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Quasi-Kramers symmetries under particle–hole conjugation

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Abstract. The application of quasispin in nuclear, atomic and ligand field theory is extended here to systems of electron and hole states in a metallic system. Conversely, results known in connection with particle-hole conjugation in metals are generalised to shell theoretic applications of quasispin. The analogy between the relationship of particle-hole conjugation with quasispin and the relationship of time reversal with ordinary spin is extended to the development of selection rules parallelling those associated through Kramers with time reversal. Hamiltonians such as the BCS Hamiltonian which are composed of quasispin operators with real or imaginary coefficients have definite conjugation signature and so have a special interest. Several old and new results for matrix elements within a half-filled shell are derived from this viewpoint.

1. Introduction

Particle-hole (PH) conjugation symmetries have been discussed in many diverse fields of physics. Usually they have been applied in nuclear or atomic shell theory, including ligand field theory, and have been of particular importance in the theory of the interactions of systems with half-filled shells, which are eigenfunctions of the PH conjugation operator. Beyond that, the symmetry (and indeed antisymmetry) of relevant terms in the Hamiltonians of interest has given useful links between systems with partial or complete mirror symmetry; for example, the nuclear spectra of ^{38}Cl and of ^{40}K may be deduced from each other (Parikh 1978). In other less obvious contexts, PH conjugation symmetries have been applied in, for example, the theory of alternation symmetry in certain organic molecules (Koutecky *et al* 1985) and in PH exchange relative to the Fermi level in a conductor, and so to symmetries in the calculation of the Kondo effect or of transport properties of a metal (Keiter *et al* 1969, Krempasky and Schmid 1979).

The links between all these diverse applications have not been adequately discussed. In particular, Keiter *et al* (1969) give an explicit representation for a PH conjugation operator in terms of second quantised operators, which seems to be unknown in the nuclear and atomic contexts. Furthermore, this explicit form is closely related to the concept of quasispin, which is well known in the atomic, nuclear and even organic molecule contexts, but conversely is unknown in the theory of metallic transport. (A formal discussion of quasi-spin groups is given by Cheng-tian Feng and Judd (1982), a review of applications in Rudzikas and Kaniausakas (1984) and further reviews and applications in Judd (1985) and Judd *et al* (1986).) It seems not to have been fully realised in any of these fields just how close is the analogy between particle-hole conjugation as it relates to quasi-spin on the one hand, and time reversal as it relates to ordinary angular momentum on the other. Some of the key relations are given by

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Judd (1967). Since these and other relationships are (for time reversal) vital in proving some important selection rules, originally associated with the name of Kramers (Wigner 1959, Abragam and Bleaney 1970), and illustrated in § 4, we anticipate selection rules of analogous form for various quantities of physical interest and arising from the algebra of quasispin and the associated PH conjugation. We extend Judd's comparison to bring out the analogy as fully as possible. For this we need to modify the PH conjugation operation of Keiter *et al* (1969) by a complex conjugation operation so as to make it antilinear. Only then, for example, do PH conjugation and quasi-spin anticommute. It transpires that, because of this modification, a physically non-trivial constraint is required of any Hamiltonian with PH conjugation symmetry (or antisymmetry). Consequently the full analogy with time reversal and spin is reserved to certain physical systems, which fortunately include many of model or practical interest. These conclusions are developed below. In a later paper we examine the consequences for the calculation of thermopower in metallic glasses in more detail.

2. Quasispin

We summarise the standard definitions of quasispin in a somewhat novel and compressed notation, which simplifies the phase choices of previous accounts and brings out many basic symmetries more clearly; some results are new.

Eigenstates $|K)$ of an unperturbed Hamiltonian H_0 are labelled by an irrep component label K of the symmetry group G_0 of H_0, corresponding to the spatial and spin degrees of freedom. We take states to be paired so that for every one-fermion state K there is a conjugate state $\bar{K}$ in which the spin projections are reversed (incidentally this guarantees that the states do not coincide) and in which also some similar transformation of the spatial parts of the eigenstates is performed. The latter transformation will correspond to a reversal of orbital angular momentum for the atomic and nuclear applications, to a reversal of momentum for superconductivity, and to a particle-hole exchange (between states on opposite sides of, and equidistant from, the Fermi surface) for thermopower applications. In most of these cases, the conjugate labels will have conjugate group theoretic character, and the unitary matrices—analogous to a contravariant metric tensor—which couple conjugate states into a group invariant correspond to the $2jm$ symbols of the relevant symmetry group. These matrices are denoted here by their component (row and column) labels (KL); since L is necessarily conjugate to K, and so uniquely defined in terms of K, we shall also write $(KL) \equiv (K\bar{K})\delta_{K\bar{L}}$. The phase $(K\bar{K})$ is unavoidable in this definition for fermion states, since the matrix is antisymmetric; hence by unitarity the $2j$ phase $\{K\} \equiv (KL)(LK)^*$ is -1. For example, if we ignore orbital labels, K reduces to the spin projection m ($m = \pm\frac{1}{2}$), the spin transformation reduces to the $2jm$ symbols of SU(2) for spin $s = \frac{1}{2}$:

$$(K\bar{K}) \rightarrow (m\bar{m}) = (-1)^{s-m}\delta_{m,-\bar{m}} \tag{1}$$

i.e. $(+\frac{1}{2}, -\frac{1}{2}) = +1$, $(-\frac{1}{2}, +\frac{1}{2}) = -1$, and so $\{s\} \equiv (+\frac{1}{2}, -\frac{1}{2})(-\frac{1}{2}, +\frac{1}{2}) = -1$. The operator a_K is an irreducible tensor operator while the annihilation operator becomes an irreducible tensor operator $\tilde{a}_K$ only when rephased by the definition $\tilde{a}_K = (KL)a_L$. These operators have the anticommutation relations

