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The theoretical basis of spin Hamiltonian theory

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Abstract. A general theory of effective Hamiltonians, or spin Hamiltonians, is presented that is based upon the theory of unitary transformations. The general properties of effective Hamiltonians are discussed and a representation independent form of perturbation theory is given that allows effective Hamiltonians to be constructed in any particular case.

1. Introduction

In magnetism in general, and in magnetic resonance in particular, much use is made of effective Hamiltonians, or spin Hamiltonians. Their efficacy in describing the perhaps complicated energy level structure of a group or sub-set of quantum states in terms of just a few parameters is well known. It is perhaps because spin Hamiltonian have such a direct practical application in summarizing experimental data that they are usually used in a somewhat intuitive way without reference to any clearly stated basis of fundamental principle. Although quite satisfactory for most practical purposes, intuitive procedures can sometimes lead to confusion and misunderstanding and for this reason alone it is surprising that otherwise definitive texts, such as that by Abragam and Bleaney (1970), do not give any very explicit account of a fundamental general theory underlying the use of spin Hamiltonians.

A notable publication dealing with such a general theory is that of Stevens (1985). Unfortunately this work makes use of a perturbation method of Bloch (1958) whose effect is to produce effective Hamiltonians that, in third and higher order at least, are not Hermitian. Soliverez (1969) has shown how the perturbation method of Bloch can be modified to give Hermitian Hamiltonians, but nevertheless this seems an unnecessarily complicated procedure on which to base a general theory of spin Hamiltonians. Here a general theory will be developed that guarantees Hermiticity but is based upon more standard quantum mechanics, namely the theory of unitary transformations.

2. General theory

Out of the whole set of quantum states that a quantum system might possess it is possible that, under some conditions, some physical properties arise entirely from a particular sub-set of these states. Such a condition will occur when only the states in the sub-set have any appreciable probability of occupancy. Under such a circumstance it is natural to seek to describe the sub-set of states separately from other states. This desirable objective is achieved if a representation of the quantum states can be found in which the Hamiltonian of

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the physical system has no matrix elements connecting states within the sub-set of interest to states outside the sub-set. Then the Hamiltonian matrix has a block diagonal form with the sub-set of states of interest forming one block and all other states forming a second block. This means that there must exist a projection operator $\hat{P}$ that divides the Hilbert space of quantum states into two sub-spaces such that

$$\hat{H} = \hat{P}\hat{H}\hat{P} + (1 - \hat{P})\hat{H}(1 - \hat{P}) \tag{2.1a}$$

or equivalently

$$[\hat{H}, \hat{P}] = 0. \tag{2.1b}$$

The projection operator $\hat{P}$ can be expressed in terms of the orthonormal basis states $|\psi_\alpha\rangle$ that define the sub-space of interest as

$$\hat{P} = \sum_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|. \tag{2.2}$$

The determination of the basis states in (2.2) is equivalent to finding the unitary transformation operator $\hat{U}$ ($\hat{U}^\dagger = \hat{U}^{-1}$) that establishes a one to one correspondence between these states and the orthonormal basis states $|\varphi\rangle$ of some known standard representation. That is, for all α in the set of interest

$$|\psi_\alpha\rangle = \hat{U}|\varphi_\alpha\rangle \tag{2.3}$$

so that $\hat{P}$ can be expressed as

$$\hat{P} = \hat{U}\hat{P}_0\hat{U}^{-1} \tag{2.4}$$

where $\hat{P}_0 = \sum_\alpha |\varphi_\alpha\rangle\langle\varphi_\alpha|$ is the projection operator for the sub-space defined by the basis states of the standard representation that correspond according to (2.3) to the states in the sub-space of physical interest.

