scheme for the irreps of the groups. We list
below the correspondence between the commonly used labellings (Bethe's
and Mulliken's) and those of Butler for the irreps of \( O \).

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</table>

The following tables use Butler's internal indices only. We shall
use them in the text whenever sub- and superscript irrep labels need to be
specified or \( j \) and \( jm \) symbols written out. For example, a specific labell-
ing of \( b_{\lambda \nu \tau}^\lambda \Gamma (I-21) \) is best given in this notation. Otherwise we use Bethe's
notation throughout. We also follow the conventional classification of
JT systems, with the exception that we do not distinguish between orbital/
spin-orbital electronic states (by using the Mulliken/Bethe labelling).
Thus an electronic triplet, \( \Gamma_5 \), interacting with lattice vibrations trans-
forming as \( \Gamma_1, \Gamma_3, \Gamma_5 \), is denoted by \( \Gamma_5 \times (\alpha_1 + \epsilon + \Gamma_2) \).

We now explain the tables. The signs of the \( 3j \) symbols (triads)
are marked after the multiplicity index as,

\[
\lambda_1 \lambda_2 \lambda_3 r^\pm
\]

The \( 2j \) symbols \( \phi_\lambda \) are just \( (\lambda\lambda00) \). Two tables of \( 6j \) symbols are given:
those of IB are relevant to Section (I.3.3) only and are explained there.
The \( 6j \)s in a column are listed in order of increasing index (top to bottom,
right to left) with

\[
\begin{align*}
\left\{ \lambda_1 \lambda_2 \lambda_3 \right\} \\
\left\{ \nu_1 \nu_2 \nu_3 \right\} \\
\end{align*}
\end{equation}

represented by

\[
\begin{align*}
r_1 \ r_2 \ r_3 \ r_4
\end{align*}
\]
where the sign changes the value of the $6j$ under an interchange of columns. (The hatch # in the tables denotes a square root).

$9j$ symbols are also required for our work. Because they are many in number we shall not reproduce them here. They can be found in Butler (1981). Alternatively, they may be calculated from a product of $6j$s according to,

\[
\begin{vmatrix}
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\nu_1 & \nu_2 & \nu_3
\end{vmatrix}
\begin{vmatrix}
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\end{vmatrix}
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8 REPRESENTATIONS, 34 TRIADS, 407 6J SYMBOLS, MAX MULT=2,

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**IA-6j Symbols**
APPENDIX II

LABELLING OF THE VIBRATIONAL STATES FOR THE JT SYSTEMS

\[ \Gamma_{5} / \Gamma_{8} \times (\epsilon=\tau_{2}) \]

Refer to Sections (1.3.2) and (1.3.3)

Following Judd (1974, Section 5), the oscillator Hamiltonian for a single vibrational quintet is written,

\[ H_{p} = \varepsilon \sum_{i=1}^{5} (a_{i}^{\dagger}a_{i} + \frac{1}{2}) \]

The occupation numbers \( n_{i} \) can be used to label the irreps of \( U_{5} \), and hence the eigenstates of \( H_{p} \), as \( |n_{1}n_{2}n_{3}n_{4}n_{5}\rangle \). For this problem the highest weights \( [n_{1}...n_{5}] \) are of the type \( \lambda_{00000} \), and this restriction on the possible irreps of \( U_{5} \) in turn restricts the \( S_{0}^{3} \) and \( S_{0}^{1} \) irreps in the complete labelling of the eigenstates of \( H_{p} \) (see table on page 1022 of Judd). Thus the \( S_{0}^{3} \) irrep \( J=1 \) never occurs, nor does the \( S_{0}^{3} \) irrep \( (11) \), and we have \( b_{1}^{1}=0 \), \( b_{2}^{2}=0 \) in the \( \Gamma_{5} \times (\epsilon=\tau_{2}) \), \( \Gamma_{8} \times (\epsilon=\tau_{2}) \) systems respectively.

We generalize the problem to a consideration of \( N \) such quintets of energies \( \varepsilon_{a} (a=1...N) \), where now,

\[ H_{p} = \sum_{a=1}^{N} \varepsilon_{a} (a_{a}^{\dagger}a_{a} + \frac{1}{2}) \]

Then there exist \( 25 N^2 \) operators of the form \( a_{la}^{\dagger}a_{\beta}^{\dagger} \), which commute with \( H_{p} \) and are closed under commutation, and can thus be taken as the generators of the group \( U_{5N} \). Amongst these generators is the set \( \{a_{la}^{\dagger}a_{ja}^{\dagger}\} \) (fixed \( \alpha \) - corresponding to Judd's example) which we take to generate the group \( U_{5}(a) \). Then for all \( \alpha \) this set will generate

\[ U_{5}^{\times N} \cong U_{5}(1) \times U_{5}(2) \times ... \times U_{5}(N) \]

a subgroup of \( U_{5N} \). Lastly we may choose a still smaller set of operators, \( \{a_{la}^{\dagger}a_{ja}\} \), to generate \( U_{5} \). Now the eigenstates of \( H_{p} \) can be labelled by the irreps of the group chain,
\[ U_{5N} \supset U_S^{xn} \supset U_5 \supset SO_5 \supset SO_3, \]

and we want to show that for \( N>1 \), the irreps of \( U_5 \) are no longer all of the type \( [\lambda 0000] \). For simplicity take the example of \( N=2 \) and 2 phonons excited. Denoting \( [\lambda^{(n-1)}] \) zeroes as \( [\lambda]_n \), the corresponding irrep of \( U_{10} \) is \( [2]_{10} \). A consideration of the possible phonon occupation numbers shows that in the decomposition,

\[
U_{10} \rightarrow U_5(1) \times U_5(2),
\]

\[
\begin{align*}
[2]_{10} & \rightarrow [2]_5^{(1)} [0]_5^{(2)} + [1]_5^{(1)} [1]_5^{(2)} + [0]_5^{(1)} [2]_5^{(2)} \\
& \quad + [2]_5 + [2]_5 + [11000] + [2]_5
\end{align*}
\]

and the result is proven. Therefore two or more quintets of different frequency allow \( b_1^1, b_2^2 \neq 0 \) for the equally coupled systems.
APPENDIX III

MULTIPLICITY CONSIDERATIONS FOR THE $\Gamma_8$ STATES

Refer to Section (1.3.3)

As $O$ is a subgroup of $SO_3$, the irreps of the latter may be used to distinguish states having the same transformation properties with respect to $O$. The states of our isolated $\Gamma_8$ electronic multiplet can then be labelled as $|x J 3 i\rangle$. (We could take $J=3/2$ corresponding to a fictitious $3/2$ spin, or equal to the free ion $J$ value). The matrix elements of an operator $O_{i\mu}^J$ can be then reduced with respect to the $SO_3$ basis as,

$$<xJ3i| O_{i\mu}^J |xJ3j> = \sum_x <xJ| O_J^i |xJ> (-1)^{J'} (3)_{ii'}^x x (JJ'J)_{3\mu3}^{(i*\mu)} ,$$

(AIII-1)

where we have factorized the resulting coupling coefficient into two $3jm$ factors. Only the $SO_3 \supset O$ factors are of interest throughout this Appendix. (We should include branching multiplicity labels in these factors but our results will be independent of these).

(A) To show that $K_{\Gamma_8}$ is diagonal in $t, p$:

The non-zero factors when $\mu = \Gamma_5$ look like (Butler 1981),

$$\begin{pmatrix} J_{e/o} & J \\ 3 & 5 \\ 3 & 0 \end{pmatrix} \text{ and } \begin{pmatrix} J_{e/o} & J \\ 3 & 5 \\ 3 & 1 \end{pmatrix}$$

(AIII-2)

where $J_{e/o}$ are even/odd valued irreps of $SO_3$. Thus the product multiplicities of $(533)$ in (AIII-1) are always separated by different $SO_3$ $3jm$s. But these $3jm$s and the reduced matrix element in (AIII-1), together form the reduced matrix elements for $O$. For the vibronic ground state, $|zJ3i\rangle$, these are related to those of $|xJ3i\rangle$ by

$$<zJ3| O_J^{5t} |zJ3> = \sum_{p} K_{\Gamma_5} (5)_{tp} <xJ3| O_J^{5p} |xJ3>$$

and this requires $K_{\Gamma_5} (5)_{tp} \sim \delta_{tp}$ for fixed $J'$. 

(B) Relations between HLK's labelling of RFs and ours for $\mu = \Gamma_4, \Gamma_5, \lambda = \Gamma_8$.

(1) $\mu = \Gamma_5$

The phase $(533r) = +,-1$ depending on whether the $r$th term of $\lambda = 5$ appears in the symmetric or anti-symmetric part of $3 \times 3$. Butler labels these as $r = 1, 0$ respectively and this corresponds to HLK's classification of $O_5^m$ into time-odd/even operators (cf. (AIII-2)). So,

$$K_{00}(\Gamma_5) = K(\Gamma_5^e)$$

$$K_{11}(\Gamma_5) = K(\Gamma_5^o)$$

(2) $\mu = \Gamma_4$

For a $J = 3/2$ basis we show that HLK's choice of standard operators has a 1-1 correspondence with the multiplicity labels appearing in our reduced matrix elements $\langle x \ 3/2 \ 3 | o^{J'=2r} | x \ 3/2 \ 3 \rangle$. The proof relies on unpublished tables of $SO_3 \supset O \ 3jms.$ (Butler) whose multiplicity separations depend upon the 6j's of Appendix IB. (This is discussed in the next subsection).

HLK's operator $O_1(\Gamma_4 \ k) = S_k$, in a $3/2$ basis, transforms as $J = 1$, i.e. it corresponds to $O_{12}^1$ of (AIII-1). For

$$O_2(\Gamma_4 \ k) = S_k^3 - \frac{1}{5} S_k^{[3S(S+1)-1]}$$

we note that the tensor product of $S_k$ to form $S_k^3$ transforms as,

$$1 \times 1 \times 1 = 3 + 2 . 2 + 4 . 1 + 0.$$ 

Now $J = 0, 2, + \eta = 2$, and by explicitly subtracting out that part of the product transforming as $J = 1$, we have $O_2(\Gamma_4 \ k) = 0_{12}^{32}$. The $3j$m's involved in the matrix elements of HLK's operators are respectively,

$$\begin{bmatrix} 3/2 & 1 & 3/2 \\ 3 & 2 & 3 \end{bmatrix}_{r=0,1} = 0, 1 \quad \text{and} \quad \begin{bmatrix} 3/3 & 3 & 3/2 \\ 3 & 2 & 3 \end{bmatrix}_{0,1} = -\frac{\sqrt{3}}{7}, 0 \quad \text{(AIII-3)}$$

for Butler's original multiplicity choice. These imply,

$$\begin{align*}
    r = 1 & \leftrightarrow \ \text{HLK's label 1} \\
    r = 0 & \leftrightarrow \ \text{HLK's label 2}
\end{align*}$$
As an aside we indicate the relationship between Koster et al's coupling coefficients, used by HLK, and the 3jms of (AIII-2,-3). For the $O$ operators, $\mu=\Gamma_4,5$, Koster et al label their coefficients by a pair of basis functions $\psi_m, \phi_m$, corresponding to $|3/2 m\rangle$. For $\mu=\Gamma_5$ we use the result of time reversal invariance,

$$<a|\tilde{0}|b> = <a|0|b^*>,$$

where the bar denotes the time reversed quantity. For time even/odd operators, $\tilde{0} = (+/-)0^\dagger$ respectively (Abragam and Bleaney), and one can show from Koster et al's tables that the matrix elements of $O^\dagger$ in the $\psi, \phi$ bases correspond to the $r=1,0$ 3jms of (AIII-2) respectively. For $\mu=\Gamma_4$, one writes the operators $O_{1,2}(\Gamma_4,k)$ in matrix form for spin 3/2. A direct comparison between these matrix elements and Koster et al's shows that $\psi, \phi$ are respectively the basis functions for $O_1, O_2$.