$$\{a_K^+, \tilde{a}_L\} = (LK). \tag{2}$$

We define a combined operator $\underline{A}_K \equiv (a_K^+, \tilde{a}_K)$, and for reasons that will become clear shortly regard this as a covariant SU(2) spinor ($Q = \frac{1}{2}$), the appropriate space, 'quasispin space', being unrelated to spin or orbital space. This spinor has as its component $A_{Kq} = a_K^+(\tilde{a}_K)$ for $q = \frac{1}{2}$ ($-\frac{1}{2}$, respectively) where q is the quasispin projection. The corresponding contravariant components are obtained using the quasispin $2jm$ symbols (equation (1)) as a metric: $A_K^q \equiv (qq')A_{Kq'}$, and so may be seen to give the Hermitian conjugate operators: $A_K^q = (KL)A_{Lq}^+$; $A_{Kq}^+ = (LK)A_L^q$. These operators have the anti-commutation relations:

$$\begin{aligned} \{A_{Kq}, A_{Lq'}\} &= (LK)(qq') \\ \{A_K^q, A_{Lq'}\} &= \begin{pmatrix} q \\ q' \end{pmatrix}(KL) \end{aligned} \tag{3}$$

the mixed metric tensor being the Kronecker delta symbol. Note the decoupling between quasispin and ordinary spin-space labels in these relations.

Quasispin generators are obtained from coupling (denoted by boldface brackets) these spinors to an invariant in space-spin labels (denoted by the leading superscript zero) and to unit quasispin ($Q = 1$):

$$\begin{aligned} Q_\alpha^K &\equiv (\mathrm{i}/\sqrt{2})[\mathbf{A}_K \mathbf{A}_L]^{01} \\ &= (\mathrm{i}/\sqrt{2})(KL)A_{Kq}A_{Lq'}\langle 1\alpha|\tfrac{1}{2}q\tfrac{1}{2}q'\rangle. \end{aligned} \tag{4}$$

The factor i ensures that these operators are Hermitian (to be precise, $(Q_\alpha^K)^+ = (\alpha\beta)Q_\beta^K$; for spin 1, a suitable cartesian basis can be chosen, as mentioned below, to give $(\alpha\beta) = \delta_{\alpha\beta}$). These close under commutation on the SU(2) Lie algebra:

$$[Q_\alpha^K, Q_\beta^K] = \mathrm{i}\varepsilon_{\alpha\beta\gamma}Q_\gamma^K \tag{5}$$

hence the name quasispin. A diagram proof is given in figure 1. The explicit form of

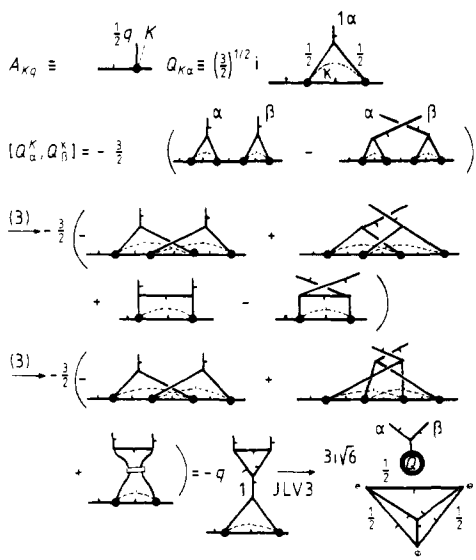

Figure 1. Definitions of fundamental spinor A_{Kq} and of quasispin Q_α^K and proof of the SU(2) Lie algebra of quasispin operators using diagrams.

the quasispin operators is

$$\begin{aligned} Q_+^K &= -(\mathrm{i}/\sqrt{2})(KL)(a_K^+ a_L^+) \\ Q_-^K &= -(\mathrm{i}/\sqrt{2})(KL)(\tilde{a}_K \tilde{a}_L) = -(\mathrm{i}/\sqrt{2})(LK)a_L a_K \\ Q_0^K &= -\mathrm{i}(KL)\{(a_K^+ \tilde{a}_L)+(\tilde{a}_K a_L^+)\}/2 \\ &= \mathrm{i}[n_K + n_{\bar{K}} - 1]/2 \end{aligned} \tag{6}$$

in spherical coordinates (i.e. the basis of the Rotenberg *et al* (1959) tables; we note that the superscript K on quasispin uniquely identifies one spin orbital K and so its conjugate $\bar{K}$, coupled to it by the $2jm$ symbol $(KL)=(K\bar{K})$ on the right-hand side). Using the contrastandard Fano-Racah transformation (see Stedman 1985, appendix B) we obtain in cartesian coordinates

$$\begin{aligned} Q_x^K &= -(KL)(a_K^+ a_L^+ - \tilde{a}_K \tilde{a}_L)/2 \\ Q_y^K &= -\mathrm{i}(KL)(a_K^+ a_L^+ + \tilde{a}_K \tilde{a}_L)/2 \\ Q_z^K &= (KL)\{(a_K^+ \tilde{a}_L)+(\tilde{a}_K a_L^+)\}/2 = [1 - n_K - n_{\bar{K}})/2 \end{aligned} \tag{7}$$

where $n_K = a_K^+ a_K$. The quasispin magnitude $Q^K = \max|Q_z^K|$ is equal to $\frac{1}{2}$ for states with $n_K = n_{\bar{K}}$ (both particle and hole states filled, or both empty) and is equal to zero for states with n_K not equal to $n_{\bar{K}}$ (just one of the particle and hole states filled). Q_+^K ladders between states with $n_K = n_{\bar{K}} = 1, 0$. We can check (figure 2) that the commutation relations of $\boldsymbol{Q}^K$ and of $\boldsymbol{A}_K$ correspond to those of a spin-1 and spin-$\frac{1}{2}$ tensor:

$$[Q_z^K, A_{Kq}] = qA_{Kq}. \tag{8}$$

The above definitions of quasispin relate to just one pair of states.

Quasispin for a shell, $(nl)^N$ say, may be defined in terms of a summation over all pairs $m_l = -l$ to l: $\boldsymbol{Q} = \Sigma'_K \boldsymbol{Q}^K$. Then

$$Q_z = \tfrac{1}{2}[(2l+1) - \hat{N}] \tag{9}$$

where $\hat{N} = \Sigma'_K (n_K + n_{\bar{K}})$. Hence Q is integral/half-integral as N is odd/even, and for a half-filled shell ($N = \langle \hat{N} \rangle = 2l+1$) the eigenvalue M_Q of Q_z is zero.

