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Effects of time-odd electron–phonon coupling in ligand field theory

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Abstract. The magnetic effects associated with ligand motion (e.g. a ligand-current-induced Zeeman coupling) might be distinguishable in the context of the spectroscopy of condensed matter through their time-odd character. In many ligand-field-related situations the time reversal signature of all interactions, taken jointly, is of importance in inducing selection rules. Time-odd coupling would give rise to novel combinations of temperature, field and excited state energy in spin–lattice relaxation times; in Raman phonon spectroscopy it would generate distinctive chiral phenomena; as noted by Fletcher it would give breakdown of Jahn–Teller reduction factor sum rules; it would also give rise to complex values of the Berry phase factor in Jahn–Teller systems. Similar characteristic evidences for time-odd coupling effects may be expected for lanthanide $4f \rightarrow 4f$ transition intensities and in virtual phonon exchange.

1. Introduction

1.1. Historical context

In pioneering work by Van Vleck in the 1930s, the splitting of free-ion electronic states by ligands was described in terms of ligand fields, notably the action of the electrostatic field from the ligand charges in splitting and mixing the electronic states of the ion. Fuller details including personal perspectives are given by Gorter and van Duyneveldt 1974, Judd 1988, and Newman and Ng 1989. With adaptation as described below for the inclusion of specifically quantum effects on electronic energies, this model has been enormously successful in a wide variety of systems.

The Van Vleck model has a natural extension to a quasistatic theory of ion–lattice coupling, in which electric (and therefore time-even) field effects are assumed to be dominant. In the early days of electron paramagnetic resonance, this mechanism quickly established its superiority and relevance over the direct spin–spin coupling originally considered by Waller (1932) (the latter being a time-odd mechanism), as the principal mechanism for spin–lattice relaxation of paramagnetic ions in crystals. Solid state workers therefore have since then tended to ignore the possibility of time-odd coupling of paramagnetic ions to the ligand field. Of the major reviews of spin–lattice relaxation since the 1960s, Gill (1975) mentions time-odd coupling: ‘it is accepted that the effect on the paramagnetic ion of the electromagnetic fields which are associated with the vibrations of the lattice is quite negligible,’ and Stevens (1967) similarly states ‘We ignore this direct spin–lattice interaction assuming it is small.’ Apart from the very early

discussion relating to Waller's specific mechanism, we have been unable to trace any analysis in the literature which attempts to justify this assumption, or any reference to the matter in the more recent reviews (Orbach and Stapleton 1972, Shrivastava 1983 for example). Fletcher (1981) and Fletcher and Pooler (1982) are unique in having raised the matter seriously. The matter has not been debated keenly partly since precise confirmation of the Van Vleck model is not easy; Stevens (1967) says: 'the fact that it has taken something like 25 years to be quite sure' (of the Van Vleck mechanism) 'is both a remarkable tribute to Professor Van Vleck's insight and an illustration of the difficulties in obtaining reliable data.' In this paper we suggest that even after a further 20 years the significance of time-odd coupling for dynamic effects is still an open and interesting question.

The potential of the dynamic effects of the ligand field for giving information about the underlying physical mechanisms has been widely recognised. The dependence of the observed ion-lattice relaxation time on temperature, field, concentration and energy splitting often identifies the type of mechanism in considerable detail. More fundamentally, it was realised several decades ago that purely electrostatic calculations of the ligand field are quite inadequate for the lanthanides, and sophisticated models (such as molecular orbital theoretic models) have been developed for the static field analysis, so refining the Van Vleck model (Newman 1971). Corresponding modifications were made to the theory of the dynamic ligand field (see for example Stedman and Newman 1971); however such models of the dynamic ligand field invariably regard this as a quasi-static extension of the static ligand field.

1.2. Rekindled interest

Recently some traditional assumptions of lattice dynamics have been reexamined. The role of rotational modes of the lattice in such topics as relaxation has long been unclear, and sometimes vigorously debated (e.g. Wurgers 1989), in the literature. Many authors (e.g. Judd 1974) dismiss the rotational modes as irrelevant. While their coupling is forbidden within the Born-Oppenheimer approximation, this cannot be invoked in the context of a nonadiabatic process such as spin-lattice relaxation. Hence the symmetry preservation under rotation in an adiabatic limit cannot be invoked (as by Galeeva *et al* (1980)) as a criticism of early papers on rotational mode effects in spin-lattice relaxation. Nor are Galeeva *et al* (1980) correct to argue that nonadiabaticity in spin-lattice relaxation is confined to Kramers doublets, as is shown by our calculations for non-Kramers systems (§ 2).

It has long been realised, at least by some workers, that rotational modes contribute to elastic constants; Nelson (1988) has recently reopened the question of the supposed irrelevance of the rotational modes in lattice dynamics (see also Pleiner and Brand 1988). The possibility of rotational mode coupling in spin-lattice relaxation was mooted two decades ago (Kumar *et al* 1970, Melcher 1972, Abragam *et al* 1972). Galeeva *et al* (1980) indeed argue that since local rotational modes are likely to be more strongly excited than (for example) shear modes, and since the obvious selection rules may be overcome by looking at higher-order coupling effects, rotational mode coupling could dominate in spin-lattice relaxation. However the possibility that rotational mode coupling could be effective at lower order in perturbation if the coupling mechanism were time-odd has not been discussed previously.

1.3. Earlier literature on rotational couplings

The situation is complicated by some confusion in these works with regard to selection rules both for rotational modes and for time-odd coupling. The best justification for the omission of rotational modes in spin-lattice relaxation is that implicit in the discussion of Kumar *et al* (1970), and is based on a time-reversal argument. It assumes that only a time-even coupling mechanism operates.

It also assumes that in all point groups, rotational modes transform in a manner which is inconsistent with time-even coupling; this is worthy of some justification. There are obvious cases when rotational coupling is forbidden on either coupling, for example E doublets in octahedral symmetry; in such cases, the Barnett effect, or magnetisation by rotation in paramagnets (Fletcher and Pooler 1982), is likely to be much reduced (Fletcher 1981). Otherwise the time-odd character of rotational couplings is guaranteed for the following reasons. Its coupling must be time odd at the O(3) level, since the appropriate rotational irrep 1^+ is never in the symmetric part of the square of any O(3) irrep such as the vector irrep 1^\pm . This is preserved in branching through a subgroup chain since symmetric and antisymmetric parts of a Kronecker product do not mix under branching provided no multiplicities arise. Multiplicities would arise only for a relatively low symmetry point group, where any degeneracy may be assigned to partners within $1^\pm(\text{O}(3))$ for the purposes of a point group Kronecker product analysis. And multiplicities in the branching rules for $1^\pm(\text{O}(3))$ always can be removed by introducing an intermediate group. Hence in particular there is no scope for enhancing the Barnett effect by considering unusual symmetries.