(C) Transformation between the 6j symbols of Appendices IA, B

Since the 6j's are elements of a unitary matrix, a transformation can be defined on each multiplicity index,

$$\{ \}_{r'r} = U_{rr'} \{ \}_{rr'} \quad U U^\dagger = I$$

The transformation (I-34) is required such that $J_{r's'} = \sum_{r'r'}\delta_{rr'}$. Setting $U = |ab\rangle_{cd}$, reality of the 0 6j's and unitarity yields the equations,

$$a^2 + b^2 = c^2 + d^2 = 1, \quad a c + b d = 0,$$

and setting, $J_{01} = 0$ gives,

$$b d - a c - 4/3 (bc+ad) = 0.$$

These imply the ratios $a/b = -d/c = 2$ or $-\frac{1}{2}$. Butler chose,

$$U = \sqrt{\frac{1}{5}} \begin{bmatrix} 2 & 1 \\ -1 & 2 \end{bmatrix}$$

(AIII-4)

The transformation (I-34) thus simplifies most of the 6j's of Appendix IB containing the triple (233). The other consequence of the transformation is the alteration of the multiplicity separation of the $SO_3 \supset O$ 3jm factors. This follows directly from the Wigner relation (Equn. (13.14) of Butler (1975)), where it can be seen that the $r$ label of these factors also appears in the 0 6j's. Thus the 3jms of (AIII-3) are transformed by (AIII-4) to the values now published by Butler.
Below are listed the reductions of the irreps of interest in the group chain $SO_5 \supset SO_3 \supset 0$. We have included the irrep labellings of $Sp_4$ (isomorphic to $SO_5$) used by Pooler and O'Brien, and a shortened notation for the $SO_5$ irreps.

$$
\begin{array}{cccc}
\text{Sp}_4 & = & \text{SO}_5 & \supset \text{SO}_3 & \supset 0 \\
<00> & & (0,0) & \equiv & 0 \\
\frac{1}{2} 0> & & (\frac{1}{2},0) & \equiv & \frac{1}{2} \\
\frac{1}{2} 2> & & (1,0) & \equiv 1 \\
<1 0> & & (1,1) & \equiv 1 + 3 \\
\end{array}
$$

The $2j$ symbols of $SO_5$ can be chosen as $\phi_\lambda = +/-1$ for $\lambda$ a true/spin irrep (Butler (1975) Table 1). Since the above irreps are simple phase (the first irrep for which this is not the case is $<31>$ (Butler)), the necessary $3j$ symbols can be determined from the symmetric and anti-symmetric parts of the Kronecker products. Indeed for the irreps of interest, a value $j_\lambda$ can be assigned to each irrep $\lambda$ such that

$$
\phi_\lambda = (-1)^{2j_\lambda}, \ (\lambda_1 \lambda_2 \lambda_3 0) = (-1)^{Ej_\lambda 1}
$$

Thus the decomposition of the product

$$
\frac{1}{2} x \frac{1}{2} = (0 + 1)_A + (2)_S
$$

gives the following table:

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>0</th>
<th>$\frac{1}{2}$</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>\lambda</td>
<td>$</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>$j_\lambda$</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$\phi_\lambda$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

†The labelling of the $Sp_4$ irreps by Wybourne (1970) (and hence Butler) is not that of Pooler and O'Brien.
6j symbols may now be determined with the aid of tables of $Sp_4$ irrep product decompositions (Wybourne (1970)) and Eqns. 9.9, 9.10, 9.11, 9.18 of Butler (1975). Those sufficient for our calculations are listed below, in the same manner as Appendix I:

\[
\begin{array}{ccc}
2 \frac{1}{2} \frac{1}{2} \frac{1}{2} & 1 \frac{1}{2} \frac{1}{2} & 0 \frac{1}{2} \frac{1}{2} \\
2 \frac{1}{2} \frac{1}{2} \frac{1}{2} & 1/20 & 1 \frac{1}{2} \frac{1}{2} & 3/20 & 0 \frac{1}{2} \frac{1}{2} & -1/4 \\
1 \frac{1}{2} \frac{1}{2} \frac{1}{2} & 1/20 & 0 \frac{1}{2} \frac{1}{2} & -1/4 \\
0 \frac{1}{2} \frac{1}{2} \frac{1}{2} & 1/4 \\
2 \frac{1}{2} \frac{1}{2} & 1/8 & 1 \frac{1}{2} \frac{1}{2} & 1/\sqrt{2} \\
\frac{11}{2} \frac{1}{2} \frac{1}{2} & \pm 1/\sqrt{50} & \frac{11}{2} \frac{1}{2} \frac{1}{2} & -1/\sqrt{20} \\
\end{array}
\]

(There is a freedom of sign for the $6j$ \( \frac{2}{1} \frac{1}{2} \frac{1}{2} \)).

The only 9j we shall require is

\[
\left\{ \begin{array}{c}
\frac{1}{2} \frac{1}{2} \\
0 \frac{1}{2} \frac{1}{2} \\
\mu \frac{1}{2} \frac{1}{2} \\
\end{array} \right\} \left\{ \begin{array}{c}
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\end{array} \right\}
\]

Using the formula given in Appendix I it reduces to:

\[
\left\{ \begin{array}{c}
0 \frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\mu \frac{1}{2} \frac{1}{2} \\
\end{array} \right\} \left\{ \begin{array}{c}
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\end{array} \right\} \left\{ \begin{array}{c}
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\end{array} \right\} + 10 \left\{ \begin{array}{c}
0 \frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\mu \frac{1}{2} \frac{1}{2} \\
\end{array} \right\} \left\{ \begin{array}{c}
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\end{array} \right\} \left\{ \begin{array}{c}
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\frac{1}{2} \frac{1}{2} \\
\end{array} \right\}
\]
Here we reduce the group-theoretic structures of some low order diagrams appearing in $d^{ijab}_{tp}$ to their component $3j, 6j$ and $9j$ symbols, with the aid of the JLVn theorems. The examples we give are taken from the main text and are sufficient in number to help reproduce our formulae. Each Feynman diagram in the accompanying figures is labelled by the letters used in the text to designate its energy denominators. In drawing its group-theoretic contribution, we assume steps 2, 3(a), Section (III.1), have been carried out. The labelling of the structures is arbitrary, and all complex conjugates, $2jm$s, etc., are included. We do not draw the final $6j/9j$ symbols in standard form for simplicity. This can be done by complex conjugating $3jm$ vertices (a stub on each line) or multiplying a vertex ($\alpha\beta\gamma$) by $\phi^*\phi^*\phi^*$ (two stubs on each line) (see Stedman (1975)). In writing out their contributions in standard form though, we use the conventions adopted in Section (I.2) - reality of $2jm$ and $2j$ symbols, neglect of $3js$ corresponding to even permutations, odd permutations equivalent, etc. We separate the examples into the three cases for which step 3(b) requires

1. JLV2 only
2. JLV3 at least
3. JLV4 at least.

(1) JLV2

Feynman graphs restricted to linear interaction vertices are the prototype for these. Those with four electron-'phonon' vertices are shown in Fig. Al. The sequence of operations on these graphs is as in Figs. 7(a-d). The phonon transformation factors are separated off as in Fig. 7(c) and can be omitted in Fig. Al provided we associate labels as $(k,v,r,r'),(l,r,s,s')$. The $3j$ phases attached to the electron-'phonon' vertices are part of the group-theoretic structure - for $A_{kl},$ for example, they disappear only because the 'phonon' lines have been twisted to give a recognizable form. If we denote the electronic irreps $\lambda_i$ by $i$, the $j$ symbols corresponding to the structures in Fig. Al are:
(2) JLV3

Fig. A2. This example is that of Figs. 13(g,k,k) (for the change of labels \( v_1 v_2 v_3 \rightarrow v^* v^* v^* \)). Conjugate phonon transformation factors, Fig. 5(k), require two stubs (2jm unitarity) placed on the 'phonon' line (\( v \) in this example) to make the group theoretic structure an invariant, suitable for further application of JLVn. All labels common to the structure and the phonon transformation diagram are summed. The former reduces to

\[
\sum_u \begin{cases} \mu^* 25* \\ 6 1 \end{cases}_{\text{trr}'u} \begin{cases} \mu 34* \\ 5 2 \end{cases}_{\text{uss}'p} (2*5\mu u) (3*4\mu p)
\]

\[
B_{k\ell}^r: \begin{cases} 6 \tau^* 5* \\ 1* 2 \nu \\ 3* 4 \end{cases} \begin{cases} s' \\ r \\ t \end{cases} \phi_2 \phi_3 (1*2\nu r) (4*5\nu r') (2*3\nu s) x (5*6\nu s') (3*4\mu p)
\]

\[
C_{k\ell}^r: \begin{cases} \mu^* 4 5* \\ 6 1 \end{cases}_{\text{trr}'p} \begin{cases} \nu 1 4 \\ \mu 2 3 \end{cases}_{\text{ups}'s} \phi \phi (2*3\nu s) (4*5\mu p) \delta_{ss'} \delta_{24}
\]

\[
D_{k\ell}^r: \sum_u \begin{cases} \nu^* 2 3* \\ \tau 4 1 \end{cases}_{\text{urr}'s} \begin{cases} \nu 5 6* \\ \mu 1 4 \end{cases}_{\text{upts}'t} \phi \phi (2*3\nu s) x (5*6\nu s') (1*4\nu u) (6*1\mu t)
\]

(3) JLV4

Fig. A3. This particular example is that of Figs. 12(f(1)) and 12(j), if the latter is relabelled as \( v_1 v_2 v_3 v_4 \rightarrow v^* r^* p^* k \). In the text we have chosen to associate the two 3j symbols labelled by \( u v \) with the phonon transformation diagram, but the choice is arbitrary. The group structure becomes

\[
\sum_{xy} \begin{cases} \sigma 2 3 1 \\ \mu^* 3 4* \end{cases}_{\text{xmmu}} \begin{cases} \sigma 6 1 \\ g^* 4* \end{cases}_{\text{txyp}} \begin{cases} \sigma 5 6 4 \\ \phi \phi \phi \phi \end{cases}_{\text{yrsv}} (4*5\nu r) x (1*2\nu u) (3*4\nu q) (4*5\nu s) (5*3\nu n) (1*5\mu t)
\]

x (1*2\nu u) (2*3\nu m) (4*5\nu p) (5*6\nu s) (3*4\mu p)
APPENDIX VI

METHODS FOR EVALUATING FEYNMAN DIAGRAMS
AND LATTICE SUMS

We first show how the contribution of any diagram to the self-energy operator $M_1(z)$ may be calculated most efficiently. As an example we choose the diagram in the figure below, which suffices to illustrate the method for more complicated diagrams. Following the rules of Section (II.1.1), one can assign any direction to the 'energy' currents, $x_i$, of the zero-order phonon propagators, provided their sum (with $z$) at any vertex is conserved. We deliberately choose these 'energies' to flow from left to right, so that they appear in the arguments of the electronic propagators prefixed by a positive sign. Then in summing over the (discrete) $x_i$, the poles of these propagators make no contribution in the Abrikosov limit.