The unitary transformation operator can be used to transform the Hamiltonian $\hat{H}$ into a form $\hat{H}_t$ that reduces into two parts with respect to the standard basis states $|\varphi\rangle$ in the same way as $\hat{H}$ does in (2.1*a*) with respect to the states $|\psi\rangle$. That is

$$\hat{H}_t = \hat{U}^{-1}\hat{H}\hat{U} = \hat{P}_0\hat{H}_t\hat{P}_0 + (1 - \hat{P}_0)\hat{H}_t(1 - \hat{P}_0) \tag{2.5a}$$

where the fact that $\hat{H}_t$ has no matrix elements from the set of standard basis states $|\varphi_\alpha\rangle$ to states outside the set can be given an algebraic expression as

$$[\hat{H}_t, \hat{P}_0] = 0. \tag{2.5b}$$

$\hat{H}_e = \hat{H}_t\hat{P}_0$ in (2.5*a*) is then the effective Hamiltonian for the set of states defined by the projection operator $\hat{P}_0$. Any eigenfunction of $\hat{H}_e$, $|A\rangle$ say, will only be a linear combination of those standard basis states that belong to the set specified by $\hat{P}_0$ and which are presumably well known and of a relatively simple nature. From the general theory of unitary transformations it follows that the corresponding eigenfunction $\hat{U}|A\rangle$ of $\hat{H}$ will have the same eigenvalue. The effective Hamiltonian does therefore provide the means for a full description of the physical properties of the set of states of interest. Together with the unitary operator $\hat{U}$, it determines the energy eigenvalues and eigenfunctions and hence the internal

dynamical processes (i.e. those processes involving only transitions between states within the set). In the special case of magnetic resonance, the states of interest are invariably a set of low-energy magnetic states having properties resembling those of free spins and then it is customary to refer to the effective Hamiltonian as a spin Hamiltonian. It should be noted that effective Hamiltonians are uniquely determined by the reduction process described by (2.5) only to within an arbitrary unitary transformation acting internally to the chosen set of states. This follows from the fact that if the unitary transformation operator $\hat{U}$ effects the reduction (2.5) then so does $\hat{U}\hat{U}_1$ if the unitary operator $\hat{U}_1$ satisfies the condition

$$[\hat{U}_1, \hat{P}_0] = 0. \tag{2.6}$$

If the set of states of interest is sufficiently well separated in energy from other states then it is clear not only that the reduction (2.5) can be carried out but also that it is physically sensible to do so since there is then likely to be a wide range of interesting physical phenomena that is purely internal to such an isolated set. For a few-body system, such as a single paramagnetic ion, the range of energy within a low-lying set of magnetic states may only be a few millielectronvolts. Since in this case the excited states may have energies of electronvolts the above condition can be well met. Although such a condition of non-degeneracy is sufficient to validate the use of an effective Hamiltonian it is by no means a necessary one. In the many-body case of a large number of paramagnetic ions, for example, the energy range of the set of magnetic states greatly exceeds the excited state energies of single atoms. Real energy conserving transitions to these latter states could however only occur through the cooperative action of thousands of individual spins, corresponding to processes described only in very high orders of perturbation. Presumably therefore the processes that lead to such statistically unlikely concentrations of energy will have exceedingly small transition probability and so their neglect need have no serious physical consequences.

Even in the case of a few-body system it is in fact unlikely that the reduction (2.5) can be carried out exactly. In any real situation the transformation operator $\hat{U}$ and effective Hamiltonian $\hat{H}_e$ will only be determined approximately. The commutator (2.5*b*), and hence the matrix elements of $\hat{H}_t$ connecting the states in the chosen set to states outside the set will not then be exactly zero, but only of a degree of smallness appropriate to a particular level of approximation. When this approximation procedure is carried out by perturbational methods it gives rise to an operator form of perturbation theory that is of interest in its own right quite apart from its importance in spin Hamiltonian theory.