Abraham *et al* (1972) comment that Melcher (1970) does not take into account correctly the rotational properties of the fictitious spin. However they in turn substitute a time-odd operator (angular momentum) for the electronic operator expressing the rotational mode coupling, on the basis that the angular momentum operator correctly duplicates its rotational properties. Nevertheless they explicitly describe the mechanism as the standard quasistatic electric ligand field model and so as time-even, substituting the corresponding coefficients into their formalism. In this way they are led to predict a sizeable effect from rotational couplings. Their argument is spurious since their formulation is inconsistent; the contribution they discuss is disallowed by the selection rules imposed by time reversal symmetry. This problem was concealed from view by the inappropriate operator substitution mentioned above.

1.4. Observability

We frankly concede that the quasi-static approach to the dynamic ligand field has as much validity as (say) the superposition model of the ligand field, and that the time-odd coupling between the ion and the lattice mode is much smaller than the time-even coupling. In this paper we emphasise that this must be weighed against the possibility that time-odd coupling effects, by breaking the selection rules under which time-even effects are constrained, could nevertheless contribute significantly to physical effects. We also pose, and to some extent answer, the interesting question as to whether the associated effects are so characteristic as to aid in their unambiguous identification. The handicaps of the conventional mechanisms of spin-lattice relaxation caused by various selection rules arising from time inversion considerations are already well known; similarly for other applications of ion-lattice coupling theory. In this paper we aim to

include time-odd coupling among the possible strategies for overcoming these handicaps.

1.5. The tasks for further analysis

In a general approach, we see four obvious tasks. First, *ab initio* estimates should be made of the magnitude of all likely contributions to the time-odd coupling ('how big is it likely to be?'). Second, the various mechanisms should be categorised with respect to their other symmetry properties and so their relevance to different physical situations ('do different time-odd coupling mechanisms have different symmetries?'). Third, the reported relevance of experimental data such as the Barnett effect should be correlated with the *ab initio* estimates ('do these estimates fit the data?'). Fourth, the special circumstances in which even a small time-odd component to the coupling might be detectable should be estimated ('how might it be recognised?'). This paper attempts the fourth of these tasks. We first comment briefly on the first two tasks.

1.6. Magnitude estimates

The comments of Gill (1975) and Stevens (1969) about the smallness of time-odd coupling reflect the early death of the Waller mechanism, and probably also the fact that back-of-the-envelope calculations of the Zeeman effect from a moving ligand, regarded as a point charge, indeed suggest a very small contribution relative to that from the change in the static field. There are four main reasons why this is not necessarily the death of our subject.

First, the matter seems not to have been seriously examined; as far as we know, no calculation of the Zeeman effect from a moving ligand has been reported in the literature. As a crude attempt to remedy this deficiency, we might guess an amplitude of vibration of $x \sim 0.5$ nm, an angular frequency $\omega \sim 10^2$ THz, giving a magnetic field $\sim 10^{-2}$ T near the lanthanide, so giving an energy shift $\sim 10^{-4}$ cm $^{-1}$, or 10^{-5} of the standard mechanism.

Second, Fletcher (1981) and Fletcher and Pooler (1982) establish a direct connection between this mechanism and the Barnett effect of magnetisation by rotation, which has been observed in a wide variety of systems (Bates 1961).

Third, it is unlikely that the obvious mechanism for such a calculation (the semi-classical Zeeman effect from a point ligand as estimated above) is dominant. Before rejecting the possible relevance of time-odd coupling one might first be expected to formulate the theory of a Dirac electron in a molecule with internal motion (say in a rotating frame). We may expect, in view of the plethora of relativistic terms which appear in the static solution of the Hamiltonian of a hydrogen atom, that such a calculation would throw up many dynamic terms of time-odd character, most of which would have no classical counterpart, and some of which would be at least comparable to the classical terms. In view of the increasing sophistication of relativistic effects in quantum chemistry, the time is ripe for such a calculation.

Fourth, back-of-the-envelope calculations of any mechanism can prove totally inadequate. For example, the static ligand field is known to be poorly predicted, and for lanthanides (higher rank parameters in particular) underestimated on a point charge model by up to two orders of magnitude. While overlap integrals between the open shell electrons of a lanthanide ion and its ligands are small (a few percent), their contribution to the ligand field dominates for the higher rank ligand field parameters (Newman 1971). Incidentally, these are the parameters which are most important for the dynamic ligand

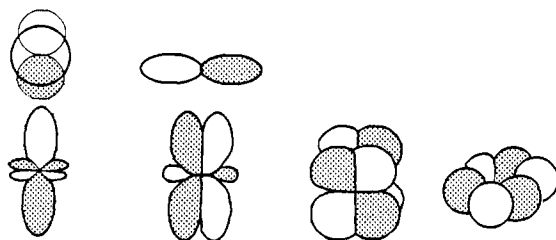


Figure 1. Analysis of the apparent angular dependence of the ligand field in the superposition model. The lower diagrams represent tesseral harmonics ($m = 0, 1, 2, 3$) for the corresponding 4f orbitals. Their electrostatic interaction energies with a point ligand are very similar; however, only the first and second ($m = 0, 1$) overlap with ligand functions (s, p_σ ; p_π respectively).

field, since their dependence on the interionic separation is stronger. Intrinsically small contributions in ligand field theory can be amplified by quantum effects to dominate the situation.

We parenthetically explain this result in simple terms, partly because this has not been previously done in the literature (though the fact has been well known for decades), and partly because this explanation may prove to have a new relevance in the present context. Thanks to the superposition model (Newman 1971, Newman and Ng 1989) it is sufficient to consider an axial arrangement of ligand and lanthanide ion (figure 1); a non-axial configuration may be reduced to an axial configuration using angular systematics. The energy of electrostatic interaction between a ligand and a lanthanide orbital (incidentally including corrections for the distribution of the charge) is relatively large; yet the overlap terms dominate the ligand field splitting. This is because the lanthanide orbital feels the ligand field through the differences in energy of the various orbitals ($m = 0, 1, 2, 3$) (figure 1). These energy differences are relatively small for the electrostatic integrals; they are also fairly uniform across the orbital set. By contrast, an $m = 0$ orbital will overlap only with an s or p_σ ligand orbital, while an $m = 1$ orbital will overlap only with a ligand p_π orbital. Hence the overlap-related contributions to the lanthanide energy splittings, which have roughly the ratio of the squared magnitudes of the overlap integrals, are strongly dependent on the orbital: all the overlap contribution appears as a difference. As a consequence the lanthanide 4f electron, acting as a probe of the anisotropy of the ligand field by way of the measurement of the energy differences between orbitals, senses a very strong angular variation in the overlap-dependent contribution to the effective ligand field. This is the physical reason that the high-rank parameters are particularly dependent on overlap-related effects.

A 'quantum enhancement' of the time-odd coupling is equally possible. The sensitivity of an overlap integral to motion is completely omitted in a classical calculation, even if (which we question) the semiclassical Zeeman-based mechanism is the dominant one.