We may construct coupled tensors of other types than the above. It is useful later to note the result $[A_K A_L]^{00} = \delta_{K\bar{L}}(n_{\bar{K}} - n_K - 1)/\sqrt{2}$, so that for example the coupled (anti)commutators have the value

$$\begin{aligned} [[A_K, A_{\bar{K}}]]^{00} &\equiv [A_K A_{\bar{K}}]^{00} - [A_{\bar{K}} A_K]^{00} \\ &= \sqrt{2}(n_{\bar{K}} - n_K) \\ [\{A_K, A_{\bar{K}}\}]^{00} &= -\sqrt{2} \end{aligned} \tag{10}$$

while

$$[[A_K, A_{\bar{K}}]]^{01}_\alpha = 0 \qquad [\{A_K, A_{\bar{K}}\}]^{01}_\alpha = -(2\sqrt{2}\mathrm{i})Q^K_\alpha. \tag{11}$$

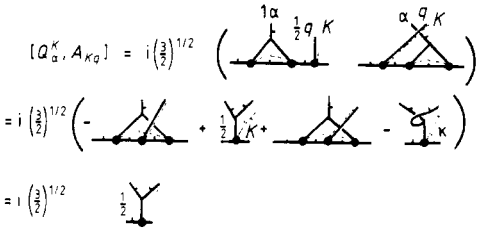

Figure 2. Commutator of quasispin and fundamental spinor.

The first result of equation (11) follows from equation (3) via the diagram reduction theorem JLV1. Judd (1967) gives an equation related to equation (11) in the form

$$[\boldsymbol{A}\,\boldsymbol{A}]^{k\kappa K} = [1-(-1)^{k+\kappa+K}][a^{+}\tilde{a}]^{k\kappa} - (-1)^{K}\delta_{k0}\delta_{\kappa 0}$$

the superscripts k, κ, K denoting orbital, spin and quasispin ranks.

The anticommutation relations

$$\{Q_i^K, Q_j^K\} = 2\delta_{ij}(Q_z^K)^2 = \delta_{ij}(1 - n_K - n_{\bar{K}} + 2n_K n_{\bar{K}}) \tag{12}$$

have a remarkably simple diagonal property, whose general proof (in the form $\{Q_\alpha^K, Q_\beta^K\}$ is proportional to $(\alpha\beta)$) is not obvious from equation (3).

An elegant and equivalent statement is the following result.

Theorem. The coupled tensor $[\boldsymbol{Q}^K\boldsymbol{Q}^K]^{02}$ vanishes. (In Judd's (1967) notation, $(X^{(100)}X^{(100)})^{200}$ vanishes.)

We comment first that $[\boldsymbol{Q}^K\boldsymbol{Q}^K]^{00}$ gives the Casimir operator $(\boldsymbol{Q}^K)^2$, while $[\boldsymbol{Q}^K\boldsymbol{Q}^K]^{01}$ gives $\boldsymbol{Q}^K$ by virtue of the Lie algebra of SU(2) ($\boldsymbol{Q}^K \times \boldsymbol{Q}^K = \boldsymbol{Q}^K$) and that the above theorem exhausts the possibility of further couplings.

Second, since a symmetriser on vector labels does not couple to spin 1, and since the coupling to spin 0 is diagonal, this theorem implies the above diagonality of the anticommutator.

Third, this theorem does not hold for isospin ($I_+ = a_K^+ a_{\bar{K}}$, $I_z = \frac{1}{2}(n_K - n_{\bar{K}})$, etc) and so is not simply a consequence of fermion bases of the spin operators. It is special to quasispin.

While not an elegant demonstration (such has eluded us), the following proof gives at least some insight.

Proof. First, the terms arising from anticommutators of the A_{Kq} in the expression $[\boldsymbol{Q}^K\boldsymbol{Q}^K]^{02}$ must vanish, since only two operators remain, and coupling two quasispin-$\frac{1}{2}$ labels to quasispin 2 is forbidden by the triangle rule of the quantum theory of angular momentum, e.g. via the diagram pinching theorem JLV3 (figure 3(*a*)). This much is true also for isospin, however.

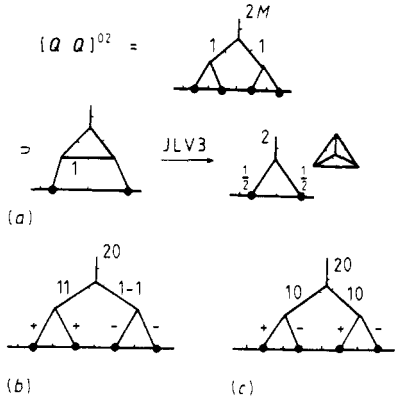

Figure 3. (*a*) Definition of a coupled tensor of rank 2 (derived from quasispin) and the proof of the vanishing of the anticommutator terms in this using the triangle rule. (*b*), (*c*) Two coupling trees which contribute oppositely to the component-zero part of the rank-2 coupled tensor.

Second, when M is non-zero (say when M is positive), $[\boldsymbol{Q}^K \boldsymbol{Q}^K]^{02}_M$ inevitably involves two operators with the same labels, including the same quasispin component (say two A_{K+} or two A_{L+}), which annihilate each other when brought together through anticommutation.

When $M=0$, terms which do not disappear for the above reason come in pairs of products of operators which have the form $A_{K+}A_{\bar{K}+}A_{K-}A_{\bar{K}-}$, $A_{K+}A_{\bar{K}-}A_{K-}A_{\bar{K}+}$ from the coupling trees of figure 3(b) and (c), respectively. While the Clebsch-Gordan coefficients in figures 3(b) and (c) are different, their products are equal and the final result is proportional to the sum of the above operator products. However this sum cancels, since the two expressions are related by an odd number of permutations of the A_{Kq} and each permutation attracts a sign from the anticommutation procedure.