3. Perturbation theory

For a perturbation treatment to be applicable it is necessary that the Hamiltonian $\hat{H}$ can be expressed as a sum of an unperturbed part $\hat{H}_0$ and a relatively small perturbation $\hat{V}$.

$$\hat{H} = \hat{H}_0 + \hat{V}. \tag{3.1}$$

The basis states of the standard representation, referred to in section 2 as $|\varphi\rangle$, can naturally be identified with the orthonormal eigenfunctions of $\hat{H}_0$ if the set of unperturbed states of interest exists as a recognizable group, well separated in energy from all other states to which this set is connected by matrix elements of $\hat{V}$. The unperturbed set of states can conveniently be taken to be a degenerate one if all the terms in $\hat{H}$ that lift the degeneracy

are included in $\hat{V}$. The projection operator for the set of unperturbed states $|\varphi_\alpha\rangle$, where $\alpha = 1\text{–}n$, say, is

$$\hat{P}_0 = \sum_\alpha |\varphi_\alpha\rangle\langle\varphi_\alpha|. \tag{3.2}$$

The effective Hamiltonian $\hat{H}_e$ is now obtained from a unitary transformation of $\hat{H}$ as described in section 2, that is

$$\hat{H}_t = \hat{U}^{-1}\hat{H}\hat{U} \tag{3.3a}$$

where according to (2.5*b*) the unitary operator $\hat{U}$ has the property

$$(1 - \hat{P}_0)\hat{H}_t\hat{P}_0 = \hat{P}_0\hat{H}_t(1 - \hat{P}_0) = 0 \tag{3.3b}$$

so that

$$\hat{H}_e = \hat{H}_t\hat{P}_0 = \hat{P}_0\hat{H}_t. \tag{3.3c}$$

The transformation (3.3*a*) so to speak 'transforms away' those terms in $\hat{H}$ that give rise to matrix elements connecting unperturbed states in the set specified by (3.2) to states outside this set.

A perturbational development of equations (3.3) can be made using the fact that any unitary operator can be expressed in exponential form (Roman 1975). Thus

$$\hat{U} = \exp\hat{T} \tag{3.4a}$$

where $\hat{T}$ is some anti-Hermitian operator ($\hat{T}^\dagger = -\hat{T}$) that can be written as a power series in the perturbation $\hat{V}$ rather than the more restricted expression used in an otherwise similar formalism by Bates *et al* (1968). That is

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots. \tag{3.4b}$$

The perturbation $\hat{V}$ will naturally contain all the terms of $\hat{H}$ that have matrix elements from unperturbed states within the set to those outside the set but it will doubtless have matrix elements internal to the set also. It makes for some algebraic simplification in the development that follows to separate out the terms that give matrix elements internal to the set by dividing $\hat{H}_0$ and $\hat{V}$ in the following way

$$\hat{H} = \hat{H}_0 + \hat{V} = \varepsilon\hat{P}_0 + (1 - \hat{P}_0)\hat{H}_0(1 - \hat{P}_0) + \hat{V}_0 + \hat{V}_1 \tag{3.4c}$$

where

$$\hat{V}_0 = \hat{P}_0\hat{V}\hat{P}_0 + (1 - \hat{P}_0)\hat{V}(1 - \hat{P}_0)$$

$$\hat{V}_1 = \hat{P}_0\hat{V}(1 - \hat{P}_0) + (1 - \hat{P}_0)\hat{V}\hat{P}_0$$

and ε is the unperturbed energy of the selected set of states.

Applying (3.4*a*) to (3.3*a*) gives $\hat{H}_t$ as

$$\hat{H}_t = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!}[[\hat{H}, \hat{T}], \hat{T}] + \ldots. \tag{3.5}$$

The various terms in the expansion (3.4*b*) can now be chosen in turn to satisfy condition (3.3*b*) up to whatever order of perturbation is required. Condition (3.3*b*) is satisfied to first order in $\hat{V}$ by

$$\hat{T}_1 = [\hat{V}_1(1-\hat{P}_0)/(\hat{H}_0-\varepsilon)] = \hat{P}_0\hat{V}(1-\hat{P}_0)/(\hat{H}_0-\varepsilon) - [(1-\hat{P}_0)/(\hat{H}_0-\varepsilon)]\hat{V}\hat{P}_0 \tag{3.6}$$