1.7. Classification of mechanisms

In the wide variety of potential mechanisms, as in the fully relativistic analysis suggested above, there will certainly be a diversity of behaviour with respect to such symmetries as particle–hole (PH) conjugation. It is often a special signature or combination of

symmetries of an interaction which lead to vital selection rules, and the PH conjugation character is especially relevant to half-filled shells. Whether or not a time-odd phonon interaction will break the symmetries satisfied by a more conventional interaction may depend on its PH conjugation character. Ceulemans (1984) proved that linear Jahn-Teller effects vanish in half-filled shells (including those of ligand field theory, e.g. d^2 in octahedral symmetry); it would take a time-odd phonon interaction with the same PH conjugation character as the time-even mechanism to couple in first order, much as the relevance of higher multipole terms than $E1$ in the spectroscopy of half-filled shells may be traced to their PH conjugation character (Stedman 1987).

1.8. Summary of approach

We discuss several physical problems whose solution depends on the time reversal symmetry of the assumed interaction between a paramagnetic ion and the lattice vibrations. In most of these cases, but not all, the conventional theory tacitly assumes a time-even coupling. We ask: for what kind of measurement, and at what kind of level, might an additional contribution from a time-odd coupling be significant? Where possible, we consider a particular observable, and compare the strengths of the time-odd contribution to it and that of any competing contribution from a conventional mechanism, defining the ratio of these terms as a *feasibility quotient* FQ. For different applications we find that the FQ value may involve the ratio of time-odd and time-even coupling amplitudes, or the square modulus of this ratio, and other factors such as energy ratios associated with the perturbation theoretic denominators arising in either mechanism. The comparison of feasibility quotients for the possible applications gives significant information about the observability of time-odd coupling. Only a brief review of the conventional mechanisms, omitting proofs, is given here.

1.9. Time reversal selection rule

The central theorem to all our applications is the selection rule

$$\mu_r \in [\Lambda \otimes \Lambda]_{\pm} \quad \text{as } \tau_{\Lambda} \tau_0 = \pm 1 \quad (1)$$

if the matrix elements

$$M_{ll'm} \equiv \langle \overline{\Lambda l} | O_m^{\mu} | \Lambda l' \rangle \quad (2)$$

of an operator O_m^{μ} in a basis $\{|\Lambda l\rangle\}$ are not all to vanish. Here we denote by an overbar the time-inverted ket or bra: $|\overline{\phi}\rangle \equiv \mathbf{T}|\phi\rangle$, where \mathbf{T} is the time inversion operator. The paired labels refer to representation (Λ, μ) and component (l, m) with respect to some symmetry group G , and the symbol \otimes to the Kronecker product of representation theory; r labels possible repetitions of μ in the Kronecker product. τ_{Λ} is the phase of the basis under double time inversion (i.e. $(-1)^n$ where n is the number of electrons), τ_0 is the time reversal signature of the operator. The proof of this rule (for various full expositions of which, see Abragam and Bleaney 1970, Stedman and Butler 1983, Stedman 1990) is based on noting that since \mathbf{T} is antilinear, $\langle \overline{\phi} | \overline{O} | \overline{\psi} \rangle = \langle \phi | O | \psi \rangle^*$, and that therefore $M_{ll'm}$ is symmetric or antisymmetric in the labels l, l' depending on the joint signature $\tau_{\Lambda} \tau_0$ of the state and operator under \mathbf{T} . It is assumed that the basis is time even, in that $|\overline{\Lambda l}\rangle$ is expressible as a linear combination of the $\{|\Lambda l'\rangle\}$; this may necessitate Λ being a reducible representation under G , hence the use of a capital Greek letter. In our applications, we should enlarge the basis to be a product $\{|\Lambda l\rangle | L\rangle\}$ of kets from the

electronic space and of kets $|L\rangle$ from the nonelectronic space (photons or phonons or both) coupled by the interaction.

We shall require an extension of this result, which is proved in a parallel way. Consider the case where $O_m^\mu \rightarrow O$ (the lack of suffices denoting the fact that the following expression has not yet been written as a sum of irreducible tensors) is an effective operator derived from perturbation theory and bilinear in two interactions A^α, B^β :

$$O \equiv \sum_{\Omega\omega L} \left(\sum_{L''} \frac{\langle L|A^\alpha|\Omega\omega\rangle\langle L''|L''\rangle\langle\Omega\omega|B^\beta|L'\rangle}{E_\Lambda - E_\Omega + E_L - E_{L''}} + \sum_{L'''} \frac{\langle L|B^\beta|\Omega\omega\rangle\langle L'''|L''' \rangle\langle\Omega\omega|A^\alpha|L'\rangle}{E_\Lambda - E_\Omega + E_L - E_{L'''}} \right). \quad (3)$$

$\{|\Omega\omega\rangle\}$ is a basis for another (or possibly the same) electronic level, also assumed to be a time-even basis. $|L\rangle$ symbolises the altered state of any non-electronic system, for example photons or phonons. The application will be to processes in which the energy change in going from $|L\rangle$ to $|L'\rangle$ in the nonelectronic system will balance the energy change in the overall electronic transition.

We have distinguished the labels L'', L''' in the two terms of equation (3) to make the point that if we are considering some process in which, say, A^α creates a quantum (photon or phonon) and B^β does something different (annihilation, as in a Raman process, or perhaps a purely electronic coupling), the states $|L''\rangle$ and $|L'''\rangle$ necessarily involve different quanta and have different energies. We allude to this circumstance for brevity as the case of *non-equivalent denominators*.

As in the proof of equation 1, on using the basic rules $\langle a|V|b\rangle = \langle\bar{a}|\bar{V}|\bar{b}\rangle^* = \langle\bar{b}|\bar{V}^\dagger|\bar{a}\rangle = \tau_V\langle b|V|a\rangle$ it is readily seen that $M_{ll'm}$ can be related to $\tau_A\tau_B\tau_\Lambda M_{l'l'm}$ to the extent that the energy denominators in the two terms of equation (3) are equivalent. Hence equations (1) and (2) apply approximately only, with $\tau_0 \equiv \tau_A\tau_B$.

It is shown by later examples that this means that the conventional time-even mechanism for many physical processes is subject to a full cancellation (in equation (2)) or a near cancellation (in equation (3)) through time reversal considerations, in the latter case a full cancellation being averted only through the inequivalence of the denominators of equation (3). The time-even process is therefore intrinsically handicapped by the ratio of the difference in the denominators to their average. The time-odd coupling, though intrinsically much weaker, does not have this handicap, and so could become significant.

Even so, the (presumably) small matrix elements relevant to time-odd coupling may make the resulting effects weaker than those for time-even coupling. The corresponding process will be identifiable experimentally only through some novel property associated with the novel time reversal character. We will want to find cases for which these novel features are maximised, and at the same time for which the amplitude loss sustained by choosing time-odd coupling is minimised. Both of these considerations make interference terms (in the square modulus of a sum over all possible transition amplitudes, which characterises all quantum probabilities) of special interest; we shall introduce the time-odd interaction in just one matrix element. If the feasibility quotients depend explicitly or implicitly on an adjustable parameter (temperature or field), the region in which interference effects are significant will be transitional, and we may expect experiment to show the effects of time-odd matrix elements in all amplitudes for appropriate choices of parameters. In that case the feasibility quotient of interest will be a second or fourth power of the feasibility quotients that we list later.