Comments. (a) This does not forbid, say, creation of ^1S of f^4 from ^1S of f^0 by the application of quasispin operator products. The seniority $v=0$ may be the same, in which case zero-rank operators could satisfy the quasispin selection rules (however, $\boldsymbol{Q}^2$ would not contain four creation operators); even when $v=4$ say, and a rank-two operator is vital, one may mix quasispin operators for different orbitals, since $[\boldsymbol{Q}^K \boldsymbol{Q}^L]^{02}$ is non-zero for $K \neq L$; alternatively (see equation (48) of Judd (1967) or equation (8.44) of Rudzikas and Kaniauskas (1984)) one may form operators with definite quasispin rank, but non-scalar in spin-space labels first (the $2jm$ symbol (KL) in equations (6) and (7) could be replaced by a $3jm$ or Clebsch-Gordan, coupling K and L to other than an invariant). We note that there will in turn be related, more complicated, restrictions on these operators and this will affect their matrix elements by the reasoning of §§ 4-5.

(b) Since the operator on the right-hand side of equation (12) commutes with quasispin, the theorem is equivalent by Schur's lemma (as well as by elimination of $Q=1,2$ ranks) to the quasispin-scalar character of the anticommutator:

$$[\{Q_i^K, Q_j^K\}, Q_k^K]=0.$$

This relation succinctly distinguishes quasispin from isospin.

3. Particle–hole conjugation

We define the particle-hole (PH) conjugation operator as

$$C \equiv (\Pi_K C_K)Z \equiv (\Pi_K [F_K + G_K])Z \tag{13}$$

where

$$\begin{aligned} F_K &= n_K(1-n_{\bar{K}})+n_{\bar{K}}(1-n_K)=1-4(Q_z^K)^2 \\ G_K &= (K\bar{K})(a_{\bar{K}}a_K - a_K^+ a_{\bar{K}}^+) = -2\mathrm{i}Q_y^K \end{aligned} \tag{14}$$

and Z is the complex conjugation operator. This definition of a PH conjugation operator (apart from the factor Z) is given explicitly by Keiter *et al* (1969), although the link with quasispin is novel. It is straightforward to prove from equations (8) and (10)-(12) that

(a) C is unitary. This follows since $F_K^2 - G_K^2 = 1$, $[F_K, G_K]=0$, these relations themselves following from $[Q_z^2, Q_y]$ being proportional to $\{Q_z, Q_x\}$, from $F_K^2 = F_K$, $G_K^2 = -4Q_z^2$ and from equation (9). Since C is also antilinear, we use the term antiunitary (as for time reversal; Abragam and Bleaney (1970)).

(*b*) C has the effect of producing an empty/filled state K if the PH conjugate state $\bar{K}$ is filled/empty (in the wavefunction on which C acts) respectively. One may define C (Bell 1959, Lawson and MacFarlane 1965) from the equations

$$C|0\rangle = \Pi_K(-a_K^+ a_{\bar{K}}^+)|0\rangle \qquad Ca_K^+ = \tilde{a}_K C \qquad C\tilde{a}_K = -a_K^+ C. \tag{15}$$

The last sign is unavoidable. The third equation follows from the second, using the antiunitarity of C, and noting that the transformations between a_K and a_K^+ generate the $2j$ phase $\{s\} = -1$. These last two equations may be summarised in the form

$$CA_{Kq} = A_K^q C. \tag{16}$$

(*c*) C anticommutes with quasispin:

$$\{C, \boldsymbol{Q}\} = 0. \tag{17}$$

This is a direct consequence of the antilinearity of C coupled with equation (9) $(i = y, j = x, z)$, $(1 - 4(Q_z^K)^2)\boldsymbol{Q}^K = 0$, $[Q_y^K, Q_y^L] = 0$. (A simple proof of the second of these relations is to note that $Q^K = \frac{1}{2}$ or 0, and that from equation (10) $Q_z^2 = \frac{1}{3}\boldsymbol{Q}^2$.) These relations imply that $C|QM_Q\rangle$, where M_Q is the eigenvalue of Q_z, is proportional to $|Q - M_Q\rangle$, since C and Q_z anticommute, and that the phase factor in this proportionality must include $(-1)^{M_Q}$, since C and Q_+ anticommute. We shall build on this shortly to give a more precise statement of the relation (equation (19)).

(*d*) C and ordinary spin commute: $[C, \boldsymbol{S}] = 0$, as mentioned above. Similarly, C commutes with spatial symmetry operations. C is made from quasispin operators, themselves of scalar character—witness the similar transformation properties of the two operators on each side of C in equation (13).

(*e*) The states $|QM_Q\rangle$ have eigenvalue ± 1 with respect to C^2:

$$\begin{aligned} C^2 &= \Pi_K[1 - 4(Q_z^K)^2 - 2iQ_y^K]^2 \\ &= \Pi_K[1 - 8(\boldsymbol{Q}^K)^2/3] = (-1)^{2Q}. \end{aligned} \tag{18}$$

Again, this is in exact analogy to the situation for time reversal and real spin, where Kramers states—states pertaining to an odd number of electrons—have negative eigenvalue under double time reversal, while a state with an even number of electrons, or non-Kramers state, has positive eigenvalue. Here, however, a state with eigenvalue $C^2 = 1$ (a 'quasi-non-Kramers' state) is one which within a shell has, curiously, an *odd* number of electrons (giving equation (9) integral eigenvalues); more generally, such a state is one with an even number of pair states K, $\bar{K}$, both filled or both empty, along with any number of half-occupied pair states. A state with an *even* number of electrons in a shell, or a state with an odd number of such pair occupancies, has $C^2 = -1$ ('quasi-Kramers'). This curious inversion between evenness and oddness for time reversal and PH conjugation is apparent throughout the later development.

Since the number of particles must be conserved, a physical operator may only connect states of the same C^2 parity at least within shell theory. Together, (*a*)-(*e*) show that PH conjugation stands in relation to quasispin precisely as time reversal stands in relation to spin (Judd 1967). In particular, equation (18) requires the Q dependence of the phase in the relation (otherwise ensured by (*c*) and by freedom of phase choice of the kets)

$$C|QM_Q\rangle = (-1)^{Q-M_Q}|Q - M_Q\rangle. \tag{19}$$

In particular, for a half-filled shell ($M_Q = 0$) all states are self-conjugate, with eigenvalues ± 1 under C as Q is even/odd.