For the ionic and phonon state labels shown, the contribution to the matrix element $(M_1(z))_{ij}$ is,

\[
\sum_{k\ell m} V_{iak} V_{bck} V_{cjm} V_{1k1m} (\tilde{N}_{sab}^{1}) x
\]

\[
x \sum_{x_1, x_2} d_k(x_1 + x_2) d_k(x_2) d_m(x_1) g_a(z + x_1 + x_2) g_b(z + x_1 + x_2) g_c(z + x_1).
\]

(AVI-1)
To perform the last summations, it is easier to rewrite the phonon propagator in (II-8) in a contracted form which leaves the sum on the phonon absorption/emission terms, \((x = \varepsilon_k/(-\varepsilon_k))\), to a later stage. Firstly we write,

\[
d_k(x) = \sum_{s_k = \pm 1} \frac{s_k}{x - s_k \varepsilon_k}
\]

We then define \(s_k \varepsilon_k \equiv k\), and take \(s_k = \sum \frac{s_k}{s_k \varepsilon_k}\) to represent the sign summation. Now \(d_k(x) = s_k (x - k)^{-1}\), and the sums to be evaluated are,

\[
\sigma_{k\ell m} \sum_{x_1, x_2} \frac{g_{\alpha \beta}(z + x_1 + x_2)}{(x_1 + x_2 - k)(x_2 - \ell)(x_1 - m)}
\]

where \(\sigma_{k\ell m} = \sigma_{k} \sigma_{\ell} \sigma_{m}\) and we have set \(g_{\alpha \beta}() = g_{\alpha}() \cdot g_{\beta}()\). The replacement of \(\pm \varepsilon_k\) by \(k\) etc. presents no problems in notation: the sum \(s_k\) in (AVI-1) is always performed after \(s_k\). The sum on a variable \(x_i\) now reduces to multiplying the residue of the sum and at a singularity \(p\) of a denominator by \(n(p)\), the phonon population factor. For example, the sum on \(x_2\) gives

\[
g_{\alpha \beta}(z + x_1 + x_2) \cdot g_{\alpha \beta}(z + \ell) - n(k) \cdot g_{\alpha \beta}(z + k)
\]

where, for \(x_2 = k - x_1\), we have used \(n(k-x) = n(k)\), since \(x = 2 \pi m / \beta\).

Finally we obtain for (AVI-2),

\[
\sigma_{k\ell m} \left\{ n(\ell) \cdot n(m) \cdot g_{\alpha \beta}(z + \ell + m) \cdot g_{\alpha \beta}(m) \right\} +
\]

\[
+ n(k) \cdot n(-\ell) \cdot g_{\alpha \beta}(z + k) \cdot g_{\alpha \beta}(z + k - \ell)
\]

\[
- n(k) \cdot n(m) \cdot g_{\alpha \beta}(z + k) \cdot g_{\alpha \beta}(z + m),
\]

with the aid of the relation,

\[
n(k-\ell) \left\{ n(\ell) - n(k) \right\} = -n(k) \cdot n(-\ell)
\]

Note that the sequence of performing the sums is important if one wishes to avoid calculating the residues of the electronic propagators. Thus, summing on \(x_1\) first in (AVI-2) produces a factor \(g_{\alpha \beta}(z+k-x_1)\), which has a pole at \(x_2 = (z+k-\theta_c)\). As \(\theta \to \infty\), \(n(x_2) \to -1\) now, \((z = (2m+1) \pi / \beta)\), and instead of the three terms as in (AVI-3), four terms are produced, one of which bears no resemblance to the phonon processes indicated by the diagram.
(although the two sequences must be equivalent). Hence our reason for avoiding such arguments. The sequence one should use, is to sum over the $x_i$'s of order of increasing appearance in the arguments of the electronic propagators. (AVI-3) can now be substituted in (AVI-1) and the contribution to $\Delta_{1}(E)_{ij}$ calculated from

$$\Delta_{1}(E) = \frac{1}{2} (M_{1}(E + io) + M_{1}(E - io))$$  

(AVI-4)

For diagrams which do not involve anharmonic vertices the energy factors in $M_{1}(2)$ can be written down directly: for phonon lines labelled $k, \ell, m...$ in a diagram, there is a term $\sigma_{km...}$, $n(k)$ $n(\ell)$ $n(m)...$, multiplied by a product of internal propagators, $a_{ij}(...)$, with arguments

$$(z + k + \ell + m + ...)$$

whenever the $k, \ell, m...$ phonon lines pass overhead, e.g. (III-7).

We now consider how the sums over $k, \ell, etc.$ may be evaluated. The standard method is to assume that the vibrational frequencies $\omega_{k}$ are sufficiently dense to approximate a continuous variable. A density of states function $D_s(\omega)$ is then defined such that $D_s(\omega).dw$ is the number of modes in the frequency range $\omega + \omega + d\omega$ for the polarization branch labelled $s$. It is given by (Kittel (1971) Chap. 6)

$$D_s(\omega) = \frac{V}{8\pi^3} \int \frac{ds}{|\text{grad}_{\omega}^{k}\omega_{ks}|}$$  

(AVI-5)

where the integral is over the surface of constant $\omega$ in $k$-space. Lattice sums can then be replaced by integrals according to,

$$\sum_{k} F(\omega_{k}) + \int_{0}^{\omega_{\text{max}}} F(\omega) D(\omega). d\omega$$

where $D(\omega) = \sum_{s} D_s(\omega)$. For our expressions, $F(\omega)$ represents a product of a frequency dependent coupling parameter (although its functional form is unknown we assume all its derivative exist), a phonon population factor and a term of $O(\omega^{-2})$. As $D(\omega)$ is also a complicated function, the following discussion is necessarily limited to the calculation of such integrals in principle. As a specific example of a lattice sum we chose the second term of (III-10), as it incorporates all the complex features to be found. In expanded form it is, to within constants,
and it converts to integrals of the form

\[
\int_{0}^{\omega_{\text{max}}} \frac{f_{1}(\omega_{k}). f_{1}(\omega_{k}). f_{2}(\omega_{k}, \omega_{l})}{(\omega_{k}+i\epsilon)^{2}} \left( \frac{f_{2}(\omega_{k}, \omega_{l})}{(\omega_{l}+i\epsilon)^{2}} \right) \frac{1}{(\omega_{k}-\omega_{l}+i\epsilon)^{2}}
\]

It is the integrations around the poles of this integral that are of concern (we assume \( f_{1} \) has no poles). Consider the integral over \( \omega_{k} \). Treating \( \omega_{k} \) as a (variable) constant \( a \), we can rewrite simply as

\[
\int_{0}^{\infty} \frac{f(x)}{(x+i\epsilon)^{2}(x-a+i\epsilon)^{2}} \quad \text{(AVI-6)}
\]

(The \( i\epsilon \) term is really the limit \( \epsilon+0^{+} \) for the double integral. We assume that the limit exists separately for each integral). (AVI-6) can be expanded in partial fractions giving particular cases of the general integral

\[
\int_{-\infty}^{\infty} \frac{f(x)}{(x-a+i\epsilon)^{n}} \quad \text{(AVI-7)}
\]

namely, \( n=1,2, a \in [0, X] \). \( f(x) \) is zero outside the domain \([0, X]\). All of our lattice sums will reduce to (successive) integrals of this type, and for RFs of higher order than the first, of order \( m \) say, values of \( n \) from 1 to \( (m+1) \) will occur. The integration around the pole at \( x=a \) for \( n=1 \) is a well known result in dispersion theory:

\[
\frac{1}{x-a+i\epsilon} = P \frac{1}{x-a} + i \pi \delta(x-a) \quad \text{(AVI-8)}
\]

where the integral of \( f(x) \) is understood to be taken on both sides, and \( P \) denotes the Cauchy principal value

\[
P = \lim_{\epsilon \to 0^{+}} \left( \int_{-\infty}^{a-\epsilon} + \int_{a+\epsilon}^{\infty} \right).
\]

\( f(a) \) must be continuous. The case of non-simple poles seldom arises in perturbation theory. However it is managed by the theory of generalized functions: these are continuous linear functionals \( (g, f) \) which associate with a sufficiently good function, \( f \), a number

\[
(g, f) = g(x). f(x) \ dx
\]

\( g(x) \) may be regular or singular and \( f \) is 'good' if it has a finite domain and is infinitely differentiable. By an analysis of these functionals
Gelfand and Shilov (1964) derive a generalization of (AVI-8) (for \(a=0\)),

\[
(x+io)^{-n} = x^{-n} + i \pi \frac{(-1)^{n-1}}{(n-1)!} \delta(n-1)(x)
\]

There is actually more detail to the integral of the real part than suggested here. In particular for \(n=2\), (AVI-7) produces a real part

\[
\text{Re} ( (x-a+io)^{-2} f(x) ) = \int_{0}^{\infty} \frac{f(x-a) + f(a-x) - 2f(a)}{(x-a)^2} \, dx \quad (\text{AVI-10})
\]

(We can set \(f(-y) = f(y)\)). Implicit in this result is the requirement that \(f^{(1)}(a)\) exists, and here we run into a difficulty: the density of states, \(D(x)\), which is included in \(f(x)\), exhibits singularities. This can be seen from (AVI-5), where the surface integral diverges at the critical frequencies as \(d\omega/dk\) approaches zero or changes sign discontinuously (when two branches cross in the dispersion curves). For 3-dimensional lattices these singularities produce slope discontinuities in \(D(x)\) at a (minimal) number of critical points, \(c\), in the range \([0,1]\) (Donovan and Angress (1971)). Provided these discontinuities are finite though, \(D^{(1)}(c)\) and hence \(f^{(1)}(c)\) can be defined, and (AVI-10) evaluated across these points. (Whether or not the integral converges will depend upon \(f(x)\) itself. If \(f(x) \sim x^m\), \(m \leq 1\) it will diverge about \(x = a\). \(f(x) = |x|\) about \(x = 0\) is an illustration). However infinite slope discontinuities can exist. For example, van Hove used topological arguments to prove that \(D^{(1)}(\omega) \to -\infty\) as \(\omega \to \omega_{\text{max.}}\), and numerical calculations of \(D(\omega)\) show sharply peaked features at a finite (and usually small) number of frequencies (though not all peaks are necessarily of the 'infinite' type. See Bilz and Kress (1979) for graphs of, and references for, \(D(\omega)\) and \(\omega(ks)\) in various structures). Thus (AVI-10) is undefined across an \(\varepsilon\)-neighbourhood of these points. Furthermore, as the second and higher derivatives of \(f(x)\) do not exist at all critical points, the use of (AVI-9) for \(n>2\) about these points is meaningless. So in general, given an exact \(D(\omega)\), we cannot perform our lattice sums exactly - with one exception. This occurs for \(a = 0\), because \(D(\omega) \sim \omega^2\) at low frequencies. Thus lattice sums which do not involve a difference of phonon frequencies in the denominator are always manageable (for all \(n\)). For \(a \neq 0\) there are two possibilities. One is to approximate the integrals around the critical points, \(\int_{C+\varepsilon}^{C+\varepsilon} f(x)\), and observe their behaviour as \(\varepsilon \to 0\). But although \(D(x)\) can be approximated about \(x = c\) by a suitable sequence of differentiable functions (these will uniformly converge to \(D(x)\) as the latter is continuous), \(D^{(n)}(x)\) is not necessarily approximated by their...
derivatives: different choices of functions will give different values for the integral in the limit \( \varepsilon \to 0 \). The other possibility is simply to ignore the contributions around \( x = c \) for some small \( \varepsilon \) (an expansion of the error in powers of \( \varepsilon \) should be possible). For example, one does not expect the removal of the singularity at \( \omega_{\text{max}} \) to affect the integral much.