For further reference, we note that if V_e denotes a time-even electronic operator and $|\bar{a}\rangle$ the time inverse of $|a\rangle$, the basic rule $\langle a|V|b\rangle = \langle \bar{b}|\bar{V}^\dagger|\bar{a}\rangle$, $\bar{V}^\dagger = \tau_V V$ gives

$$\langle a|V_e|a\rangle = \langle \bar{a}|V_e|\bar{a}\rangle \quad \langle a|V_e|\bar{a}\rangle = 0 \text{ if } \tau_a = -1. \quad (4a)$$

Many but not all of the interesting applications in this work pertain to Kramers (odd-electron) systems, for which $\tau_\Lambda = -1$ and incidentally $|\Lambda|$ is even; even-electron or non-Kramers systems have $\tau_\Lambda = +1$.

2. Spin-lattice relaxation in Kramers systems

For material reviewed briefly below, the reader should consult, for example, Orbach and Stapleton (1972), Shrivastava (1983). In EPR experiments on Kramers systems, the relaxation of interest occurs between two states in the set $\{|\Lambda l\rangle\}$ which corresponds to some level and which are degenerate in the absence of the magnetic field. For simplicity we consider a doublet ground state $|a\rangle \sim |\frac{1}{2}, \frac{1}{2}\rangle$, $|\bar{a}\rangle \sim |\frac{1}{2}, -\frac{1}{2}\rangle$.

First we consider the dependence of the time-odd coupling matrix element on phonon frequency. This suggests a direct experimental test for time-odd coupling, and is also highly important in determining the temperature dependence of a spin-lattice relaxation process. Whatever the detailed mechanism may be, the ligand operator will be derived from a velocity rather than a position operator in the time-odd case, and so will contain one more power of phonon frequency.

Searches have been made for frequency dependence of the spin-lattice coupling constants G_{ij} for S-state ions or of the effects of stress on spectral splittings (e.g. Black 1971, Clare and Devine 1980); comparisons can be complicated by other effects (Weber and Luchner 1981), such as phonon-phonon interaction, bottlenecking or cross-relaxation. No evidence for a frequency dependence characteristic of any time-odd mechanism has been reported to our knowledge; it is perhaps noteworthy, and at least indicative of the kind of reevaluation of experimental data which we would like to see, that a discrepancy between EPR splittings and so spin Hamiltonian parameters for Gd^{3+} :LaES at differing frequencies reported by Bleaney *et al* (1951) has still not been resolved. Such investigations set at least an upper limit for time-odd coupling effects which merits detailed comparison with the lower limit associated with the Barnett effect; we do not attempt this here.

The temperature and magnetic field dependence of ion-lattice relaxation is often characteristic of the mechanism: whether via long- or short-wavelength phonons, whether field-assisted, or involving admixtures of excited states etc. We show that characteristic changes can be expected for time-odd coupling. The prediction of the temperature dependence demands a knowledge of the dependence of the matrix element of the fundamental interaction V on the phonon frequency ω , since the connection with temperature arises through an integral over frequency with a given density of states (usually a Debye density) together with a phonon population factor involving the ratio of frequency and temperature.

For time-even coupling to long-wavelength phonons, $V \propto \sqrt{\omega}$; we might expect $V \propto \omega$ in that any relative motion or strain from acoustic phonons must be linear in wavevector and hence frequency; the compensating factor $1/\sqrt{\omega}$ arises from the normalisation of the Fourier expansion of the strain operator in terms of normal mode amplitudes. Different frequency and so temperature dependences are observed for optical or short-wavelength phonons (Shrivastava 1983).

For time-odd coupling, the differential momentum of lanthanide and ligand introduces a k - and therefore ω -factor for acoustic phonons as for the time-even case; second, the extra factor ω from the velocity as opposed to position dependence; third, that the remaining normalisation factor is $1/\sqrt{\omega}$ as for the time-even case. (The second and third contingency just mentioned may be verified by comparing the frequency dependence of the position and momentum operator for a simple harmonic oscillator.) This means that whenever a time-odd interaction matrix element replaces a time-even interaction, at least one extra factor of frequency and so of temperature is automatically acquired.

Many other phenomena (e.g. cross relaxation and phonon bottlenecks) can also give rise to increased temperature dependences. In a site with inversion symmetry, the linear terms in wavevector are inadequate to couple the odd modes of vibration, which may nevertheless be argued to couple significantly at higher order in wavevector and with a correspondingly enhanced temperature dependence (Klimachev 1973). Another questionable assumption is that in discussing these frequency factors we always assume a Debye density of states with an associated factor ω^2 . The temperature dependence of ion-lattice relaxation is therefore sensitive to the dimensionality of the system, an observation which has led to an ingenious if difficult test for the presence of lower dimensional and even fractal geometry (Stapleton *et al* 1982, Shrivastava 1982, Liu 1985; note however that this lowers the temperature dependence). The observed temperature dependence has therefore already been used as an indicator for the process, the geometry of the lattice, the phonon wavevector dependence, and indeed the impurity concentration. In proposing yet another mechanism for increasing the temperature dependence we propose at most a careful reevaluation of the literature in the light of a previously ignored alternative explanation.

2.1. Direct process

Consider first a single-phonon or direct process relaxation mechanism. The electronic operator corresponding to the phonon interaction plays the role of O_m^μ . This immediately gives the selection rule that the mediating phonons are restricted to representations μ compatible with equation 1. Inspection of the Kronecker product rules for both true and spin point group representations Λ shows that in most groups it is rotational modes, and those with similar transformation properties, which can never mediate relaxation processes, in the conventional choice $\tau_0 = +1$, i.e. a time-even phonon coupling mechanism. The reason for the special character of rotational modes in this context is discussed in section 1.3.

The spin-lattice relaxation contribution to the longitudinal relaxation time τ_1 necessarily involves a population change and so coupling between the time-conjugate states of the Kramers ground doublet, i.e. the matrix elements M_{ij} and so only the symmetric part of the Kronecker product of equation (1). Hence (either from equation (1) or equation (4)) the direct process of spin-lattice relaxation is strictly forbidden for the case of time-even phonon coupling in Kramers systems.

The conventional approach at this point is to include the effects of admixtures of higher electronic states (at a relative energy Δ) by the magnetic field B associated with the EPR experiment. This gives rise at moderate temperatures to a direct relaxation process with the field and temperature dependence B^4T/Δ^2 ; one factor ω and hence B (from $\omega = g\beta B/\hbar$) comes from the square of the matrix element, a factor ω^2 from the phonon density of states, a factor $(B/\Delta)^2$ from the admixtures necessary in each amplitude and a factor $(2n + 1)$ (so generating T/B at high temperatures) from the

relative population factors arising in the rate equation, where n is the Bose–Einstein function for the phonons. Experiments have confirmed this temperature dependence and to some extent the field and energy dependence, in various systems. If the effect of admixtures within the ground doublet only is considered, we have $\Delta \sim B$ so that there is a B^2T dependence.