so that, up to second order in $\hat{V}$, $\hat{H}_e$ is given from (3.3*c*) and (3.5) as

$$\hat{H}_e = \hat{H}_0\hat{P}_0 + \hat{P}_0\hat{V}\hat{P}_0 + \tfrac{1}{2}[\hat{V}_1, \hat{T}_1]\hat{P}_0 \tag{3.7a}$$

or, equivalently

$$\hat{H}_e = \varepsilon\hat{P}_0 + \hat{P}_0\hat{V}\hat{P}_0 - \hat{P}_0\hat{V}[(1-\hat{P}_0)/(\hat{H}_0-\varepsilon)]\hat{V}\hat{P}_0. \tag{3.7b}$$

Satisfaction of (3.3*b*) up to second order is achieved by further having $\hat{T}_2$ in (3.4*b*) as

$$\hat{T}_2 = [[\hat{V}_0, \hat{T}_1], (1-\hat{P}_0)/(\hat{H}_0-\varepsilon)] \tag{3.8a}$$

so that $\hat{H}_e$ becomes, up to third order of accuracy

$$\hat{H}_e = \hat{H}_0\hat{P}_0 + \hat{P}_0\hat{V}\hat{P}_0 + \tfrac{1}{2}[\hat{V}_1, \hat{T}_1]\hat{P}_0 + \tfrac{1}{2}[\hat{V}_1, \hat{T}_2]\hat{P}_0 \tag{3.8b}$$

or

$$\begin{aligned}\hat{H}_e = {} & \varepsilon\hat{P}_0 + \hat{P}_0\hat{V}\hat{P}_0 - \hat{P}_0\hat{V}[(1-\hat{P}_0)/(\hat{H}_0-\varepsilon)]\hat{V}\hat{P}_0 \\ & + \hat{P}_0\hat{V}[(1-\hat{P}_0)/(\hat{H}_0-\varepsilon)]\hat{V}[(1-\hat{P}_0)/(\hat{H}_0-\varepsilon)]\hat{V}\hat{P}_0 \\ & - \tfrac{1}{2}\hat{P}_0\hat{V}\hat{P}_0\hat{V}[(1-\hat{P}_0)/(\hat{H}_0-\varepsilon)^2]\hat{V}\hat{P}_0 \\ & - \tfrac{1}{2}\hat{P}_0\hat{V}[(1-\hat{P}_0)/(\hat{H}_0-\varepsilon)^2]\hat{P}_0\hat{V}\hat{P}_0.\end{aligned} \tag{3.8c}$$

The similarity between (3.8*c*) above for $\hat{H}_e$ and the third line of equation (36) in Bloch's expression (Bloch 1958) for a corresponding quantity $\hat{A}$ is close but not exact. $\hat{H}_e$ and $\hat{A}$ have the same eigenvalues but, as a direct comparison of the expressions shows, only $\hat{H}_e$ is Hermitian in third and higher order.

One immediate and very simple application of these results is to the special case of a set consisting of a single number, having unperturbed state $|0\rangle$ say. In this particular case, $\hat{H}_e = E|0\rangle\langle 0|$ and it may be assumed that ε is chosen so that $\hat{P}_0\hat{V}\hat{P}_0 = \langle 0|\hat{V}|0\rangle|0\rangle\langle 0| = 0$ and then (3.8*c*) gives

$$E = \varepsilon - \sum_{n\neq 0}\frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{(\varepsilon_n-\varepsilon)} + \sum_{\substack{n\neq 0\\ m\neq 0}}\frac{\langle 0|V|n\rangle\langle n|V|m\rangle\langle m|V|0\rangle}{(\varepsilon_n-\varepsilon)(\varepsilon_m-\varepsilon)}.$$

This is a standard result of non-degenerate perturbation theory, but here it appears as a special case of a formulation that applies equally well to degenerate and non-degenerate perturbations.