While mathematically imprecise, these are the only methods available for handling an exact \( D(x) \). The saving grace is that \( D(x) \) is never precisely known: the shape of a singularity about \( x = c \) may be, but its magnitude, \( D(c) \), must still be estimated on a lattice dynamical model, (see Maradudin et al. (1963) for methods of calculation). The latter are designed to reproduce the observed dispersion curves, \( \omega(k) \), by calculating with a large number of \( k \) values in the Brillouin zone. Thus in any numerical calculation of our lattice sums, which is probably the easiest method given the complexity of \( D(\omega) \), the mesh size, \( \Delta \), between discrete values \( k, \frac{\Delta}{2} = k + \Delta, \ldots \), will set limits on the smallness of quantities like \( \omega_k - \omega_{\frac{k}{2}} \) near the critical points and elsewhere. The behaviour of the summation for smaller \( \Delta \) would then have to be observed. Similar problems have been considered before in lattice sums (Maradudin and Fein (1962)).

In summary, for any realistic calculation, all our lattice sums are manageable. The presence of (a finite number of) critical points in the density of states does not affect our conclusions about the role of resonating denominators in these sums.
APPENDIX VII

ELIMINATION OF THE LINEAR INTERACTION

TRANSFORMING AS $\Gamma_1$

This can be achieved for any isolated electronic multiplet by using the canonical transformation method of Section (IV.1.1). Consider first the Hamiltonian,

$$H = H_0 + V_l$$

$$= \sum_i \theta_i a_i^+ a_i + \sum_k \varepsilon_k (b_k^+ b_k + \epsilon_k)$$

$$+ \sum_{i,k} V_{iik} a_i^+ a_i \phi_k + \sum_{i,j,k} V_{ijk} a_i^+ a_j \phi_k$$

where the state labels, $i$, are quite arbitrary for the moment. The result of Section (IV.1.1) is that the diagonal part of the interaction here can always be absorbed into a new zero-order Hamiltonian. We do this for the symmetrized part of $V_{iik}$ transforming as $\Gamma_1$ alone. The symmetrized form of the coefficient $V_{ijk}$, (IV-1), allows us to write,

$$V_{ijk} = \sum_{r,v} V^{(r,v)}_{ijk}$$

The operator $u_k$ in (IV-3) can then be expanded as $\sum_{r,v} u^{r,v}_k$, and we perform the canonical transformation, $SO^*_2$, of an operator $O$, for $v = \Gamma_1$ only, i.e.

$$S = \exp\left(\sum_{r,v} u^{r,v}_k \tau_r\right), \quad u^{r,v}_k = \sum_{i,k} V^{(r,v)}_{iik} a_i^+ a_i \epsilon_k$$

The fermion and boson operators then transform as in (IV-4), but with $u_k + u^{r,v}_k$, $z_i \rightarrow z^{r,v}_i$. The effect on (AVII-1) is to replace:

(i) $\theta_i$ by $\theta'_i = \theta_i - \sum_k |V^{(r,v)}_{iik}|^2 \epsilon_k$,

(ii) the diagonal interaction by

$$\sum_{i,k} V^{(r,v)}_{iik} a_i^+ a_i \phi_k (\epsilon_k - 2 u^{r,v}_k)$$
(iii) and the off-diagonal interaction by,

\[ \sum_{i\neq j} \sum_{kr\neq 0} V_{ijk} \hat{a}_i \hat{a}_j e^{(z_i^O - z_j^O)} (\phi_k - 2u_k^O). \]

The product in (ii), \( \sum_k \sum_{ijk} V_{ijk}^O \), \( v \neq 0 \), is zero by Schur's lemma (cf. (II-39)); similarly for (iii). And within a multiplet \( (x_i, x_j, y_i, y_j) \), \( V_{ijk} = V_{jjk} \), so \( z_i = z_j \). For this case then the total interaction is simply,

\[ \sum_{i\neq j} \sum_{kr\neq 0} V_{ijk} \hat{a}_i \hat{a}_j \phi_k \]

and the effect of the \( \Gamma_1 \) 'phonon' is only to be found in the zero-order Hamiltonian. For our RF calculations the total Hamiltonian which must be transformed is,

\[ H_0 + V_{\Gamma 1} + H_s \]

For an isolated multiplet \( H_s \) is unchanged, and the calculation of \( d_\lambda^\pi (\mu) \) proceeds as if the coupling via the \( \Gamma_1 \) 'phonon' did not exist (the replacement of \( \theta_i \) by \( \theta_i' \) is of no consequence within a multiplet). Our RFs will thus be independent of this component of the linear interaction. (Strictly, we should still indicate the presence of this coupling by labelling the JT systems as \( \lambda x (a_1 + v) \), but the convention is to ignore it altogether and we follow this).

When higher-order interactions are included in (AVII-1) the \( \Gamma_1 \)-type coupling always exists. Consider the terms \( V_2, V^{(3)} \) of (II-16,-17). In the first place it is impossible to eliminate \( V_{ijkl}^{(o)} \) from \( V_{ijkl} \); in the second, the above transformation inserts \( V_{ijk}^{(o)} \) into new terms alongside \( V_{ijkl} \) and \( V_{klm} \). Nevertheless the transformation remains useful as we now show. Consider \( V_2 \).

With \( \phi_k + \phi_k - 2u_k^O \), it gives rise to a term linear in the phonon operators,

\[ -2 \sum_{ijkl} V_{ijkl} \hat{a}_i \hat{a}_j (\phi_k u_k^O + \phi_k u_k^O). \]

We interchange \( k,l \) in the second term, use \( V_{ijkl} = V_{ijlk} \), and substitute for \( u_k^O \) to obtain a coefficient,

\[ -4 \sum_{ijkl} V_{ijkl} \epsilon_{ik}^{-1} \epsilon_{jl}^{-1} = -4 \sum_{iajk} \epsilon_a^{-1} \epsilon_{jk}^{-1}, \]

where we have artificially included an intermediate state, \( a \), so that the diagram representation of this coefficient can be made obvious. Besides
this linear term, the usual quadratic interaction (II-16) is produced, as well as a purely electronic operator,

$$V' = \sum_{ij} V'^{ij}_{aa} a_i^+ a_j^+ , \quad V_{ij} = \sum_{k, kl} V^{(o)}_{ikj} V^{(o)}_{jkl} \phi_k^\epsilon \phi_l^\epsilon \epsilon^{-1}$$

By Schur's lemma $V_{ijk\ell}$ must transform as $\Gamma_1$, so $V'_{ij}$ is diagonal and contributes to $\theta'_1$. Likewise, $V^{(3)}_{ij}$ transforms to operators containing $(\phi_k^\epsilon)^n$, $n=0,1,2,3$, but diagonal in the electronic states. $n=0$ gives an addition to $\theta'_1$ of

$$-\frac{4}{3} \sum_{k, kl} V^{(o)}_{ik} V^{(o)}_{i\ell} V^{(o)}_{k\ell} \epsilon^{-1}$$

and $n=3$ gives $V^{(3)}_{ij}$ back again. We now gather the $n=1,2$ terms with those from $V_2$ and (AVII-3), to obtain effective linear and quadratic interactions,

$$V'_1 = \sum_{ijk} V'_{ijk} a_i^+ a_j^+ \phi_k^\epsilon , \quad V'_2 = \sum_{ijk\ell} V'_{ijk\ell} a_i^+ a_j^+$$

with

$$V'_{ijk} = V^{(rvf)}_{ijk} - 4 \sum_{k, kl} V^{(o)}_{ik} V^{(o)}_{j\ell} \epsilon^{-1}$$

$$+ 2 \sum_{k, kl} V^{(o)}_{ia} V^{(o)}_{aj} \epsilon^{-1}$$

and

$$V'_{ijk\ell} = V^{(o)}_{ijk\ell} - \sum_m V^{(o)}_{ijkm} \epsilon^{-1}$$

Thus $V'_1$ is the sum of terms at order $V_1$, $V_2 V_1$, and $V^{(3)} V_1$ where only the last two orders can have a $\Gamma_1$-type dependence. Provided we are prepared to redefine all electron-phonon interaction vertices in this way, we can always accommodate the removal of $V^{(o)}_{ilk\ell}$ from $V_{ijk}$, for any order of non-linearity and anharmonicity. The Hamiltonian prior to the transformation

$$H_0 + (V_1 + V_2 + V^{(3)} + \ldots) + H_s$$

simply becomes,

$$H'_0 + (V'_1 + V'_2 + V^{(3)} + \ldots) + H_s$$

afterwards.
REFERENCES

Abou-Ghantous M. and Bates C. A. 1980 J. Physique Letts. 41, L263

Abou-Ghantous M., Bates C. A., Fletcher J. R. and Jassaud P. C.


Abragam A. and Bleaney B.

Abrikosov A. A.
1965 Physics 2, 5.

Abrikosov A. A., Gor'kov L. P. and Dzyaloshinski I. E.

Bates C. A.

Bates C. A., Brauns P., Fletcher J. R., Jassaud P. C.
1976 J. Physique 37, 763.

Bates C. A., Chandler P. E. and Stevens K. W. H.

Bates C. A., Maynard C. M., Rampton V. W. and Shellard I. J.

Bates C. A. and Steggles P.

Bersuker I. B. and Polinger V. Z.

Biernacki S. W.

Bilz H. and Kress W.
1979 Phonon Dispersion Relations in Insulators (Springer-Verlag, New York).
<table>
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<th>Author(s)</th>
<th>Year</th>
<th>Publication Details</th>
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<tbody>
<tr>
<td>Butler P. H.</td>
<td>1975</td>
<td>Phil. Trans. R. Soc. A277, 545.</td>
</tr>
</tbody>
</table>
Judd B. R. 1976 Colloque Int. du CRNS, Spectroscopie des Eléments lourds dans Les Solides (Lyon).
Messiah A. 1965 Quantum Mechanics (North-Holland, Amsterdam).
Muramatsu S. 1977 Solid St. Comm. 21, 125.


A preliminary account of the preceding work has been published in

Journal of Physics C: Solid State Physics

Vol 10, L671-675 (1977)

We include the article below. We also present for examination the article entitled, 'Ion-lattice coupling, spectral moments and transition interference in Fe$^{2+}$:MgO', published in

Journal of Physics C: Solid State Physics

Vol 10, 1549-1559 (1977)

This work was carried out in collaboration with Dr G.E. Stedman.
LETTER TO THE EDITOR

A diagram approach to reduction factor calculations in Jahn–Teller systems

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Received 15 August 1977

Abstract. A general technique is developed for calculating reduction factors in the weak coupling limit for interaction with a phonon continuum. The many-body theoretic approach of Gauthier and Walker is combined with a diagram representation of symmetry constraints. As an application, reduction factors are calculated for a triplet state in cubic symmetry, correct to fourth order in linear coupling at zero temperature. For example, in the T \otimes t_1 problem it is shown that on coupling to lattice modes of unequal energy, K(E) + \frac{1}{2}K(T_{1,3}) = K(T_{1,1}) < 1 at fourth order.

The qualitative effects of coupling a Jahn–Teller active ion to more than one lattice mode have been of recent interest. For E \otimes e coupling in cubic symmetry, the linear relation between the reduction factors p, q predicted by single-mode theories is not obeyed in a multimode theory (e.g. Gauthier and Walker 1973, 1976); this has led to experimental confirmation of the necessity of the multimode theory. Similar theoretical treatment of reduction-factor relations in systems of different symmetry have been given by Ham (1972), Leung and Kleiner (1974), Ham et al (1976). We extend these results by applying the method of Gauthier and Walker (1976) to an arbitrary system, generalising the group-theoretic aspects of their analysis using the diagram notation of Stedman (1975). This has the important advantage of a coherent and systematic presentation since the group theoretic information is latent in the Feynmann diagrams considered by Gauthier and Walker. The details of the diagram representation will be indicated by parenthetical description in the following paragraphs.