A time-odd coupling escapes this cancellation and so provides an interesting alternative origin for a direct relaxation process; rotational modes for example could couple time-conjugate states directly. The above calculation of the T , B and Δ dependence is then simply modified by the addition of another T factor, and the removal of a B/Δ factor, for every replacement of a time-even by a time-odd interaction. This yields a process depending as B^3T^2/Δ (for an interference term) or B^2T^3 (for a fully time-odd coupling), rather than B^4T/Δ^2 , for example. One possibility therefore is to search for contributions to spin–lattice relaxation times with this revised temperature and field dependence. A test of the Δ dependence is difficult but not inconceivable (Krygin *et al* 1986).

The feasibility quotient in this situation may be taken as

$$\text{FQ}_1 \equiv |V_o/V_e|(\Delta/g\beta B)$$

where V_o , V_e represent a typical matrix element of the time-odd/even interaction and $g\beta B$ is the Zeeman splitting. There is an implicit temperature dependence in this and similar following expressions through the different frequency dependence of V_o and V_e .

The B^4T dependence of the direct process is confirmed in many systems (Pashinin and Prokhorov 1963, Davids and Wagner 1964 for example). A T^2 dependence has indeed been reported in some systems, and is often taken to indicate the presence of a phonon bottleneck. Our analysis gives one alternative to a bottleneck interpretation, and particularly if the exponent rises above 2. Whether this mechanism should then be taken seriously becomes a matter for further theoretical and experimental investigation.

2.2. Dephasing time

A second relaxation time may be measured in such experiments as linewidth studies: the transverse relaxation time τ_2 , corresponding to the dephasing of the spin through lattice interaction. Since it depends on the diagonal matrix elements of the ion–lattice interaction within the ground doublet, which are non-zero for time-even coupling, it might be expected that the conventional mechanism suffers no handicap in this case. However, quantum interference effects (see for example Stedman 1970a) require a coherent composition, in fact a subtraction, of the relevant matrix elements for the two states in the doublet. Since a time-even interaction equates these matrix elements (just as these states are degenerate in a time-even static ligand field) this process also cancels to first order.

Again a time-odd coupling thereby becomes a competitor; its diagonal matrix elements are opposite in sign (just as a magnetic field splits the doublet), and their subtraction gives a finite result. As before, the characteristic signature of time-odd phonon coupling will be a contribution to the direct relaxation process with a stronger temperature dependence and a weaker field dependence; a similar feasibility quotient can be expected for the transverse as for the longitudinal relaxation time.

2.3. Raman process

If two phonon interactions are involved, we are not restricted to the coupling of time conjugate states in each phonon interaction. We consider operators of the form of equation 3 where A^α and B^β are both one-phonon couplings. Let A^α describe the creation of a phonon in mode k , and B^β the annihilation of a phonon in mode l ; $|L''\rangle, |L'''\rangle$ represent states with one more, or one less, phonon respectively, and the corresponding denominators contain $\hbar\omega_k, -\hbar\omega_l$.

As shown in § 1, the matrix elements arising in a second order calculation will satisfy a symmetry or antisymmetry restriction which is exact to the extent that the denominators in equation (3) are equivalent.

First we consider the case that $\Omega \neq \Lambda$, i.e. that the intermediate electronic state is an excited ligand field level. It is then a reasonable approximation to set the denominators equal to the energy difference $\Delta \equiv E_\Lambda - E_\Omega$; phonon energies are ignored. In equation 3, this yields equivalent denominators. As a consequence, Raman contributions to the longitudinal relaxation time in Kramers doublets are approximately forbidden for time-even phonon coupling. In the present context this phenomenon is well known and is called the Van Vleck cancellation (Orbach and Stapleton 1972). The amplitude for the conventional process of relaxation is therefore handicapped by the ratio of the sums of the phonon energies to a typical electronic energy difference. The reciprocal of this ratio contributes to a feasibility quotient for the visibility of an interference term involving a time-odd interaction given by:

$$FQ_2 \equiv |V_o/V_e|(\Delta/\hbar\omega).$$

When the average over the phonon spectrum is taken, the extra factors of phonon frequency induce a new and characteristic temperature dependence. In general if, after all near cancellations are accounted for, the amplitude of any Raman relaxation process is of degree p in phonon frequencies, the corresponding observable varies at T^{7+2p} . Instead of giving a T^7 process, as found for non-Kramers systems, the Van Vleck cancellation leads to a T^9 dependence, which is clearly distinguishable in experiment. Alternatively, magnetic field modification of the wavefunctions of the ground doublet permit a process with a T^7B^2 dependence. This is weaker by the ratio $(g\beta B/\hbar\omega)^2$, where ω is a typical phonon frequency. Such dependences are clearly verified experimentally (Orbach and Stapleton 1972, Pouw and van Duynevelkt 1976, Shrivastava 1983).

The question as to whether there is a clear experimental signature for the presence of a time-odd coupling takes a new and interesting form. In a non-Kramers ion, the effect of time-odd coupling is to convert a T^7 process to a T^8 - T^{11} process depending on how many of the four time-even matrix elements are replaced by time-odd matrix elements, simply because of the different frequency dependence of these matrix elements. In a Kramers ion, the problem is more subtle; the replacement of one matrix element avoids the Van Vleck cancellation with the associated power of ω , but reintroduces the same factor ω through its different frequency dependence. If no more than one matrix element in each amplitude is replaced, then, the temperature dependence is unchanged. If both are replaced, a Van Vleck cancellation reappears. Temperature dependences of T^{11} have been seen, and variously explained (Klimachev 1985 for example considers time-even coupling to an odd mode in second order of the wave-vector). As for the direct process of relaxation, this discussion may be extended to the transverse relaxation time with similar conclusions.

The feasibility quotient now depends critically on the nature of the competing mechanism. For non-Kramers ions, the latter is the standard T^7 process, and the feasibility quotient is

$$FQ_3 = |V_o/V_e|$$

distinguishable if at all through the implied difference in temperature dependence. For Kramers ions, the feasibility quotient *vis-à-vis* the standard T^9 process is FQ_2 , the feasibility quotient *vis-à-vis* the B^2T^7 process is FQ_1 , and that *vis-à-vis* the T^{11} coupling to phonons in second order of wavevector k is

$$FQ_4 = |V_o/V_e|(1/ka)$$

where a is the ion–ligand separation.

2.4. Semidiagonal Raman process

In semidiagonal relaxation (Walker 1968, Stedman 1969), the intermediate electronic states are those of the ground doublet: $\Omega = \Lambda$. Here we clearly cannot have equivalent denominators in equation (3); rather, the denominators are nearly opposite, since $\hbar\omega \gg g\beta B$ and energy conservation requires the phonons to have approximately equal energies. (For non-Kramers ions, this gives a T^5 dependence.) Nevertheless, time inversion selection rules still handicap the contributions of the time-even interaction for two reasons, both of which derive from equation (4).