4. Transformation of associated operators

The Hamiltonian is not the only operator of interest to an investigation of the properties of a physical system. Operators representing the internal symmetries of the system are also of considerable importance, as are those describing coupling to experimental probes (external electromagnetic fields, neutron beams etc). It is important therefore to recognise that a consistent use of effective Hamiltonians requires that these operators be subjected to the same transformation $\hat{U}$ that generates $\hat{H}_t$ from $\hat{H}$. For every operator $\hat{Q}$ there is therefore a transformed operator $\hat{Q}_t$ given by

$$\hat{Q}_t = \hat{U}^{-1}\hat{Q}\hat{U}. \tag{4.1a}$$

The effective operator $\hat{Q}_e$ that acts purely internally to the set of states defined by $\hat{P}_0$ is then

$$\hat{Q}_e = \hat{P}_0\hat{Q}_t\hat{P}_0. \tag{4.1b}$$

Unlike $\hat{H}_t$ in (3.3*a*), $\hat{Q}_t$ above may have significant matrix elements connecting states in the set $\hat{P}_0$ to states outside the set.

4.1. Symmetry operators and uniqueness

In general $\hat{Q}_t$ in (4.1*a*) will not be the same as $\hat{Q}$. Operators that represent symmetry operations are however a special case. A unitary operator $\hat{S}$ will be a member of the symmetry transformation group of the Hamiltonian $\hat{H}$ if it has the special property

$$\hat{S}\hat{H}\hat{S}^{-1} = \hat{H}$$

or, equivalently

$$[\hat{S}, \hat{H}] = 0. \tag{4.2}$$

Since unitary transformations preserve algebraic relationships such as (4.2) it follows that the same symmetry will be shown by $\hat{H}_t = \hat{U}^{-1}\hat{H}\hat{U}$, but described by the operator $\hat{S}_t$, that is

$$[\hat{S}_t, \hat{H}_t] = 0$$

where

$$\hat{S}_t = \hat{U}^{-1}\hat{S}\hat{U}. \tag{4.3}$$

It is generally regarded as intuitively obvious that, for symmetry operators, $\hat{S}_t = \hat{S}$. The assumption of the invariance of symmetry operators is important in practical applications where spin Hamiltonians are usually constructed directly, in a phenomenological way, guided by symmetry considerations rather than the formal theory of (3.3). It can easily be shown that, for effective Hamiltonians given by the perturbation theory of section 3 at least, this assumption is justified when certain very natural conditions are satisfied. Firstly it is natural to suppose that the division of $\hat{H}$ in (3.1) is such that $\hat{H}_0$ has the symmetry of $\hat{H}$. The unperturbed Hamiltonian $\hat{H}_0$ may have higher symmetry than $\hat{H}$ but not less (no reasonable perturbation will increase the symmetry, only reduce it). It is also natural, indeed necessary,

to suppose that the set of unperturbed states defined by $\hat{P}_0$ forms a representation of the symmetry group common to $\hat{H}_0$, $\hat{H}$ and $\hat{V}$ (not necessarily an irreducible representation). These conditions imply therefore that for any symmetry operator $\hat{S}$ of the symmetry group

$$[\hat{H}, \hat{S}] = [\hat{H}_0, \hat{S}] = [\hat{V}, \hat{S}] = [\hat{P}_0, \hat{S}] = 0. \tag{4.4}$$

The unitary transformation operator $\hat{U}$ in (3.3*a*) need only be a function of the operators occurring in (4.4) above, that is

$$\hat{U} = \hat{U}(\hat{H}_0, \hat{V}, \hat{P}_0) \tag{4.5}$$

so that

$$[\hat{U}, \hat{S}] = 0$$

and therefore

$$\hat{S}_t = \hat{U}^{-1}\hat{S}\hat{U} = \hat{S} \tag{4.6}$$

showing that symmetry operators are indeed invariant. The symmetries of the effective Hamiltonian are therefore described by the same operators that describe the symmetries of $\hat{H}$, that is

$$[\hat{H}_e, \hat{S}_t] = [\hat{H}_e, \hat{S}] = 0 \tag{4.7}$$

and the properties of (4.4) furthermore show that (4.7) will apply to each term separately in the perturbation expansion (3.8*b*) of $\hat{H}_e$.