We start with eigenstates of an electronic Hamiltonian \( H_0 \) (whose propagators are represented by solid lines) labelled by the irreducible representation \( \lambda \) (in general, a Greek letter) and component \( \alpha \) (the corresponding Latin letter), with respect to the point group \( G \). Phonons (wiggly lines) interact with Hamiltonian \( V \) in all orders with these states to give a dressed excitation (double lines) in a one-particle theory (figure 1(a)). This single-particle approximation is known to be inadequate in general, but may be expected to be rather more satisfactory for the commonly studied singlet–multiplet spectrum than the multiplet–multiplet spectrum (Stedman 1976a). In the weak-coupling limit we apply first an electronic perturbation \( H_s \), expandable (broken line) in terms of irreducible tensor operators:

\[
H_s = \sum_{\mu} h_{s_{\mu}} O_{s_{\mu}}
\]
Figure 1. Components of the diagram formulation, and construction of the reduced matrix elements $d^{\mu}(\mu)$ defining the reduction factors $K^{\mu}(\mu)$.

Figure 2. Group-theoretic reduction of a typical diagram for the evaluation of its contribution to the reduction factors.

This perturbation modifies the electronic states (solid line with double arrows, figure 1(c)), and the phonons modify it further (double line with double arrows, figure 1(d)).

The self-energy operator $\Sigma$ (cross-hatched circle) in this Dyson equation may be expanded in orders of $H_{\xi}$; the first-order term $\Sigma_{1}$ in this expansion, (figure 1(e)) is of immediate interest in calculating reduction factors. It is an invariant diagram under
the operations of $G$; the transformation from lattice phonon to symmetry coordinate basis (e.g.: $f_{\alpha}$ of Gauthier and Walker in the $E \otimes e$ problem $\leftrightarrow$ circle labelled $f$ in figure (2) is an invariant node (Stedman 1976b). We may then use the Wigner–Eckart theorem in its diagram form (the extended Jucys theorem JLV 3) on figure 1(e) to obtain figure 1(f), in which the upper diagram contains a coupling (Clebsch–Gordan) coefficient for $G$ and the lower diagram a reduced matrix element, related to $d^{\mu}(\mu)$ (figure 1(g)). For the purpose of this Letter, we may suppress the multiplicity index $r$. It then follows from an obvious generalisation of the argument of Gauthier and Walker (1976) that the reduction factor $K^{\mu}(\mu)$ for an operator in $H_\lambda$ of symmetry $\mu$ acting within a manifold of electronic states of symmetry $\lambda$ is

$$K^{\mu}(\mu) = (1 + d^{\lambda}(\mu))/(1 + d^{\mu}(1))$$  \hspace{0.5cm} (1)$$

where $1$ is the identity irreducible representation of $G$. Figure 1(e, g) and equation (1) define a diagram method for calculating reduction factors to arbitrary order in the ion–lattice interactions. We shall concentrate on the linear interaction within the electronic multiplet $\lambda$:

$$V = \sum_{\ell m} f^{\lambda \alpha}(m) U^*_{\alpha \ell} \phi_k$$  \hspace{0.5cm} (2)$$

where $\phi_k = b_k + b^*_k$ is a lattice mode operator, $U^*_{\alpha \ell}$ an electronic tensor operator in the normalisation of Payne and Stedman (1977) and $f^{\lambda \alpha}(m)$ the corresponding matrix element, generalising the coefficients $V_\alpha$, $V_\gamma$ of single-mode theories and the coefficient $f_{\alpha \ell}$ of Gauthier and Walker (1976). Results obtained by restricting $\nu$ in equation (2) will be denoted by a subscript $K^{\mu}(\nu)$.

Each term in figure 1(e) is reduced to its group-theoretic essentials—$6j$ symbols and reduced matrix elements—by application of the diagram reduction theorems JLV n. In the case of Gauthier and Walker (1976) $G = O$, $\lambda = \nu = E$, $K(A_2) = p$, $K(E) = q$. The first term, for example, in $\Sigma_1$ successively reduces as in figure 2. The tetrahedral figure is the $6j$ symbol

$$A(\mu) = \begin{bmatrix} \mu & F & E \\ F & E & E \end{bmatrix}$$

tabulated by Griffith (1962). Since multiplicity labels and $2 - jm$ vertices have trivial values here, and since $A(E) = 0$, $A(A_1) = -A(A_2)$ there are several simplifications in this problem. For example we find that: (i) figure 3(a) contributes to $d^{E}(1)$ and $d^{F}(A_2)$, and in equal proportions, the relative sign being determined by the number of vertices between the broken and other external lines; (ii) figure 3(b) contributes just to $d^{E}(E)$; and (iii) diagrams not expressible in one of these forms (e.g. figure 3(c, d)) do not contribute to any reduction factor. In this way we may confirm quite rapidly the results of Gauthier and Walker (1976) for general coupling in fourth order at zero temperature, except indeed for a correction to their value for $p$ (in the term of fourth order in the linear interaction, their equation 4·14a) in favour of their earlier value (Gauthier and Walker 1973). We agree with all earlier workers that $2q = 1 + p$ for general coupling to isoenergetic lattice modes.

While the particular simplifications mentioned above do not generalise, we find the diagram formalism to be superior in all problems of reasonable complexity.

We have calculated second- and fourth-order contributions to reduction factors in the system $T \otimes (e + \ell)$, at zero temperature and in linear coupling (equation (2))
for simplicity. At second order

\[ K_{e+1}(E) = 1 - \sum_k 3h_k/\varepsilon_k^2 \]  \hspace{1cm} (3)
\[ K_{e+1}(T_1) = 1 - \sum_k 3(3g_k + h_k)/\varepsilon_k^2 \]  \hspace{1cm} (4)
\[ K_{e+1}(T_2) = 1 - \sum_k (3g_k/2 + h_k)/\varepsilon_k^2 \]  \hspace{1cm} (5)

where \( \varepsilon_k \) is the energy of a phonon in lattice mode \( k \),

\[ g_k \equiv \sum_n = \alpha_k |f_k^n(E_n)|^2/|E| \] (figure 3(c)) and

\[ h_k \equiv \sum_n = \alpha_k |f_k^n(T_2)|^2/|T_2|. \]

(For coupling to a single mode of either symmetry,
\[ \sum_k g_k \rightarrow \hbar V_k^2/2\omega, \quad \sum_k h_k \rightarrow \hbar V_k^2/2\omega. \]

![Diagram](image)

\textbf{Figure 3.} (a)-(d). Generalisations to higher orders of interaction of the diagrams contributing to \( \Sigma_{T_2} \); (e), diagram definition of the basis transformation (Stedman 1976b) from lattice mode to local symmetry coordinate \( E \).

The effective mass has been set equal to unity. As shown by Bates \textit{et al} (1974) and Ham (1965, 1972) these second-order contributions satisfy the sum rules \( K_{e+1}(E) = K_{e+1}(T_1) \) and \( K_{e+1}(E) = K_{e+1}(T_2) \) are obeyed.

Fourth-order contributions to these reduction factors are given in table 1. From these we readily deduce the following statements as special cases:

(i) The sum rules mentioned above are invalid at fourth order, as expected. In particular, the inequality of \( K_{e+1}(T_1) \) and \( K_{e+1}(E) \) is a consequence of the vanishing of the \( 9 - j \) symbol derived from figure 3(b) when \( \mu = T_1 \), but not when \( \mu = E \).

(ii) The general relations \( K_{e+1}(E) = 1, K_{e+1}(T_1) = K_{e+1}(T_2) \) are obeyed.

(iii) For equal coupling to two isoenergetic modes of \( E \) and \( T_2 \) symmetry \( (g_1 \rightarrow g_2, \delta_{11}, h_1 \rightarrow h_2, g_1 = 4h_1/3 \) \( \mu = T_1 \)), the sum rules \( K_{e+1}(E) = K_{e+1}(T_2) \), \( 5K_{e+1}(E) = 3K_{e+1}(T_1) = 2 \) which are associated with the \( R_3 \) symmetry of this special case (O'Brien 1971, Romestain and Merle d'Aubigne 1971, Judd 1974) are satisfied.

(iv) If we define \( \bar{K}_{e+1} = K_{e+1}(E) - 1 + 3/2[K_{e+1}(T_2) - K_{e+1}(T_1)] \), at fourth order

\[ \bar{K}_{e+1} = 3 \sum_k h_k^2 (\varepsilon_k - \varepsilon_0) / \varepsilon_k^2 (\varepsilon_k + \varepsilon_0)^2. \] (6)
Letter to the Editor

Table 1. Fourth-order contributions to the reduction factors $K_{ii}^{(0)}$ in linear coupling at zero temperature. Except when subscripted, $k = e_i; m = e_i + e_i. \delta K_{ii}^{(0)} = \sum \Sigma_{i=1}^{\infty} P_i Q_{ii}(\omega)/k^2m^2 - \delta Q^{(0)}(1)K^{(0)}(0)$.

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<tr>
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<td>$-3kl - 12lm - 6km$</td>
<td>$-3kl - 6km + 3km$</td>
<td>$-3kl + \frac{1}{2}k^2$</td>
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<tr>
<td>$Q_i(\omega)$</td>
<td>$-\frac{3}{2}kl - 3lm - 3km$</td>
<td>$-3kl - 12lm - 6km$</td>
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<td>$Q_i(\omega)$</td>
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<td>$-\frac{3}{2}kl - 6km + 3km$</td>
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Leung and Kleiner (1974) discussed the sum rule $K_i^{(0)} = 0$. In a single-mode theory they found that $K_i^{(0)} = 0$ up to (our) eighth order, and that to all orders $K_i^{(0)} = 0$ because of the $R_3$ sum rules in the equal coupling case. From equation (6), $K_i^{(0)} = 0$ to fourth order if and only if the lattice modes are isoenenergetic. If $e_i \neq e_i$ we find (by summing each term against the corresponding term with $k, l$ interchanged) that $K_i^{(0)} < 0$.

The sum rules $K_i^{(0)} = 0$ and $2q = 1 + p$ (of the $E \otimes e$ problem) thus break down under identical circumstances. Since the breakdown of the latter sum rule has been observed experimentally (e.g. Abou-Ghantous et al. 1974) there is more likelihood of observing a non-zero value for $K_i^{(0)}$ (in weakly coupled systems with $V_{fi} \ll V_f$) than might be anticipated from the analysis of Leung and Kleiner (1974).

We are grateful to Dr M C M O'Brien for drawing our attention to errors in an earlier script, and to Dr P H Butler for discussions. S H P is grateful to the New Zealand University Grants Committee for a Postgraduate Scholarship.

References

Judd B R 1974 Can. J. Phys. 52 999-1044
Ion–lattice coupling, spectral moments and transition interference in Fe²⁺:MgO

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Received 8 November 1976

Abstract. We determine the magnitude of phonon-induced transition interference in the ESR and far-infrared spectra of Fe²⁺:MgO. The ion–lattice coupling constants required in our analysis are predicted for Fe²⁺:MgO using the ligand superposition model. An improved formulation of the theory of spectral moments is included. The broadening component associated with phonon-induced transition interference has a sign dependent on the mechanism for the optical coupling (E₂ or M₁), a temperature dependence identical to that of the conventional contributions, and a magnitude typically of 20% of the corresponding conventional contributions.