The first reason (I) is that a time-even interaction may not couple a state within the ground doublet with its time inversion conjugate in the absence of field-induced mixing from higher levels (which destroys the conjugacy). The second (II) is that the equality of the diagonal matrix elements for a state and for its conjugate within the ground doublet generates a new form of Van Vleck cancellation which is exact in the limit that the phonon energies are the same, i.e. that the ground state Zeeman splitting is negligible. Time inversion selection rules thus conspire to limit maximally the effectiveness of the conventional time-even coupling mechanism both for longitudinal and transverse relaxation (Stedman 1970b). The effect is to reduce the semidiagonal amplitude in Kramers systems by a factor $(g\beta B)^2/(\Delta\hbar\omega)$, thus giving a T^3B^4/Δ^2 process. In this expression, the factor $g\beta B/\hbar\omega$ is associated with I, and the factor $g\beta B/\Delta$ with II.

This double cancellation gives a special interest to the possible role of a time-odd coupling in such a system. The reciprocals of the above factors for mechanisms I and II contribute to the feasibility quotient appropriate for estimating the significance of time-odd coupling in this problem. Hence the feasibility quotient FQ_1 is to be associated with the bypassing of I through introduction of a time-odd phonon coupling between the time-conjugate states of the ground doublet. If the time-odd interaction is used to differentiate the diagonal matrix elements (bypassing II) and/or to give a finite off-diagonal matrix element (bypassing I) we obtain the respective feasibility quotients

$$FQ_3 = |V_o/V_e| \hbar\omega/g\beta B$$

and FQ_1 . To remove either source of handicap we need a time-odd interaction in one amplitude; to remove both we need two such. The feasibility quotients are different, and are multiplied when both replacements are made.

These time-odd coupling effects are distinguishable through their unique combination of temperature and field dependence; FQ_3 introduces two powers of temperature per amplitude, so returning a T^7 semidiagonal process in Kramers systems. Since

relevant phonon energies are typically less than electronic ligand field splittings, we have the hierarchy $\Delta E > \hbar\omega > g\beta B$, so that $FQ_1 \sim FQ_3 \gg FQ_2$. The role of the time-odd coupling mechanism in semidiagonal relaxation could therefore be of special importance.

3. Phonon Raman spectroscopy

We extend the formulation of phonon Raman scattering (for example Churcher and Stedman 1981) to include time-odd phonon coupling. By this is meant a Raman effect with photons of polarisation e, e' in which the electronic system eventually returns to the original level, while a phonon in mode κk is emitted with an energy $\hbar\omega_k$ equal to the difference $\hbar(\omega - \omega')$ of the photon energies. For convenience we write labels in vector form: $\Omega \equiv (\omega, \omega', \omega_k), \bar{\Omega} \equiv (\omega', \omega, -\omega_k), s \equiv (l, l', k), \bar{s} = (l', l, k)$.

Three interactions are involved, and equation (3) needs to be generalised accordingly. The Raman spectral feature has an intensity

$$I_{ee'}(\Omega) = \sum_s \left| \sum_{\rho\rho'} e_\rho M_{ll'}^{\rho\rho'}(\Omega) e_{\rho'} \right|^2$$

where the relevant matrix elements $M_{ll'}^{\rho\rho'}(\Omega)$ are related as in section 1 to an effective operator of the form

$$O^{\rho\rho'} = \sum_{\substack{M\mu N\nu \\ L''L'''}} \{ \langle L|D^\rho|M\mu\rangle\langle L''\rangle\langle L''|\langle M\mu|D^{\rho'}|N\nu\rangle\langle L'''\rangle \\ \times \langle L'''\rangle\langle N\nu|V_k|L'''\rangle / (E_\Lambda - E_M + \hbar\omega)(E_\Lambda - E_N - \hbar\omega) \dots \}$$

The omitted terms correspond to five alternative orderings of the three operators: the electric dipole operator components $D^\rho, D^{\rho'}$ and the ion-lattice interaction V_k , with corresponding changes to the denominators. The analysis of section 1, extended to this matrix element, leads to the symmetry

$$M_{ll'}^{\rho\rho'}(\Omega) = \tau_\Lambda \tau_\nu M_{l'l}^{\rho'\rho}(\bar{\Omega})$$

In the equivalent denominator approximation, which in this context means that the replacement $\Omega' \rightarrow \Omega$ has a negligible effect on the denominators, we obtain the selection rules

$$\mu \in [1 \otimes 1]_\eta \quad \nu \in [\Lambda \otimes \Lambda]_{\eta\tau_\nu\tau_\Lambda} \quad \mu^* \in \kappa \otimes \nu$$

where μ is the coupling symmetry of the photon interactions, κ the symmetry of the phonon and ν a coupling symmetry for phonon and photons. This generalises the selection rules of Churcher and Stedman (1981) to time-odd ($\tau_\nu = -1$) as well as time-even coupling.

As an example, we give in table 1 Raman active phonon modes for either coupling and for the true irreps of the tetrahedra group T. It is clear from an inspection of this table that some phonon symmetries are Raman active for time even coupling only, some for time-odd coupling only, some for both, and some for neither. Symmetric phonons ($\kappa = 0$) are never Raman active for time-odd coupling within states of a true irrep; the symmetric or identity irrep satisfies $\chi^0(g^2) = \chi^0(g)^2 = 1$ and so is never present in the antisymmetric square of a true irrep.

Table 1. Raman active phonons for the tetrahedral group.

		Time-even coupling:					Time-odd coupling:				
		μ	0	2	$\bar{1}$	1	μ	0	2	$\bar{1}$	1
Λ	κ						Λ	κ			
0	0		✓				0	1			✓
	2			✓			1, $\bar{1}$	1	✓	✓	✓
	$\bar{1}$				✓			2		✓	✓
1, $\bar{1}$	1			✓	✓	✓		$\bar{1}$		✓	✓
	2, $\bar{1}$		✓	✓	✓	✓		0		✓	✓
	0			✓			2	1		✓	✓
2	0		✓	✓				2		✓	
	1				✓			$\bar{1}$			✓
	2		✓	✓				0	✓		
	$\bar{1}$				✓	✓					
	0					✓					✓

On the face of it, breakthrough (Raman activation) of previously forbidden phonons would be a clear denomination of time-odd coupling. As such it competes against other sources of breakthrough, including instrumental problems (such as Snell's law effects at boundaries: Lai *et al* 1987) and the breakdown of the assumption of equivalent denominators. This assumption requires the difference of the photon energies $\hbar\omega$, $\hbar\omega'$, which by energy conservation is itself the phonon energy, to be negligible. Since these are optical photons, this is likely to be an excellent assumption for non-resonant Raman scattering processes in comparison with ion-lattice relaxation. We may therefore expect a feasibility quotient of the form:

$$FQ_4 \equiv |V_o/V_e|(\omega/\omega_k)$$

as compared to breakthrough from a breakdown of the assumption of equivalent denominators, if the time-odd coupling acts in just one amplitude. This looks promising, given that the frequency ratio in FQ_4 is $\sim 10^3$ – 10^4 in standard applications.