We note that since $\langle C\rangle_{Q=0}=1$, C commutes with $Q=0$ terms such as $(a_K^+\tilde{a}_L-\tilde{a}_K a_L^+)$, or equations (8) and (12).

4. Physical consequences of time reversal symmetry

4.1. Review of standard applications

If CP violation is ignored, all Hamiltonians are invariant with respect to time reversal. When such Hamiltonians are divided into operators acting on one or other of two subsystems, such as a radiation field and the matter on which it acts, each operator in an interaction has its own time reversal signature; the signs must cancel on forming the product. We review the significance of this in a condensed matter context. More details may be found in Abragam and Bleaney (1970), Payne and Stedman (1983) and Stedman (1985), for example.

For example, the Zeeman interaction involves two time-odd quantities; in this case it is important that time reversal and angular momentum anticommute, i.e. that spin is time-odd. Similarly, the radiation-matter interaction $\boldsymbol{A}\cdot\boldsymbol{p}$ has time-odd operators coupled into a time-even (and rotationally invariant) product. However the interaction $\boldsymbol{E}\cdot\boldsymbol{r}$ with a static electric field involves time-even operators only. These results lead directly to novel selection rules, based on application of the identity for antiunitary operators T:

$$\langle a|H|b\rangle=[(\langle a|T^{-1})(THT^{-1})(T|b\rangle)]^*=\langle\bar{a}|\bar{H}|\bar{b}\rangle^* \tag{20}$$

(the bars denoting the transformed quantities) (Messiah 1960). Since not all of these are well known we mention some examples. The eigenvalue of any state $|a\rangle$ with respect to double time reversal will be written as $\{a\}$ and is $+1$ for a non-Kramers state (even number of electrons) and -1 for a Kramers state (odd number of electrons). $\{a\}$ is determined by the product of $2j$ phases $\{s\}$ for the constituent electrons, and corresponds to $\{K\}$ or the $2j$ phase in the full parentage labelling from SO(3). Results special to Kramers (non-Kramers) systems will be labelled K (NK, respectively).

From equation (20), a time-even (odd) coupling $E(O)$ in a subsystem gives the constraints

$$\begin{aligned}&\langle a|E|a\rangle=\langle\bar{a}|E|\bar{a}\rangle \qquad &&\langle a|E|\bar{a}\rangle_K=0\\ &\langle a|O|a\rangle=-\langle\bar{a}|O|\bar{a}\rangle \qquad &&\langle a|O|\bar{a}\rangle_{NK}=0.\end{aligned} \tag{21}$$

Hence $|a\rangle$ and $|\bar{a}\rangle$ are degenerate under a time-even interaction and are distinct in the Kramers case (for otherwise $\{a\}=1$). Only a time-odd interaction can separate time conjugate states. However, it may not couple such states. For example, single-photon interactions may not couple time-conjugate states $|a\rangle, |\bar{a}\rangle$ even in a non-Kramers system, irrespective of the multipole of coupling. Similar results hold at higher order of perturbation. Such second-order contributions as

$$P=\Sigma_c[\langle a|H_l|c\rangle\langle c|H_k|\bar{a}\rangle/\{E_a-E_c+\omega_k\}+\langle\bar{a}|H_k|\bar{c}\rangle\langle\bar{c}|H_l|a\rangle/\{E_a-E_c-\omega_l\}] \tag{22}$$

(k, l referring to boson—photon or phonon—modes coupled by the interaction and a, c to electronic states) suffer cancellation of the numerators (dubbed the 'van Vleck cancellation' in the literature) in Kramers systems. Hence, for example, Raman spin-lattice relaxation in a Kramers system has a T^9, rather than T^7, dependence on temperature. In two-particle matrix elements (as for virtual phonon exchange between

Kramers ions (McKenzie and Stedman 1979)) the analogous cancellations take on a complex but elegant structure, and again are directly responsible for physically distinguishable properties such as temperature dependence.

Let $|a\rangle$ and $|b\rangle$ belong to some manifold of states which are degenerate under a spatial symmetry group of the unperturbed Hamiltonian. The manifold will be labelled by some irreducible representation λ, say, of the spatial symmetry group. The Hamiltonian is assumed to be time-even. All matrix elements within that manifold of states $\{\langle a|H|b\rangle\}$ may be written as linear combinations of the set $\{M_{ab}=\langle\bar{a}|H|b\rangle\}$, since $|\bar{a}\rangle$ is in this manifold, and (whether or not it is distinct from $|a\rangle$, i.e. for either Kramers or non-Kramers systems) $\{|\bar{a}\rangle\}$ as well as the set $\{|a\rangle\}$ is a basis for the manifold. However, the above constraint gives that $M_{ab}=\{a\}M_{ba}$ for a time-even coupling, and $M_{ab}=-\{a\}M_{ba}$ for a time-odd coupling. Hence the allowed spatial coupling symmetries are restricted to those irreducible representations appearing in the symmetrised and antisymmetrised Kronecker product $[\lambda\times\lambda]_{\pm\{a\}}$ respectively.

In the case of non-resonant Raman (photon) scattering, Raman active (phonon) modes couple via singlet electronic states only to even coupling symmetries ($J=0, 2$) of the two photons. More generally the symmetric and antisymmetric Raman couplings (the latter arising from coupling to electronic multiplets) may not interfere.

For the same basic physical reason (time-even phonon coupling) Jahn–Teller active phonons are those contained in an appropriately symmetrised part of the Kronecker square of the electronic state symmetry. The physical origin of some important sum rules for reduction factors in Jahn–Teller systems may be traced to this.

4.2. Relevance of time reversal to PH conjugation

Since the basic equations leading to all these important results all have analogues for PH conjugation and quasispin, we expect a similar set of results to be obtained in quasispin applications. The only requirement not already established is that the interaction operators involved should have a definite PH conjugation signature (i.e. $CH=\pm HC$). We describe such an operator H as C-even or C-odd (and label them $\mathscr{E}$, $\mathscr{O}$) respectively. Given such operators, we have

$$\begin{aligned} &\langle a|\mathscr{E}|a\rangle=\langle\tilde{a}|\mathscr{E}|\tilde{a}\rangle \qquad && \langle a|\mathscr{E}|\tilde{a}\rangle_{QK}=0 \\ &\langle a|\mathscr{O}|a\rangle=-\langle\tilde{a}|\mathscr{O}|\tilde{a}\rangle \qquad && \langle a|\mathscr{O}|\tilde{a}\rangle_{QNK}=0 \end{aligned} \tag{23}$$

where the tilde (not to be confused with the rephasing of an annihilation operator) is used instead of a bar, a script letter in place of Roman characters and Q (quasi-) added to subscripts (Kramers, non-Kramers) to emphasise the analogy but not the equivalence with equation (21).