1. Introduction

Transition interference may occur in systems in which two different pairs of electronic levels have the same separation. In the absence of phonon interaction, the spectrum will contain two delta-function parts that superimpose at the common transition frequency. On including phonon interaction, each line will broaden and shift, and sidebands will appear. However, it is generally assumed that the spectrum will still be a superposition. Under certain conditions, additional effects arise representing interference between the spectra (Stedman 1976, to be referred to as I). The argument in this paper was purely qualitative, however, and it is of interest to estimate the importance of this effect in a realistic situation.

The ground state of Fe²⁺:MgO is a triplet (T₂g) with an isotropic g-factor in cubic symmetry (which we assume throughout); the first excited states are a doublet (E_g) and a triplet (T₁g), and all these states are Jahn–Teller-active (Ham et al 1969). Since the far-infrared transition (A in figure 1) from the ground triplet to the two excited multiplets is seen (Meyer et al 1974, Hjortsberg et al 1975) and is magnetic dipole in origin, this is exactly the type of system discussed in I as a candidate for a study of transition interference. We shall estimate the various contributions to the second moment of the far-infrared absorption band in §4.

The ESR transitions (B in figure 1) between the levels of the ground triplet also coincide in energy and suggest the possibility of transition interference under different restrictions and with different effects to that discussed in I. There has already been some discussion of the possibility that an unusual lineshape could result from a full-blown treatment of phonon effects on the spectrum in this case (Stevens and Persico 1966, van Eckelen and Stevens 1967). We find that, in such circumstances, the contribution of transition inter-
ference to the broadening of the zero-phonon line occurs via inelastic interaction with the lattice and can therefore proceed via the direct process of spin-lattice relaxation, in a lower order of perturbation theory than the Raman elastic processes discussed in I. In this particular system, the dominant features of the observed spectrum are due to strain broadening (Ham 1968), but since in other spectral regions laser fluorescence studies can examine phonon broadening effects normally masked by strain, this type of problem may have more than academic interest.

We take this opportunity to improve two bodies of theory required by the analysis. First, the basic ion-lattice interaction constants for Fe$^{2+}$:MgO have never been satisfactorily explained (Ham et al 1969). The situation is confused by disagreement between a number of authors who have published formulae for the ion-lattice constants on a point-charge model for cubic symmetry. We show that the observed signs and magnitudes of static and dynamic parameters are consistent with the ligand superposition model of ligand-field theory developed by Newman (1971). This also enables us to predict the ion-lattice coupling constants in the excited multiplets of Fe$^{2+}$:MgO required by our analysis and unavailable experimentally. Second, we give details of an improved formulation (alluded to in I) of the theory of spectral moments, in particular removing an unwarranted assumption in the standard treatment of negative frequencies.

2. Superposition model interpretation of ion-lattice coupling constants in cubic symmetry

2.1. Normalization conventions

We define the strain tensor by $e_{ij} = \frac{1}{2}(\partial u_i/\partial r_j + \partial u_j/\partial r_i)$, where $u(r)$ is the displacement of the medium at $r$. On symmetrization with respect to the cubic group, we have strains $e_{ij} = e_{x^2} - \frac{1}{2}(e_{xx} + e_{yy}), e_z = \frac{1}{2}\sqrt{3}(e_{xx} - e_{yy})$ for the $E_g$ irreducible representation, and $e_{ij} = e_{yz}, e_z = e_x = e_y$ for the $T_{2g}$ irreducible representation. We define the corre-
Transition interference in Fe²⁺ : MgO

sponding normal coordinates for octahedral symmetry by \( Q_\alpha = 2R_e e^{\sqrt{3}}/3, Q_\epsilon = 2R_e e^{3/3} \), \( Q_z = R_z \) etc, where \( R \) is the distance to the nearest neighbour. The above conventions correspond to the definitions of, for example, Ham et al (1969). The harmonic linear ion–lattice coupling Hamiltonian will be written

\[
V = V_0(Q_\alpha E_\alpha + Q_\epsilon E_\epsilon) + V_T(Q_z T_z + Q_\eta T_\eta + Q_\zeta T_\zeta).
\]

Here \( V_0 \) and \( V_T \) are essentially reduced matrix elements of the ion-lattice interaction for the irreducible representations \( E_\alpha \) and \( T_\zeta \). The electronic operators \( (E_\alpha, E_\epsilon) \) and \( (T_\eta, T_\zeta, T_\chi) \) have the corresponding symmetry. Authors differ in their choice of these operators. For example, for unsymmetrized crystal-field operators, a list in Racah normalization is given by Smith and Thornley (1966) and in Stevens normalization by Newman and Urban (1975). A list of Stevens operators, symmetrized for cubic symmetry, has been given by Calvo et al (1969). Most authors use the symmetrized Racah operators, in particular the list of Blume and Orbach (1962). These operators have the major defect that the \( T_\zeta \) operators are not Hermitian; the origin of this appears to be that table A19 of Griffith (1961) for kets has been translated into operators without ensuring Hermiticity. Since a Hermitian choice must eventually be specified (by dropping a factor \( \pm i \)) to gain a real answer, we conclude that previous calculations are liable to have incorrect signs for \( V_0 \).

Within a triplet \( (E_\alpha = 1) \), we define the symmetrized effective spin operators by (Ham et al 1969)

\[
E_{ij} = \frac{3L_{ij}^2}{2} - \frac{1}{2}, E_{ij} = \frac{3(L_{ij}^2 - L_{ij}^2)}{2}, T_z = (L_{\eta}, L_{\zeta}) \) etc, and within a doublet \( (E_\alpha = \frac{1}{2}) \) by (Bates et al 1971) \( E_\alpha = L_{\eta}^2, E_{\epsilon} = L_{\zeta}^2, T_\eta = 0 \). We shall take the \( L_{\zeta} = \frac{1}{2} \) state to be the \( |E_\alpha E_\epsilon \rangle \) state, to conform to Griffith’s (1962) conventions. The additional operator equivalent factors needed to reduce the symmetrized Racah crystal-field operators to the above spin operators are listed in Bates et al (1962) in the form \( \{r_{\eta}, n = 2, 4 \} \). The operators of Baker and van Ormondt (1974) are defined by substituting \( Z^{(4)}_{\eta, \epsilon, \chi} \) of Table IV of Hutchings (1964) for the combination \( (n, m) \pm (n, -m) \sqrt{2} \) in Griffith’s table; hence, for example, \( C(T_\eta, 2, 0) = \alpha E_\alpha C(T_\zeta, 2, 0) = \frac{1}{2}\sqrt{3}T_\eta \alpha \).

Levels 1–8 in figure 1 are assigned the symmetries \( E_\alpha, T_\zeta, E_\epsilon, S_\eta, S_\zeta \) and \( S_\chi \) respectively.

2.2. Superposition model of ion–lattice interaction

There is now a considerable body of evidence that the ligand superposition model of the static and dynamic crystal field should be used in lieu of the point-charge or indeed any electrostatic model, in view of the simplicity and general applicability of the model (Newman 1971). Some of this evidence relates to transition-metal ions (Stedman 1969a, b, Newman and Siegel 1976).

Superposition-model expressions for ion–lattice coupling constants have been given by Newman and Urban (1975). If we cast this work into the normalization conventions of § 2.1 we obtain

\[
R \begin{bmatrix} V_0 \\ V_T \end{bmatrix} = \begin{bmatrix} -2 \sqrt{3}L_{kE}^2 & 4\sqrt{5}L_{kE}^4 \\ 6L_{kE}^2 & -4\sqrt{15}L_{kE}^4 \end{bmatrix} ^{\alpha B_2} \begin{bmatrix} \beta B_2 \\ B_2 \end{bmatrix}.
\]

† In this reference, the caption to table 2.1 should have \( \{X, Y\} \) as the anticommutator of \( X \) and \( Y \).

‡ Allen (1973) has pointed out an inconsistency in the physical interpretation of Stedman (1969b). We correct this as follows: if \( B_z \) decreases down the series \( V^{4+} \) to \( V^{4+} \) due to charge penetration, for example, the reduction in its contribution to \( \sigma \) will explain the observed decrease in this parameter. Either this reduction in \( B_z \) or the increase in \( B_d \) associated with \( \Delta \), or both, will explain the observed increase in \( \eta \). Note that \( \sigma B_2 < 0 \).
where $x$ and $\beta$ are the standard operator equivalent factors (Bates et al 1971), $B_4$ is the axial crystal-field parameter in Stevens normalization for one ligand at a distance $R$ along the $z$-axis, and the factor $t_n$ describes $B_4$'s dependence on $R$ (Newman 1971). In the point-charge model, $t_n = n + 1$ and $B_4 = -|e| q < r^n > / (R^{n+1} X_4)$, where $X_2 = 2$, $X_4 = 8$.

On comparing expressions for $V_E$ and $V_T$ on a point-charge model for Fe$^{2+}:$MgO we have the experimental values for $V_E$ and $V_T$ (Watkins and Feher 1962):

$$V_E = \frac{1}{R} \left[ \sqrt{3} G_{1/2} \right] = \frac{1}{R} \left[ \frac{680}{540} \right] \text{ cm}^{-1}.$$  

If we use the estimates of Ham et al (1969) for the Jahn–Teller reduction factors ($K_E = K_T = +0.09$), we have the 'corrected' values $RV_E = 7800 \text{ cm}^{-1}$, $RV_T = 6000 \text{ cm}^{-1}$. Ham et al (1969) comment that the signs of these expressions are at variance with the point-charge model predictions. The order-of-magnitude agreement in size is scarcely significant when the point-charge model disagrees with the observed magnitude of the main static crystal-field parameter, $\Delta$. If the single-ligand crystal-field parameter $B_4$ is derived from $\Delta$, the observed magnitudes and signs for $V_E$ and $V_T$ can be obtained by judicious balancing of the contributions of the $n = 2, 4$ dynamic crystal-field terms. In other words, the point-charge model not only gives an incorrect order of magnitude for $B_4$ but predicts the wrong relative contribution of the $n = 2, 4$ terms.

Since $\Delta (=-80B_4/21) = 10850 \text{ cm}^{-1}$, we obtain $B_4 = 813 \text{ cm}^{-1}$ for this system. Hence, from equation (2), (in units of cm$^{-1}$) $RV_T = -1.71 B_2 + 3100$. Using the raw data for $V_T$, we find $B_2$ to be positive; using the data as adjusted by the Ham et al (1969) reduction factors, we would find $B_2$ negative. Ligand-field theory for transition metals would normally predict a positive $n = 2$ single-ligand crystal-field parameter, and it is possible that Ham et al (1969) have underestimated the reduction factor $K_2$: a value $K_2 = 0.17$ or greater would make $B_2$ positive. As an order-of-magnitude estimate, we conclude that $B_2 \approx 1000 \text{ cm}^{-1}$. (Much larger values of $B_2$ have been predicted by D J Newman (private communication) in pyrope garnet.) Similarly, $RV_E = -0.99 t_2 B_2 + 1790 t_4$. For oxygen ligands, a value of $t_4 = 5$ is a reasonable estimate (Burns and Axe 1966) and we conclude that, on either the raw or adjusted data for $V_T$, $t_2 B_2$ is positive, again as expected from ligand-field theories. The uncertainties in $K_E$ and $t_n$ preclude estimates of more than an order of magnitude for $B_4$, but there is no problem in principle in interpreting the data for $\Delta$, $V_E$ and $V_T$ on the ligand superposition model, as opposed to the point-charge model.