The validity of (4.6) demonstrated above for one specific but generally applicable case shows that (4.6) can be assumed for effective Hamiltonians obtained by other more phenomenological means. By so doing the arbitrariness of the reduction process referred to in (2.6) is lessened but not entirely eliminated. If (4.6) is to be satisfied in all cases, then $\hat{U}_1$ in (2.6) must also be invariant under the action of the operators of the symmetry group of $\hat{H}$. For low symmetry and high spin quantum numbers this condition alone will not be sufficient to enforce the condition $[\hat{U}_1, \hat{H}_e] = 0$ that is necessary to ensure the uniqueness of the effective Hamiltonian $\hat{H}_e$. In general therefore uniqueness of $\hat{H}_e$ demands the imposition of other conditions, such as the 'simplest' representation of the Zeeman terms in $\hat{H}_e$.

5. Rotational covariance and fictitious spins

Because the reduction process (2.5) is independent of any particular representation, the effective Hamiltonians it produces will also be in a representation independent form, as in (3.8*b*). Expressions such as (3.8*b*) apply therefore in any coordinate system and so they give the effective Hamiltonian in a form invariant or rotationally covariant way that makes manifest the tensorial nature of the various parameters that occur in $\hat{H}_e$. This can be seen to be generally true by noting that if $\hat{H}$, $\hat{U}$, $\hat{H}_t$, $\hat{H}_e$ and $\hat{P}_0$ referred to one particular coordinate

system satisfy (2.1) then so do the corresponding operators $\hat{H}'$, $\hat{U}'$, $\hat{H}_t'$, $\hat{H}_e'$ and $\hat{P}_0'$ referred to a rotated coordinate system, where

$$\begin{aligned}
\hat{H}' &= \hat{R}\hat{H}\hat{R}^{-1} \\
\hat{U}' &= \hat{R}\hat{U}\hat{R}^{-1} \\
\hat{H}_t' &= \hat{R}\hat{H}_t\hat{R}^{-1} \\
\hat{P}' &= \hat{R}\hat{P}\hat{R}^{-1} \\
\hat{H}_e' &= \hat{R}\hat{H}_e\hat{R}^{-1}.
\end{aligned} \tag{5.1}$$

The unitary operator $\hat{R}$ describing the relationship between the coordinate systems is given explicitly in standard texts (e.g. Brink and Satchler (1968) p 20).

Although it is unlikely that $\hat{H}$ in (3.1) will have the symmetry of the full rotation group it is quite possible that $\hat{H}_0$ does. In this case the set of states defined by $\hat{P}_0$ will form a representation of the rotation group with the result that $\hat{P}_0' = \hat{P}_0$ in (5.1). When, as is invariably the case, the set of states forms an irreducible representation, the Wigner–Eckart theorem (Brink and Satchler 1968, p 56) ensures that all the operators in $\hat{H}_e$ in (2.1) can be expressed in terms of the 'real' spin or angular momentum operator associated with such states.

Cases of the opposite kind, where $\hat{P}_0' \neq \hat{P}_0$ in (5.1), are commonly encountered when dealing with ions having an odd number of electrons (Kramers ions). If the different Kramers doublets that occur are well isolated it is possible to construct effective Hamiltonians for each doublet separately. Since only an external magnetic field $\boldsymbol{B}$ is capable of lifting the Kramers degeneracy, an effective Hamiltonian for a Kramers doublet will take the general form

$$\hat{H}_e = w\hat{P}_0 + \sum_{i=x,y,z} B_i[a_i(|1\rangle\langle 1| + |2\rangle\langle 2|) + b_i(|1\rangle\langle 2| + |2\rangle\langle 1|) + c_i(|1\rangle\langle 2| - |2\rangle\langle 1|)] \tag{5.2}$$

where $|\varphi_1\rangle$ and $|\varphi_2\rangle$ (here written $|1\rangle$ and $|2\rangle$ for simplicity) are orthonormal basis states for the doublet. They do not form a representation of the rotation group since, for example, $\hat{R}|1\rangle$ cannot be expressed as a linear combination of $|1\rangle$ and $|2\rangle$ alone.