In systems where particle and hole labels are related by time reversal symmetry, the PH conjugacy signature necessary for use of equation (23) is guaranteed and the PH signature of an interaction is closely linked to its time reversal signature. This comes about since charge conjugation essentially time-inverts the state labels. Detailed proofs of this statement are deferred to § 5, since fermion anticommutation rules and similar phase factors affect the precise form of the connection in different ways for different operators. However one general introductory step is now taken.

The effect of time reversal on the matrix elements (and thus on the coefficients in a second quantised Hamiltonian) of a time-even (odd) operator is that of complex conjugation. From equation (20) (cf Stedman and Butler (1981) for a detailed account)

this may be equally described as the combination of operations: (*a*) a $2jm$ transformation (or time reversal) of state labels and (*b*) the introduction of a sign η for a time-odd operator. If $\bar{K}$ is the time-reversal conjugate to K, etc,

$$H_{KL} = \eta(K\bar{K})(L\bar{L})(H_{\bar{K}\bar{L}})^* = H^*_{LK} \tag{24}$$

where $\eta = +1$ for time-even operators E, and -1 for time-odd operators O; the last relation follows from Hermiticity.

5. Application to one-particle Hamiltonians

5.1. General

Consider a general one-particle interaction Hamiltonian

$$F = \Sigma_{LM} f_{LM} a^\dagger_L a_M = \Sigma_{LM} g_{LM} a^\dagger_L \tilde{a}_M \tag{25}$$

where $g_{LM} = (M) f_{L\bar{M}}$. Using equations (15), (3), (21), (1):

$$CF = -\{\Sigma_L f_{LL} + \Sigma_{LM}(L\bar{L})(M\bar{M}) f_{\bar{M}\bar{L}} a_L a_M\} C.$$

Hence if the trace term vanishes the operator F is C-even or C-odd as

$$f_{LM} = \mp(L\bar{L})(M\bar{M}) f_{\bar{L}\bar{M}} = f^*_{ML} \tag{26}$$

respectively; the last equation follows from hermiticity. (Removal of the trace term amounts to the extraction of any component of the number operator $N = \Sigma_K n_K$ from F. A similar calculation shows that for the trace term

$$C\hat{N} = (N_0 - \hat{N})C \tag{27}$$

where N_0 is the number of states in the set $\{K\}$.) From equations (24) and (26), *if the paired states K, $\bar{K}$ are related by time reversal*, the coefficients f_{LM} are C-even as the interaction is time-even or odd and the coefficients are antisymmetric (and so imaginary) or symmetric (and so real) respectively; conversely for a C-odd operator:

$$\mathscr{E}_{KL} = -\eta \mathscr{E}_{LK} \qquad \mathscr{O}_{KL} = \eta \mathscr{O}_{LK}. \tag{28}$$

Equation (28), which may be contrasted with equation (24), corresponds to theorem 7-1 of Watanabe (1966) in the context of ligand field theory, with the important difference that, to obtain anticommutation with quasispin, we are forced to add complex conjugation to Watanabe's PH conjugation operator (as also to that of Keiter *et al* (1969), these authors using essentially $C' = CZ$) and so put a constraint on our C-even/odd operators with non-trivial physical consequences. The above symmetry would have been guaranteed by hermiticity if combined with complex conjugation; but then the above analogy with Kramers or time-reversal symmetries would be lost.

This raises the general question: is it worth adding complex conjugation Z to the PH conjugation operator C'? The price we pay is a restriction to a physically constrained form of interaction with symmetric (and real) or antisymmetric (and imaginary) matrix elements. The advantage we gain is that all earlier equations apply, and stronger selection rules may be proved. Quasispin operators at least are indeed C-odd and Hamiltonians constructed from quasispin operators have definite C-parity; the matrix elements of their eigenstates are subject to these stronger rules. This is known to include several Hamiltonians of considerable physical interest (see §§ 5.3 and 6) and the constraint is physically interesting.

This problem of the plurality of PH conjugation operations and the consequent need for a trade-off between respective advantages and disadvantages is known in previous applications. We have already mentioned the application in ligand field theory by Watanabe (1966); several of the results of § 3 have parallels in Watanabe's equations. We note the formalisms of Herrick (1981), Herrick and Liao (1981) and Koutecky *et al* (1985) where several C-operators are defined, along with quasispin operations, in the context of alternant symmetry in linear polyenes.

One caution is warranted at this stage. PH conjugation in the above senses is not to be identified with the particle physicists' particle—antiparticle conjugation operator; its action is not merely to reverse the charge of the constituent particles, for example. The primary reason why the ligand field for substitutional ions in solids is C-odd (Newman 1971) is not that the classical electrostatic potential is linear in charge but that it is time-even and real. Clearly some connection with charge reversal is implied by equation (27), but this link is secondary for our purposes.

In some applications the paired states are defined more arbitrarily than by time reversal and equation (26) is more fundamental.

5.2. Examples of one-particle operators with C-parity

We give three examples. Consider first the Hamiltonian

$$H_0 = \Sigma'_K E_K (a_K a_K - a_{\bar{K}} a_{\bar{K}}). \tag{29}$$

The prime denotes that the sum over K is over each pair. Physically, this would hold for a time-odd perturbation (e.g. Zeeman splitting) of states with differing spin projection in an orbital, for nuclear or atomic shell theory; states with opposite projection would shift by opposite amounts (equation (17)). It could also correspond to paired states K, $\bar{K}$ in a metal with opposite energies $E_K = -E_{\bar{K}}$ relative to the Fermi surface (Keiter *et al* 1969). Since K and $\bar{K}$ are not now time-reversal conjugate, a definition of paired labels must be chosen to conform to equation (17). Note also that the number operator has been extracted.