For the first excited doublet, we require one ion–lattice interaction parameter, $V_E$. Substituting $t_2 = 4$, $t_4 = 5$ and $B_2 = 1000 \text{ cm}^{-1}$ and using the appropriate set of operator equivalent factors in equation (2), we obtain $RV_E = -21000 \text{ cm}^{-1}$. Even allowing then for the possibility of Jahn–Teller reduction of stress-induced splitting,
the superposition model predicts a strong ion–lattice coupling of \( E_g \) symmetry in the excited doublet, and definitely of negative sign.

Similarly, for the second excited multiplet (\( T_{1g} \) triplet), we predict \( RV''_B = +6200 \text{ cm}^{-1} \), \( RV''_T = +7100 \text{ cm}^{-1} \).

3. Moments of the optical spectrum

One may write closed expressions for the moments of an optical spectrum in terms of a trace over a set of operators. The primary references in this area are van Vleck (1948), Lax (1952), Henry et al (1965), Pake (1962) and Abragam (1961). In each of these works an unwarranted approximation is made, and a correction seems desirable.

We start with the Golden Rule form of the spectrum on which all our work is based:

\[
X(E) = \sum_{A,B} (\rho_B - \rho_A) |M_{AB}|^2 \delta(E_A - E_B - E),
\]

(A and \( B \) represent coupled electron–phonon (i.e. vibronic) eigenstates of the complete crystal Hamiltonian \( H \) with eigenvalues \( E_A \) and \( E_B \), and \( M \) is the optical interaction. We shall take \( \beta \propto \exp(-\beta H) \), i.e. we neglect the effects of optical pumping on the population of vibronic levels. The difference \( \rho_B - \rho_A \) takes account of emission as well as absorption. Since the spectral function has physical meaning only if \( E > 0 \) (\( E_A > E_B \)), we define the physical spectrum as

\[
\sigma_\pm(E) = \theta(E)X(E) = \sum_{A,B} (\rho_B - \rho_A) |M_{AB}|^2 \delta(E_A - E_B - E),
\]

where \( \theta \) is the unit step function. It is convenient to define

\[
Y(E) = \sum_{A,B} (\rho_B + \rho_A) |M_{AB}|^2 \delta(E_A - E_B - E)
\]

with a positive-frequency part \( \sigma_+(E) = Y(E)\theta(E) \). If the optical approximation were made, i.e. all excited vibronic levels unpopulated \( (\rho_B \ll \rho_0 \text{ where } B \neq \text{ ground state}, 0) \), \( \sigma_+(E) = \sigma_-(E) \equiv \sigma(E) \).

The (unnormalized) moment of the spectrum may be defined by

\[
\langle \omega^n \rangle_x = \int_{-\infty}^{\infty} E^n \sigma_+(E) \, dE = \int_{0}^{\infty} E^n X(E) \, dE,
\]

and similarly for \( \langle \omega^n \rangle_y \).

The works previously referred to make one of the following approximations: either the lower limit in equation (6) is written as \(-\infty\) rather than zero, or equivalently \( \sum_{E_B < 0} \) in equation (4) is replaced by \( \sum_{E_B \neq 0} \) (It is also common to assume that \( Y(E) = X(E) \)). These steps overlook the fact that the negative-frequency parts of \( X \) and \( Y \) are just as sizeable as the positive-frequency parts; indeed these functions are respectively odd and even in \( E \).

We define

\[
F_{\pm}(t) = \text{Tr} \rho [M(0), M(t)]_{\pm},
\]

\[
F(t) = \text{Tr} \rho M(0) M(t),
\]
where $M(t)$ is the Heisenberg operator and the signed bracket denotes a commutator or anticommutator. Using

$$\delta(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\Omega t) \, dt,$$

one may take the energies inside the matrix elements and re-order the operators inside the trace to give

$$X(E) = \frac{1}{ni} \int_{-\infty}^{\infty} dt \sum_{A,B} \rho_{AB} M_{BA} \exp(iE_A t) M_{AB} \exp(-iE_B t) \sin(Et)$$

$$= \frac{1}{ni} \int_{-\infty}^{\infty} dt \, F_-(t) \sin(Et). \tag{7}$$

Hence, by Fourier inversion,

$$F_-(t) = 2i \int_{0}^{\infty} X(E) \sin(Et) \, dE, \tag{8}$$

$$\left[ \left( \frac{d}{dt} \right)^{2n+1} F_-(t) \right]_{t=0} = 2i(-1)^n \langle \alpha^{2n+1} \rangle_{\gamma} \tag{9}$$

We may evaluate the left-hand side using

$$\left( \frac{d}{dt} \right)^p M(t) = i^p \left[ H, \left[ H, \ldots \left[ H, M(t) \right] \ldots \right]_p \right], \tag{10}$$

where the suffix denotes $p$ nested commutator brackets, to give

$$\langle \alpha^{2n+1} \rangle_{\gamma} = \frac{1}{2} \text{Tr} \rho \left[ H, \left[ H, \ldots \left[ H, M \right] \ldots \right]_{2n+1} \right]. \tag{11}$$

Similarly,

$$F_+(t) = 2 \int_{0}^{\infty} Y(E) \cos(Et) \, dE, \tag{12}$$

$$\langle \alpha^{2n} \rangle_{\gamma} = \frac{1}{2} \text{Tr} \rho \left[ H, \left[ H, \ldots \left[ H, M \right] \ldots \right]_{2n} \right], \tag{13}$$

which, following Grant (1964) for example, can be written as

$$\langle \alpha^{2n} \rangle_{\gamma} = (-1)^n \text{Tr} \rho \left[ H, \left[ H, \ldots \left[ H, M \right] \ldots \right] \right]_n^2. \tag{14}$$

Adding equations (8) and (12), we obtain in the optical approximation

$$F(t) = \int_{-\infty}^{\infty} \sigma(E) \exp(iEt) \, dE, \tag{15}$$

from which all moments may be written in the form

$$\langle \alpha^n \rangle = \text{Tr} \rho M \left[ H, \left[ H, \ldots \left[ H, M \right] \ldots \right] \right]_{\alpha}. \tag{16}$$

This agrees with the exact moments of equations (11) when $n$ is odd, and with the moments of equation (13) when $n$ is even and the optical approximation is made.
4. Interference contribution to the second moment of the far-infrared spectrum

We evaluate the second central moment using equation (16), in the form of equation (23) of I. Since the excited multiplets are at 107 cm\(^{-1}\) above the ground state, their relative population at 10 K is exp \((-15)\) \((\ll 1)\). Hence the optical approximation of §3 is certainly appropriate. The interference terms we shall include are those with \(a, d\) in one multiplet and \(b, c\) in another (in the notation of equation (23) of I), i.e. we ignore all effects arising from coupling of the multiplets by phonon interaction. The representation of equation (1) also ignores the breathing mode \(A_{1g}\), which is normally a dominant source of band-broadening. In the present case, the far-infrared splitting between the multiplets is predominantly due to spin–orbit coupling (although there is some crystal-field dependence (Ham et al 1969)) and the difference in the shifts of these multiplets \((a, b)\) under hydrostatic strain \((\propto (V_{ab} - V_{bb}))\) is not expected to be as great as for asymmetric modes. In view of this and other complications we shall ignore \(A_{1g}\) contributions.

When summing over phonon modes \(kJ = k\), we shall assume a factorization of the form

\[
\sum_{kJ} \rightarrow \sum_{jk} \sum_{\Gamma_\gamma} \sum_{ij} \sum_{r^e_s}
\]

where \(|k|\) is the magnitude of wavevector, \(j\) is the polarization and \(\Gamma_\gamma\) are the symmetry labels for a complex mode. This approximation avoids a complicated problem in lattice dynamics and is in the spirit of phenomenological computations of spin–lattice relaxation rates. However, the combined effect of these two approximations is to introduce some spurious symmetries. For example, the product of terms \(V_{68}, V_{78}\) \((y\) labels the phonon symmetry in \(T_2g\)\) vanishes. The effect of this is to cancel contributions to the interference part that are strictly non-zero, and our estimate of transition interference is therefore to be regarded as a lower bound.

We take a linear ion–lattice interaction (from I):

\[
V = \sum_k \mathcal{C}_k (b_k + b_k^+) h.
\]

\[
\mathcal{C}_k = \sum_{mn} V_{mn} a_m^+ a_n.
\]

From Griffith (1962), the parameters of §2 are related to this interaction by

\[
V_E = \langle T_{2g} | \mathcal{C}^{(3a)} | T_{2g} \rangle / \sqrt{3F}, \quad V_T = \langle T_{2g} | \mathcal{C}^{(1a)} | T_{2g} \rangle / 6F \quad \text{(and similarly for } V'_E, V'_T) \quad \text{and}
\]

\[
V'_{68} = \langle E_g | \mathcal{C}^{(6a)} | E_g \rangle / F, \quad \text{where } F = \left[ \frac{h}{2N(\Omega M, \omega)} \right]^{1/2} \sin \left( \frac{1}{2} \omega k \right) \quad \text{(Ham et al 1969).}
\]

If the light were \(\sigma\)-polarized (with respect to some choice of \(z\)-axis, e.g. by adding a magnetic field) we find that in the above approximations some interference terms (those in \(T_{2g} \rightarrow E_g\) vanish. We shall assume no polarization of the incoming radiation, and define the reduced matrix elements of the optical interaction by

\[
M = \langle 1 | M_{x} | 4 \rangle = -\frac{1}{2} \langle T_{2g} | M^{(T_{2g})} | E_g \rangle,
\]

\[
M' = \langle 1 | M_{x} | 7 \rangle = -\frac{1}{2\sqrt{6}} \langle T_{2g} | M^{(T_{2g})} | T_{1g} \rangle.
\]

Ham et al (1969) compute numbers related to \(M, M'\) on a crystal-field model, which we use later.

We discuss the two sets of transitions separately. For the transition to the \(E_g\) doublet, we find for the second central moment

\[
\langle \omega^2 \rangle (E_g) = \sum_{jk} (2n_k + 1) \rho_1 |M|^2 F^2 \left[ \frac{1}{2} V'_E + V'_E V'_E + \frac{1}{6} |V'_E|^2 - \frac{1}{3} |V'_E|^2 + 2V'_E|^2 \right.
\]

\[
+ 2|V'_E|^2 + |V'_E|^2 + 8|V'_{T}|^2 + 2V'_E V'_{E} / \text{Tr } \rho |M|^2,
\]

(18)
and for the transition to the \( T_{1g} \) triplet

\[
\langle \omega^2 \rangle_x(T_{1g}) = \sum_{\text{ff}} \left\{ \frac{1}{2}(2n_i + 1)\rho_{ii} |M'|^2 F^2([V''_E + 2V_E|^2 + |V''_E + V_E|^2 + |V''_E - V_E|^2 +
+ 3[V''_E + V_E|^2 + |V_E|^2 + |V''_E|^2]
+ 24[V''_T|^2 + |V_T|^2] - 12V_YV''_T)/\text{Tr} \rho |\mathcal{N}|^2. \right\}
\]  

(19)

In equations (18) and (19), cross terms which arise from expanding internal brackets represent non-additive broadening contributions, and the last term in each case represents transition interference. The terms have been calculated using a Debye model for the lattice; corrections arising from terms in \( \langle \omega^2 \rangle_x \) containing the zero-order Hamiltonian are negligible.

We find that \( \langle \omega^2 \rangle_x \) is proportional to \( T \) at high temperatures for all contributions and that the total width has a low-temperature limit of 80 cm\(^{-1}\), which is an order of magnitude greater than the observed bandwidth (Meyer et al 1974). In view of the above approximations, better agreement cannot be expected.