The best hope for detection of time-odd coupling through Raman scattering may still rest with those phonon symmetries which are Raman active for both couplings though in different polarisations, since as in our discussion of spin-lattice relaxation interference between time-odd coupling in one amplitude and time-even coupling in the conjugate amplitude makes the feasibility quotient linear rather than quadratic in the (presumably small) ratio $|V_o/V_e|$.

4. Jahn-Teller reduction factors

Fletcher (1981) has already pointed out the significance of time-odd lattice coupling for sum rules between Ham reduction factors $K(\lambda)$. The latter express the extent to which matrix elements of any electronic operator of given point group symmetry λ are reduced by lattice interaction with Jahn-Teller active lattice modes. These modes in turn are those non-symmetric modes that couple to an electronic manifold characterised by a definite point group irrep Λ . As such, Jahn-Teller active modes are precisely those consistent with equation 2 and with time-even coupling. Raman active modes also

include the symmetric modes. We note that Ceulemans (1984) showed that in half-filled shells the Jahn-Teller coupling vanishes to first order for reasons to do with its joint particle-hole conjugation and time reversal character; as mentioned in section 1, the situation for general time-odd coupling mechanisms in this rule deserves fuller study.

Sum rules between reduction factors, limiting their relative magnitudes, hold in special circumstances—second order coupling only, or coupling isoenergetic lattice modes. In each of these circumstances it is possible to use the point group 6j symbol orthogonality relations to transform between reduction factors and the reduced matrix elements of the lattice mode interaction as essentially dual parametrisation schemes (Payne *et al* 1983). Since time reversal considerations limit the possible symmetry types of the participating phonons (the other reduced matrix elements vanishing), they also interrelate the dual parameters, the reduction factors. Payne *et al* (1983) discuss this in $T \times \tau$ etc.

Time-odd interactions permit new mode symmetries to be Jahn-Teller active. Hence the sum rules are violated at lower order of perturbation than might otherwise be expected. Fletcher (1981) has illustrated this in the $E \times \varepsilon$ system (doublets in cubic symmetry). As a related and a particularly simple example, consider the planar square system of Stedman (1983) with $SO(2)$ as well as D_4 symmetry. In second quantisation the Hamiltonian is

$$\begin{aligned}
 H = & E(f_1^\dagger f_1 + f_2^\dagger f_2) + \hbar\omega_a(a^\dagger a + \frac{1}{2}) + \hbar\omega_b(b_1^\dagger b_1 + b_2^\dagger b_2 + 1) \\
 & + V_b[(f_1^\dagger f_1 - f_2^\dagger f_2)(b_1 + b_1^\dagger) + (f_1^\dagger f_2 + f_2^\dagger f_1)(b_2 + b_2^\dagger)] \\
 & + V_a(f_1^\dagger f_2 - f_2^\dagger f_1)(a - a^\dagger). \quad (4b)
 \end{aligned}$$

a^\dagger creates a phonon in the A_2 mode of the molecule, b_1^\dagger, b_2^\dagger create phonons in the B_1 and B_2 modes respectively, and f_1^\dagger, f_2^\dagger create electrons in the two E states (p_x, p_y). The corresponding coupling constants and energies are labelled in an obvious fashion, and the eigenkets of the Hamiltonian by $|i n_a n_1 n_2\rangle$, the labels giving the state of the electron and the populations of the A_2, B_1 and B_2 modes in the corresponding unperturbed state $|i n_a n_1 n_2\rangle_0$. It is a simple exercise in first order perturbation theory to derive

$$K(B_1) = K(B_2) = \langle 1000 | f_1^\dagger f_1 - f_2^\dagger f_2 | 1000 \rangle = 1 - 2V_b^2/\omega_b^2 - 2V_a^2/\omega_a^2$$

$$K(A_2) = \langle 1000 | (f_1^\dagger f_2 - f_2^\dagger f_1) | 2000 \rangle = 1 - 4V_b^2/\omega_b^2.$$

The time-odd coupling V_a clearly has the effect of violating the sum rule $2K(B_1) = 1 + K(A_2)$.

This violation competes with the other sources of violation implied by the above discussion: a spectrum of lattice mode frequencies, contributions fourth order in ion-lattice coupling, etc. Since real molecules and solids almost invariably have a broad vibration spectrum, testing the validity of sum rules between reduction factors is not a good way of looking for the effects of time-odd coupling.

5. Complex geometric phase factor in Jahn-Teller systems

When the ligand states are altered over a closed path in some parameter space of the Hamiltonian, the associated electronic wavefunctions do not necessarily return with their original phase. The non-dynamical part of the phase change, or Berry phase, is topological in character, since it does not depend on the manner in which the system is

taken along the closed path in parameter space. Chancey and O'Brien (1988) have shown that a Berry phase of π (a sign change of the electronic wavefunction) is appropriate to the $E \times \varepsilon$ Jahn–Teller system under an $SO(2)$ rotation of 2π on the ligand states; see also O'Brien (1989). This sign reversal is clear in the explicit perspex-and-string model of Stedman (1983) for the $SO(2) \rightarrow D_4$ molecule discussed in section 5: since the ligand arrows rotate at twice the angular speed of the electronic state (there is a 2:1 reduction on one pulley system), the central p electronic state rotates only by π for a 2π ligand rotation, and (since it is a p electron) changes its sign. However, this discussion as well as that of Chancey and O'Brien (1988) ignores the effect of time-odd or A_2 mode coupling. In another context Kivelson and Rokhsar (1988) explicitly argue that the π phase change is the only possibility when the Hamiltonian is time-even.

In general, we may rewrite the electronic part of equation (4) in terms of spin operators ($s = \frac{1}{2}$) for the fermion doublet: $H = EI + V_b(\sigma_z Q_1 + \sigma_x Q_2) + V_a \sigma_y P_a$ where $Q_i \equiv (b_i + b_i^\dagger)$, $P_a \equiv i(a - a^\dagger)$. Under a coordinate transformation

$$V = \begin{bmatrix} 1 & i \\ -i & 1 \end{bmatrix} / \sqrt{2}$$

this becomes $H = EI + \mathbf{B} \cdot \boldsymbol{\sigma}$ where $\mathbf{B} \equiv (V_b Q_\theta, V_b Q_\varepsilon, -V_a P_a)$ is an effective operator magnetic field for the spin.

Berry (1984) treated this problem in the adiabatic limit. If we first assume V_a is zero, \mathbf{B} is in the xy plane. The cone drawn by the spin in its space during an adiabatic evolution is a plane, and subtends a solid angle 2π ; hence the Berry phase γ , which is half this solid angle, is π . When we allow time-odd coupling, the cone subtends a smaller solid angle, and the geometric phase factor $\exp(i\gamma)$ is complex in general.