From equation (8) this Hamiltonian is a quasispin invariant. It is also PH conjugation invariant (C-even) from the above theorem (the coefficients are clearly symmetric, since diagonal, and are 'time'-odd). One could equally have argued the C-even character from its quasispin content (see the last part of § 3).

As another example, take the exchange interaction of Keiter *et al* (1969) for an electron in a metal interacting with an impurity spin (Kondo problem) $K = (k\kappa)$:

$$H_{ex} = \Sigma_{kl\kappa\lambda} J_{kl} a^+_{k\kappa} \boldsymbol{s}_{\kappa\lambda} \cdot \boldsymbol{S} a_{l\lambda}. \tag{30}$$

This Hamiltonian is C-even under the constraint, assumed explicitly by Keiter *et al* (1969) (note C commutes with the spin operator $\boldsymbol{S}$ (§ 3))

$$J_{kl} = J_{\bar{k}\bar{l}}. \tag{31}$$

It is not obvious that this symmetry is realistic, since this condition is not guaranteed by time-reversal considerations (K and $\bar{K}$ are not time-reversal conjugate; even if they were, a reality condition is also implied).

Third, an electron–phonon interaction whose parameters have the symmetry of equation (31) will be C-odd. Krempasky and Schmid (1979) illustrate the potential importance of such a symmetry in thermopower calculations; this will be analysed more fully in a following paper.

Fourth, the ligand field (Newman 1971) is time-even and is real, and so C-odd. In the operator equivalent formalism, the Hermitian ligand field operators of the form of a function of J_z times $(J_+^M + J_-^M)$, or $(J_+^M - J_-^M)/i$, have real coefficients A_N^M.

Fifth, the standard one-photon interaction $\boldsymbol{A}\cdot\boldsymbol{p}$ may be expanded in terms of E1 $(\boldsymbol{A}_0\cdot\boldsymbol{p})$, M1 $(\boldsymbol{m}\cdot\boldsymbol{L})$, where $\boldsymbol{m}$ is the magnetic polarisation and $\boldsymbol{L}$ the angular momentum operator, see Stedman 1985) and E2 multipole moments, etc. All terms are time-odd, because the vector potential $\boldsymbol{A}$ is time-odd. Successive multipoles are real and imaginary, because of the imaginary factor in the exponent of $\boldsymbol{A} = \boldsymbol{A}_0 \exp(i\boldsymbol{k}\cdot\boldsymbol{r})$. The E1 term is real, while E2 and M1 are imaginary. Hence the E1 interaction is C-even, while the M1 and E2 interactions are C-odd, etc.

5.3. Analogues to selection rules from time reversal

First we consider analogues to the constraints on diagonal matrix elements of an operator in PH conjugate states. From equation (23) these are equal/opposite as the operator is C-even/odd. In a half-filled shell in LS coupling, each state is an eigenstate of the PH conjugation operator (§ 3). Hence C-odd operators, such as the spin-orbit interaction and the ligand field, have no matrix elements in a half-filled shell in LS coupling. This result with other more general results is proved by Judd (1967) in an elegant manner, except for the appeal to the vanishing of the (quasispin) $3jm$ symbol

$$\begin{pmatrix} K & Q & K' \\ 0 & 0 & 0 \end{pmatrix}$$

when Q is odd. His proof notes that a C-odd operator may be expanded in terms of (C-odd) quasispin operators of rank Q, say, and that its matrix elements are proportional to this $3jm$ symbol. In more conventional applications, its vanishing implicitly uses time-reversal constraints, via the Derome-Sharp lemma (Stedman and Butler 1981). The above proof makes this link directly and so avoids particular numerical properties of $3jm$ symbols. We note that the pioneering work of Racah on such cancellations in a half-filled shell assumed a reality/symmetry constraint for the Hamiltonian matrix elements and that a C-even operator could not be expanded using the tensor operator $\boldsymbol{X}$ applied by Judd (1967) in this context, and so evades the above theorem. This is paralleled by the way in which, for time-reversal reasons, spin operators must replace spherical harmonics for expansions of time-odd operators if certain diagonal matrix elements are not to cancel (Stedman and Butler (1981), for example; the reduced matrix element of a spherical harmonic is proportional to a similar $3jm$ symbol).

More generally of course, equations (23) proscribe the relation between matrix elements in conjugate ions within a transition or lanthanide series.

While first-order diagonal matrix elements may be forbidden, second-order ones may be allowed, subject to the kind of partial cancellation described in connection with equation (24). Just such partial cancellations have importantly affected two-photon spectral calculations for gadolinium (Judd and Pooler 1982). We might describe these cancellations, therefore, as quasi-van Vleck cancellations.

We now consider the corresponding results for first matrix elements of the photon interaction. To a first approximation (ignoring odd-parity ligand field mixing) E1 transitions are forbidden within a shell multiplet (say the ground multiplet $S_{7/2}$ of Gd^{3+}) for parity reasons. However M1 and E2 are allowed by parity and may be expected to dominate. These multipoles are C-odd, and therefore can give rise only

to antisymmetric matrix elements ($M_{ab} = -M_{ba}$, cf § 4.1). The antisymmetric part of the orbital space of $^{2S+1}L_J$, $[L \times L]_-$, contains only odd angular momenta. Hence a rank-2 interaction such as E2 cannot couple states within a multiplet of a half-filled shell in *LS* coupling.

6. Application to two-particle operators

A two-particle operator of the form

$$G = \Sigma_{KLMN} g_{KLMN} a_K^+ a_L^+ a_M a_N \tag{32}$$

has the coefficient symmetries $g_{KLMN} = g_{LKNM} = -g_{LKMN} = g^*_{MNKL}$. Under a similar analysis to that of § 5.2, it will be *C*-even/odd as a whole if

$$g_{KLMN} = \pm(K\bar{K})(L\bar{L})(M\bar{M})(N\bar{N}) g_{\bar{K}\bar{L}\bar{M}\bar{N}} \tag{33}$$

and if $\Sigma_K g_{KLKN} = 0$.