The relative magnitudes are our immediate interest. We find that transition interference gives 30% and 13% of the conventional contributions to the second moment for the transition to the \( E_g \) and \( T_{1g} \) multiplets, respectively. If, instead of regarding a lattice mode \( kj \) as activating a single mode of the complex, we use equation (17) for each occurrence of the label \( k \) in such products as \( V_6 V_{76} \), these magnitudes become 25% and 47%, respectively. The truth probably lies between these approximations of extreme coherence and extreme incoherence. We may conclude that a width calculation aiming at 30% accuracy should certainly include interference terms.

All these contributions are negative, i.e. interference effects tend to decrease the bandwidth (by up to a factor of 2). If a magnetic field were applied, the interference terms might be expected to decrease rapidly in magnitude, since the transitions would no longer be isoenergetic. At the point at which the spectrum showed clearly separated transitions, the interference terms would be expected to be negligible; the associated Green functions (cf § 5) would no longer have the coincident resonances which enhanced their importance. This would suggest that, other things being equal, the width of the \( T_{2g} \rightarrow T_{1g} \) transition should increase with magnetic field, since a negative contribution was being reduced in magnitude. In fact, the opposite trend was noted by Hjortsberg et al (1975). One explanation for this is that on increasing the field the band shifts out of the energy regime of the acoustic phonons and that conventional broadening mechanisms are thereby greatly reduced.

5. Interference effects in the ESR spectrum of Fe\(^{2+} \):MgO

From equation (2) of I, the optical spectrum can be written as

\[
\sigma(E) \propto \sum_{\text{f}} \text{Disc} M_{ab} M_{cd} G_{ab,cd}(E)
\]

(20)

where \( a, b, c, d \) label electronic levels and \( G_{ab,cd}(E) \) is a two-particle Green function whose external lines are labelled by these states. The terms \( G_{ab,b}(E) \) are denoted diagonal Green functions and give rise to the conventional terms in the spectrum; the remainder, \( c \neq b \) or \( a \neq d \), are denoted interference Green functions. In the three-level system of figure 1, the transitions 1 \( \leftrightarrow \) 2 and 2 \( \leftrightarrow \) 3 have a common energy \( E_0 \) (in the absence of ion-lattice interaction). The major contribution to the ESR (zero-phonon) line will come from those
Green functions which resonate at this energy. These will include \( G_{21',12}(E) \) and \( G_{32',23}(E) \) even in the absence of ion–lattice interaction; on expanding the Green functions to second order, we find resonances at \( E_0 \) in each of the terms of figure 2.

\[
G_{ab,ba}^{00} = \begin{pmatrix} a & \rightarrow & b \\ b & \leftarrow & a \end{pmatrix}
\]

\( (a, b) = (2, 1), (3, 2) \)

\[
G_{12',23}^{(2)} = \begin{pmatrix} 1 & \rightarrow & 2 \\ 2 & \leftarrow & 1 \end{pmatrix}
\]

\[
G_{21',23}^{(2)} = \begin{pmatrix} a & \rightarrow & c \\ b & \leftarrow & d \end{pmatrix}
\]

\[
G_{21,23}^{(2)} = \begin{pmatrix} b & \rightarrow & a \\ c & \leftarrow & d \end{pmatrix}
\]

\[
G_{22,12}^{(2)} = \begin{pmatrix} b & \rightarrow & a \\ c & \leftarrow & d \end{pmatrix}
\]

Figure 2. Green functions giving non-zero contributions to direct-process broadening of the \( \Delta L_q = 1 \) ESR transitions of Fe\( ^{2+} \):MgO. Interference terms correspond to the last two diagrams, \( G_{21',23}^{(2)} \) and \( G_{22,12}^{(2)} \).

It follows that interference effects arise in the zero-phonon line at second order of perturbation, rather than fourth order as in I, and all our earlier general conclusions need revision because of the different structures of the isoenergetic transitions. This situation was anticipated in a footnote in Stedman (1972), and by revising the arguments in that paper in the indicated manner, we find:

(i) vertex corrections (of the type \( G_{21',23} \)) contribute to the width but not the shift of the zero-phonon line; and

(ii) this width contribution arises from ion–lattice interaction processes in which a net amount of energy \( E_0 \) is released to or gained from the lattice. Hence the direct process of ion–lattice relaxation can give a non-zero contribution to the interference-induced width.

The relative values of the matrix elements \( M_{ab} \) in the ground triplet can be obtained by applying time reversal under which \( \hat{M} \rightarrow \epsilon \hat{M} \), where \( \epsilon = \pm 1 \), as \( \hat{M} \) is an electric or magnetic multipole operator. Equation (20) becomes

\[
\sigma(E) \propto \text{Disc} \left| M_{12} \right|^2 \{ G_{21,12}(E) + G_{32,23}(E) + \epsilon [G_{32',12}(E) + G_{21',23}(E)] \}.
\]

The sign of the interference terms in this expression will depend on the mechanism of the optical transition.

Proceeding as in Stedman (1972), we find second-order contributions to the half-width at half-power of the zero-phonon line at \( E_0 \) as

\[
\Gamma = \Gamma_0^{(1)} + \Gamma_1^{(1)} + \Gamma_0^{(2)}
\]

\[
= \frac{\pi}{4} \sum_k \left\{ \delta(E_0 - \omega_k) \left[ \left| V_{12k} \right|^2 - 2\epsilon V_{23k} V_{12k} \right] + R_{23}(n_k + 1) \left| V_{32k} \right|^2 - 2\epsilon V_{23k} V_{21k} \right\}
\]

\[
+ \delta(2E_0 - \omega_k) \left| V_{13k} \right|^2 \left[ R_{13} n_k + R_{23}(n_k + 1) \right],
\]

\[
(22)
\]
where $\Gamma^{(1)}$, the interference terms, are those proportional to $\epsilon$, $\Gamma^{(2)}_d$ represents the term proportional to $\delta(2E_0 - \omega)$ (arising from direct relaxation between levels 1 and 3) and $\Gamma^{(1)}_d$ the remaining terms arising from diagonal Green functions and direct-process relaxation between levels 1 and 2 or 2 and 3. $R_{ab} = (\rho_a - \rho_b)/(\rho_1 - \rho_3) \approx 1 (\beta E_0 \ll 1)$ and $\rho_a$ is the population of electronic state $a$. $n_k$ and $\omega_k$ are the population and single quantum energy, respectively, of lattice mode $k$, and $V_{obk}$ is the coefficient of the linear ion–lattice interaction (to which we restrict ourselves) in the second quantization (cf I).

Again we ignore $A_{1g}$ mode interactions; semidiagonal contributions to the zero-phonon linewidth (see the references in I) are certainly non-zero but do not contribute to direct-process relaxation.

Using equation (17) for summation over lattice modes, we find

$$\Gamma = \left(3\pi10^9\hbar c^2 R^2 E_0^2 kT/2N M_v \epsilon_k^2\right) (7V_t^2 + 3V_e^2 - 2\epsilon V_{1g}^2).$$

Therefore, the contribution from the interference term to the width is $\sim 17\%$ of the conventional contributions. The magnitude of $\Gamma$ for a typical case ($T = 4 K, E_0 = 0.3 \text{cm}^{-1}, 2 \times 10^{-5} \text{ cm}^{-1}$, is of course much less than that of the observed strain-broadened line ($7 \times 10^{-2} \text{ cm}^{-1}$, Low and Weger 1960).

6. Conclusions

The observed ion–lattice interaction constants in the ground triplet of Fe$^{2+}$:MgO are consistent with the ligand superposition model, and values have been predicted from this model for the constants in excited multiplets. For the $T_{1u}$ multiplet, the constants are similar to those in the ground multiplet, but $V_{1g}$ for the $E_g$ multiplet is negative.

The contribution of interference between transitions to fine- or band-broadening can be $20\%$ or more, and thus should be included in a careful calculation for multiplet–multiplet transitions. Since the symmetry properties of these terms are quite different from those of the conventional contributions (they may change sign under a change in multipole of optical interaction and for general site symmetry they are strongly polarization-dependent), they may play a proportionally greater part in, for example, MCD spectra.

Acknowledgments

We are grateful to Dr C A Bates and Dr J M Baker for correspondence clarifying §2. SHP is grateful to the New Zealand University Grants Committee for a Postgraduate Scholarship.

References

Abragam A 1961 The Principles of Nuclear Magnetism (Oxford: Clarendon)
Transition interference in Fe$^{2+}$: MgO

Grant W J C 1964 Phys. Rev. 135 A1265–8
Griffith J S 1961 The Theory of Transition Metal Ions (Cambridge: Cambridge UP)
Ham F S 1967 Phys. Rev. 160 328–33
Hutchings M T 1964 Solid St. Phys. 16 227–73
Lax M 1952 J. Chem. Phys. 20 1752–60
Pake G E 1962 Paramagnetic Resonance (New York: Benjamin)
van Vleck J H 1948 Phys. Rev. 74 1168–83
ACKNOWLEDGEMENTS

I am indebted to my supervisor, Dr. E. E. Stedman, for his assistance and encouragement throughout the course of this work. I would like to thank Dr. P. H. Butler for his considerable help in all matters group-theoretic, and the provision of necessary tables for my calculations; also, Professor B. G. Wybourne for his interest in my progress. I am grateful to Dr. W. B. Wilson for discussions.

Of my fellow research students, I would especially like to acknowledge the encouragement of Murray Smith.

A very special and deserved thanks is due to Margaret and Kenneth Davies, who have provided me with a 'second home' for several years, and have given me their friendship and support.

For financial assistance, I am grateful to the New Zealand University Grants Committee for the award of a Postgraduate Scholarship, and the University of Canterbury for the Kidson and Charles Cook Scholarships.

Finally, I would like to thank Miss B. V. Nottingham for typing this thesis.

p.6  -(I-8)  - \( \sum_{x} \lambda_{y} \)

- next eqn.  - \( \sum |2k> \lambda(g)_{ik} \)

p.17  - line 1  - ... \( SO_3 \Rightarrow 0 \) 3jms ...

5 found previously.

p.20  - last eqn.  - sub- and superscript pairs 2'2 should be z'z

p.23  - line 1  - ... Brillouin zone ...

p.26  - line 4  - ... Fourier transform ...

\( (II-8) \)  \( d_{k}(x_{\nu}) \)

p.40  - 2nd last line  - ... \( x_{i} = x_{c} \) for \( \lambda_{i} = \lambda_{c} \), ...

p.43  - line 7  - ... such that \( k \in \nu_{a} \times \lambda_{j} \).

p.53  - line 7  - ... \( g_{k} \rightarrow \frac{h\nu}{E/\omega_{E}} \delta_{k} \)

p.55  - line 5  - ... 2j phase, \( \phi_{s} \), ...

p.65  - line 10  - ... \( \mu = \Gamma_{1}, \Gamma_{2} \)

p.76  - line 14  - ... setting \( \nu = \Gamma_{1} \) in 7(c) ...

p.81  - line 23  - ... must have \( b_{7} \Rightarrow 0 \), ...
p.90 - (IV-16) $a_i a_j$

p.127 1st eq. $V_{l,k}^i$

2nd eq. $e^{-\frac{1}{2}(x_{il} + x_{kj})}$

p.145 - (2)JLV3 ... Figs. 13(g,k,l) ...

p.150 - line 10 ... residue of the summand ...

p.153 - (AVI - 9) $\delta^{(n-1)}(x)$