We may solve the time dependent Schrödinger equation exactly for the case $\mathbf{B} = (B_b \cos \omega t, B_b \sin \omega t, B_a)$. The arbitrary initial state

$$\Psi(0) = \begin{bmatrix} p \\ q \end{bmatrix}$$

evolves into

$$\begin{aligned} \Psi(t) = \exp(-iEt/\hbar + i\omega t/2) & \left[\cos(\delta t/\hbar) \begin{pmatrix} p \exp(-i\omega t) \\ q \end{pmatrix} \right. \\ & + ((i/\delta)(\hbar\omega/2 - B_a) \sin(\delta t/\hbar) \begin{pmatrix} p \exp(-i\omega t) \\ -q \end{pmatrix} \\ & \left. - (iB_b/\delta) \sin(\delta t/\hbar) \begin{pmatrix} q \exp(-i\omega t) \\ p \end{pmatrix} \right] \end{aligned}$$

where $\delta \equiv \sqrt{[B_b^2 + (B_a - \frac{1}{2}\hbar\omega)^2]}$. Physically $B_b \gg B_a$ and in the adiabatic limit $B_a \gg \hbar\omega$. $H(t)$ has the instantaneous eigenvalues $\lambda^\pm = E \pm \varepsilon$, where $\varepsilon \equiv (B_a^2 + B_b^2)^{1/2}$ with corresponding (unnormalised) eigenstates $\varphi^\pm = ([\pm \varepsilon + B_a] \exp(-i\omega t)/B_b, 1)^T$ so that if $\psi(0)$ is the normalised eigenstate $q\varphi^\pm(0)$ of $H(0)$, it is easily shown that $\psi(t)$ is given by

$$\begin{aligned} \psi(t) = q \exp(-iEt/\hbar + i\omega t/2) & \{ [\cos(\delta t/\hbar)] \mp i \sin(\delta t/\hbar) (1 - \hbar^2 \omega^2 B_b^2 / 4\delta^2 \varepsilon^2)^{1/2} \} \varphi^\pm(t) \\ & - i(\hbar\omega/2\delta) \sin(\delta t/\hbar) (1 \pm B_a/\varepsilon) \varphi^\mp(t). \end{aligned}$$

For cyclic adiabatic evolution $t = 2\pi/\omega$ so that $H(t) = H(0)$. Keeping only terms of zero

order in $\hbar\omega/B_b$ we obtain $\psi(2\pi/\omega) = -\exp(-2\pi i(E \pm \delta)/\hbar\omega)\psi(0)$. The dynamical phase is given by

$$-\int_0^{2\pi/\omega} \langle \psi(t) | H(t) | \psi(t) \rangle dt / \hbar = -(2\pi/\hbar\omega)(E \pm \varepsilon)$$

giving a Berry phase $\beta = \omega(\pi \pm B_a/\varepsilon)$, in agreement with $\beta = \mp \Omega/2$ (Berry 1984), where Ω is the solid angle subtended by \mathbf{B} in parameter space.

This verifies that the geometric phase factor $\exp(i\beta)$ is complex if the time-odd phonon coupling B_a is finite. This, like the sign of the Berry phase (Jiao *et al* 1989), will certainly be of experimental importance. We may expect these consequences to be distinguishable from the effects (such as coupling to modes of very different frequencies) whose action rivalled the other manifestations of time odd coupling in Jahn-Teller systems (section 4).

6. Other consequences of time-odd coupling

6.1. Ligand field induced absorption

The Judd-Ofelt theory expresses the oscillator strengths of $f^n \rightarrow f^n$ transitions, when associated with electric dipole radiation interaction together with an odd parity ligand field interaction (the latter to satisfy the parity selection rule), as a sum over k of terms proportional to the reduced matrix elements of effective operators Λ_q^k whose rank k is even and not greater than six (as for ligand field interaction within the f^n configuration). This parametrisation has been successful also when the ligand field interaction is necessarily dynamic (for lanthanide ions at a site with inversion symmetry) as well as static. The oscillator strengths are averaged over polarisation, and the denominators associated with the intermediate state energies are assumed to be rotational scalars, i.e. ligand field splittings of the virtual states are ignored.

The analysis of section 2 implies that a time-odd dynamic ligand field would require the presence of odd-rank (even parity) operators in the Judd-Ofelt formalism. The matrix elements relevant to the oscillator strength may be written in an $f^n LSJM_J$ basis: $f \propto \langle JM_J | \Lambda^k | JM_J \rangle^2$, and M_J plays the role of l in equation (2); there are no further energy denominators to be approximated. In fact, the requirement of even rank is strictly a consequence of time reversal, rather than parity, considerations. Of course it would be impossible to detect the presence of a time-odd dynamic coupling in practice by such a reparametrisation.

However, the situation is more hopeful if the polarisation is not averaged. Newman, Richardson, Reid and coworkers have discussed the extra information that may be obtained about the dynamic and the static contributions of the ligand field to oscillator strengths, using a tensorial expansion scheme with more parameters but also with much more predictive power. This is of special interest since we may expect a time-odd coupling to mimic the action of an internal magnetic field as far as selection rules are concerned, so inducing such chiral effects as optical activity which are not included in an analysis which averages over polarisation (see Berry *et al* 1986a, b, Richardson *et al* 1986).

Optical activity induced by a time-odd ligand interaction in systems with inversion symmetry will have as its competitor the mechanism for natural optical activity. i.e. interference between electric and magnetic dipole coupling terms; the relevant selection

rules for chiral interactions such as (natural or induced) optical activity (Ross *et al* 1988) are equally satisfied by a change in time reversal phase or the incorporation of one more power of the photon wavevector in one interaction term. At this level of argument the feasibility quotient for the observability of the time-odd dynamic coupling effects becomes

$$FQ_5 \equiv |V_o/V_e| \langle E1 \rangle / \langle M1 \rangle$$

where the last terms denote the relative size of electric and magnetic dipole matrix elements. This estimate does not however make allowance for other possible methods of identification, which we do not study here: as well as inducing a chiral effect, the time-odd ligand coupling may be associated with a characteristic set of the tensorial operators, much as Berry *et al* (1986a, b) and Richardson *et al* (1986) have discussed those features peculiar to M1 transition moments and ligand field effects in conjunction with f^n spectra.

6.2. Virtual phonon exchange

McKenzie and Stedman (1979) show that complicated Van Vleck cancellations occur in the analysis of virtual phonon exchange. Clearly these may be avoided as in section 2 by introducing interference with time-odd coupling terms. These will have the effect of changing the temperature and excited state energy dependence of the mechanism in a similar manner to that for the Raman spin-lattice relaxation processes.

6.3. S-state ion spectra

The selection rules special to half-filled shells, both of atomic and of molecular orbitals, limit the effects from time-even operators such as Jahn-Teller coupling (Ceulemans 1984). Clearly there may be breakthrough from time-odd coupling mechanisms whose other symmetries are appropriate.

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