If the two-particle operator acts between particles in different shells or configurations, say, one may derive conditions similar to those of § 5.2 for the one-particle tensors into which *G* may be factorised (on a term-by-term basis) by applying PH conjugation operations to just one shell. In this manner we may reproduce the results of, for example, Racah (1942, 1943) who showed that in *LS* coupling, under PH conjugation, matrix elements changed by a phase $(-1)^{S+k+1}$ where *S*, *k* are the spin and spatial ranks. (Hence *T*-even operators are *C*-odd, and vice versa; see also Parikh (1978) and Arima (1983).) In particular, even rank multipole coupling operators were PH-conjugation-odd, and vice versa. Racah concluded that electrostatic energies are identical within conjugate configurations, electrostatic couplings between a fixed configuration and a second is altered in sign when the second is conjugated and diagonal matrix elements within a half-filled shell vanish if $S + k$ is even. For example, diagonal matrix elements of a spin-orbit coupling within a half-filled shell vanish. Arima (1983) shows that matrix elements of quadrupole operators which are diagonal in seniority vanish in a half-filled shell. Arima (1983) and Parikh (1978) discuss conservation of quasispin for the odd rank terms in a multipole expansion of the Coulomb interaction. This may be extended (Arima 1983) to the point interaction approximating one-pion exchange in the nucleus, but not the quadrupole or other even rank couplings.

As another example, consider the BCS Hamiltonian in the form (Kittel (1963) and Doniach and Sondheimer (1974) with some notational changes)

$$H = \Sigma_K 2E_K Q_z^K + \Sigma_{KL} V_{KL} Q_+^K Q_-^L. \tag{34}$$

The first (unperturbed) term, H_0, is linear in quasispin and so is *C*-odd if $E_K = E_{\bar{K}}$; hence *C*-conjugate states have opposite unperturbed energies. (For example, a filled pair state and an empty pair state have opposite energies relative to an origin, suitably defined—at the energy of a half-filled state.) The perturbation *V* is quadratic in quasispin and is *C*-even; hence *C*-conjugate states have the same diagonal matrix elements. Hence all pair states can experience the same lowering (and in fact binding) effect on their energies under the interaction. *C*-parity arguments thus support the possibility of a superconducting transition. Incidentally, quasispin gives an elegant

reformulation of the Bogoliubov-Valatin operators (Taylor 1970)

$$\gamma_K = u_K a_K - v_K a_{\bar{K}}^+ = U_K A_{\bar{K}}$$
$$\delta_K = u_K a_{\bar{K}}^+ + v_K a_K = U_K A_K \tag{35}$$

where the quasispinor $U_K \equiv (-v_K, (\bar{K})u_K)$; for example, their anticommutation relations follow directly from equation (3) and $C\gamma_K = (K\bar{K})\delta_K^+ C$. The standard pairing interaction in nuclei is also of the above form.

7. Conclusions

If the Hamiltonian of interest is made of quasispin operators with real (or with imaginary) coefficients, selection rules analogous to those from time reversal symmetries (§ 4) may be derived.

In all such applications, quasi-Kramers symmetries give an alternative and elegant explanation and unification of the origin of a wide variety of selection rules.

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References

Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Metal Ions* (Oxford: Clarendon)
Arima A 1983 *Symmetries in Nuclear Structure* ed K Abrahams, K Allaart and A E L Dieperink (New York: Plenum) pp 93-117
Bell J S 1959 *Nucl. Phys.* **12** 117-24
Cheng-tian Feng and Judd B R 1982 *J. Phys. A: Math. Gen.* **15** 2273-84
Doniach S and Sondheimer E H 1974 *Green's Functions for Solid State Physicists* (Reading, MA: Benjamin) p 232
Herrick D 1981 *J. Chem. Phys.* **74** 1239-55
Herrick D and Chung-Lin Liao 1981 *J. Chem. Phys.* **75** 4485-95
Judd B R 1967 *Second Quantization and Atomic Spectroscopy* (Baltimore, MA: Johns Hopkins) ch 7
—— 1985 *Rep. Prog. Phys.* **48** 907-53
Judd B R, Lister G M S and Suskin M A 1986 *J. Phys. B: At. Mol. Phys.* **19** 1107-14
Judd B R and Pooler D R 1982 *J. Phys. C: Solid State Phys.* **15** 591-8
Lawson R D and MacFarlane M H 1965 *Nucl. Phys.* **66** 80-96
Keiter H, Muller-Hartmann E and Zittartz J 1969 *Z. Phys.* **223** 48-53
Kittel C 1963 *Quantum Theory of Solids* (New York: Wiley) p 157
Koutecky J, Paldus J and Cizek J 1985 *J. Chem. Phys.* **83** 1722-35
Krempasky J J and Schmid A 1979 *J. Low Temp. Phys.* **34** 197-214
McKenzie B J and Stedman G E 1979 *J. Phys. C: Solid State Phys.* **12** 5061-75
Messiah A 1960 *Quantum Mechanics* vol II (Amsterdam: North-Holland)
Newman D J 1971 *Adv. Phys.* **20** 197-256
Parikh J C 1978 *Group Symmetries in Nuclear Structure* (New York: Plenum)
Payne S H and Stedman G E 1983 *J. Phys. C: Solid State Phys.* **16** 2679-703
Racah G 1942 *Phys. Rev.* **62** 438-62
—— 1943 *Phys. Rev.* **63** 367-82

Rotenberg M B, Bivins R, Metropolis N and Wooten J K 1959 *The 3j and 6j symbols* (London: Lockwood)
Rudzikas Z and Kaniauskas J 1984 *Quasispin and Isospin in Atomic Theory* (Vilnius: Mokslas)
Stedman G E 1985 *Adv. Phys.* **34** 513–87
Stedman G E and Butler P H 1981 *J. Phys. A: Math. Gen.* **13** 3125–40
Taylor P L 1970 *A Quantum Approach to the Solid State* (Englewood Cliffs, NJ: Prentice-Hall) ch 7
Watanabe H 1966 *Operator Methods in Ligand Field Theory* (Englewood Cliffs, NJ: Prentice-Hall) pp 63 ff
Wigner E P 1959 *Group Theory* (Engl. transl. J J Griffin) (New York: Academic) pp 332–48