An operator of 'fictitious' spin $\tilde{\boldsymbol{S}}$ can be introduced by the substitutions

$$\begin{aligned}
\tilde{S}_z &= \tfrac{1}{2}(|1\rangle\langle 1| - |2\rangle\langle 2|) \\
\tilde{S}_x &= \tfrac{1}{2}(|1\rangle\langle 2| + |2\rangle\langle 1|) \\
\tilde{S}_y &= (1/2\mathrm{i})(|1\rangle\langle 2| - |2\rangle\langle 1|)
\end{aligned} \tag{5.3}$$

that allows (5.2) to be put into the form

$$\hat{H}_e = w\hat{P}_0 + \sum_{i,j=x,y,z} g_{ij}\mu_B B_i \tilde{S}_j \tag{5.4}$$

where μ_B is the Bohr magneton.

It can be verified from (5.3) that the components of 'fictitious' spin satisfy the same commutation rules as the components of real spin and have the same eigenvalues within

the doublet states as real spin components do within states having spin quantum number $S = \frac{1}{2}$. They also are reversed in sign under time reversal just like the components of real spin, since $|1\rangle$ and $|2\rangle$ are Kramers conjugate states (i.e. $|2\rangle = \hat{\vartheta}|1\rangle$ and $|1\rangle = -\hat{\vartheta}|2\rangle$ where $\hat{\vartheta}$ is the time reversal operator).

Despite these similarities, $\tilde{S}$ is not a true vector since its components (5.3) do not form a representation of the rotation group if the set of states $|1\rangle$, $|2\rangle$ do not. The freedom that exists in choosing the basis states, referred to earlier in (2.6), can however be used to make the similarity of $\tilde{S}$ to a true vector as close as possible. If (5.3) applies in one particular coordinate system with basis states $|1\rangle$ and $|2\rangle$ then the same relationships can be applied in any rotated system to define $\tilde{S}'$ in terms of $|1\rangle'$ and $|2\rangle'$, the chosen basis states for the rotated system. It is possible to choose to define $|1\rangle'$ and $|2\rangle'$ in terms of $|1\rangle$, $|2\rangle$ and the rotation operator $\hat{R}$ so as to ensure that

$$\hat{R}\tilde{S}_i\hat{R}^{-1} = \sum_{j=x,y,z} D_{ij}(R)\tilde{S}'_j \tag{5.5}$$

where $D(R)$ is the same matrix that describes the rotational transformation of the components of a true vector, such as the magnetic field $\boldsymbol{B}$:

$$B_i = \sum_{j=x,y,z} D_{ij}(R)B'_j.$$

The usual expression 'g tensor' for the set of coefficients g_{ij} in (5.4) can therefore be justified since, with the above definition of $\tilde{S}$, the g_{ij} referred to one coordinate system are related to the corresponding coefficients g'_{ij} referred to another system in the standard way that defines a second-rank tensor. However, as pointed out by Abragam and Bleaney (1970, p 652), in practical applications (5.4) is usually used only as a vehicle for expressing the angular variation of the eigenvalues E of $\hat{H}_e$, which are given as the roots of the quadratic equation

$$(E - w)^2 = \sum_{i,j,k=x,y,z} g_{ik}g_{jk}B_iB_j. \tag{5.6}$$

The coefficients G_{ij}, given from (5.6) as

$$G_{ij} = \sum_{k=x,y,z} g_{ik}g_{jk} \tag{5.7}$$

are therefore quantities of more direct practical relevance. Since in (5.6) $(E - w)$ is a scalar and B_i, B_j are components of a true vector it follows that the coefficients G_{ij} do form a tensor, irrespective of the choice made for the matrix $D(R)$ in (5.5).

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