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A quantum approach to paramagnetic resonance

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Abstract. In the semi-classical theory of the problem of interaction of radio-frequency (r.f.) field with electron or nuclear spin, the application of quantisation is restricted to the spin system only, the r.f. field being treated classically. In this paper, a purely quantum approach is discussed for a system with spin $> 1/2$ using a Glauber vector to describe coherent excitations of the r.f. field. It is illustrated here for the case of spin 3/2. One finds that this quantum approach contains the classical one.

Keywords. Paramagnetic resonance; quantum approach; canonical transformation.

1. Introduction

In the generally accepted (Abragam 1961) semi-classical treatment of magnetic resonance, the r.f. field is treated classically and quantisation is applied only to the spin-system, though recently some workers (Allegrini *et al* 1971; Daniels 1964; Mystre *et al* 1974) have noticed the importance of invoking the quantum properties of the field.

According to the semi-classical theory, a significant energy exchange between the r.f. field and the spin system can occur when (i) the circular frequency of the r.f. field H_1 is equal to the Larmor frequency in the steady field H_0 and (ii) the sense of rotation of the rotating magnetic field H_1 is the same as that of Larmor precession, the rotating vector H_1 being continuously in step with the transverse projection of the spin magnetic moment vector. Usually, in the laboratory, one generates a linearly polarised field which can be decomposed into two circularly polarised fields rotating in opposite sense. The spin system then chooses the component which has the same sense of rotation as the Larmor precession and is also in step with it, while the component rotating in the opposite sense contributes only towards a broadening of the resonance signal (Abragam 1961). Thus, for significant energy transfer the r.f. excitations must bear a phase coherence with each other. In other words, the uncertainty in the phase of the r.f. field should be low, a fact that has to be taken cognisance of in the development of a quantum mechanical formalism of the problem.

As is well known, the quantum mechanical uncertainty product $(\triangle n \triangle \phi)$ where n is the number of photons per unit frequency range and ϕ is the phase angle of the excitation of the r.f. field, is of the order of 1. In r.f. spectroscopy n is very large ($\sim 10^{17}$), hence even when $\triangle\phi$ is very low, $\triangle n$ is a very small fraction of n. It thus becomes possible to define simultaneously with fairly high accuracy both n and ϕ without contradicting the uncertainty relation. This supplies the required

nearly single-phase component of the r.f. field and makes its classical description possible. The problem is further handled using canonical transformations.

2. Inadequacy of the semi-classical treatment

The canonical transformation used is generally to a ' rotating ' coordinate frame of reference. For the spin 1/2, the transformation is through a unitary operator $\exp(i\omega I_z t)$ which is a transformation to a coordinate frame of reference rotating about the z-axis at the frequency ω. In the case of spin 3/2, the transformation used is through an operator $\exp(iAt)$ where $A = (\frac{1}{2}\omega)[S_z^2 - \frac{1}{3}S(S+1)]$. This transformation does not have any simple geometrical interpretation, though it is also referred to as a transformation to a ' rotating frame '. As has been observed by some workers (Goldman 1970), there is some arbitrariness involved in the choice of such a ' rotating frame '. Further, the approach based on the rotating frame has some limitations. For example, certain transitions under an adiabatic fast passage (as in the case of atomic hydrogen) cannot be explained by it (Daniels 1964). Again for sufficiently large interaction times, the semi-classical approximation is inadequate in the case of large field intensities as is revealed in some cases such as Rabi flipping (Mystre *et al* 1974).

3. The quantum treatment

The interaction of a system (which is the origin of paramagnetism) with an r.f. field can be looked upon as a spin coupled to an oscillator and a formal quantum theory for such an interacting system can then be developed. The choice of the entity $2H_1$ the magnetic field in the x-direction, as the coordinate of the oscillator leads to a simple treatment. Daniels (1964) has developed a theory on this basis for a system of spin 1/2. The study of spin greater than 1/2 is important for the following reasons: (i) As mentioned earlier the canonical transformations used in these cases are somewhat arbitrary and have no simple geometrical significance like a ' rotating frame ' ; (ii) Certain features like the quadrupole splitting come into play which are absent for the spin 1/2 case.

Taking into consideration the different interactions involved the Hamiltonian for an oscillator coupled to a system of spin higher than 1/2 in the presence of a static magnetic field H_0, will be as follows if the relaxation effects are ignored for the sake of simplicity:

$$H = \gamma\hbar H_0 S_z + (\xi^\dagger \xi + \tfrac{1}{2})\hbar\omega + \hbar\gamma\mu(\xi^\dagger + \xi) S_x + D[S_z^2 - \tfrac{1}{3}S(S+1)] \quad (1)$$

In this equation, $\xi^\dagger$ and ξ are the creation and the annihilation operators for the oscillator excitations and μ is the r.m.s. value of the field $2H_1$ when the oscillator is in its ground state.

The first term on the right hand side of eq. (1) represents the interaction of the spin system with the static field H_0 supposed to be in the z-direction. The second term represents the oscillator Hamiltonian. The third term represents the coupling between the spin and the r.f. oscillator and is therefore very important (Daniels 1964). Since the r.f. field is mostly coherent, it can be described by the Glauber vector, which is an eigen-ket of the annihilation operator ξ and is given by (Glauber 1963; Klauder and Sudarshan 1968):

$$|Z\rangle = \exp\left(-\frac{1}{2}|Z|^2\right) \sum_{n=0}^{\infty} \frac{Z^n}{\sqrt{n!}} |n\rangle. \tag{2}$$

It can be seen that the expectation value of the interaction term in the Hamiltonian in the state described by the Glauber vector leads to the corresponding classical term, *i.e.* $\gamma\hbar 2H_1 \cos\omega t \cdot S_x$ when μZ is identified with H_1 (Daniels 1964).

The fourth term represents the interaction between the quadrupole moment of the spin system and the crystal field deemed to possess an axial symmetry about the z-axis for the sake of simplicity.

We illustrate, for the case of spin 3/2, a matrix representation of this Hamiltonian in the occupation number basis, the base vectors being simultaneous eigenkets of the occupation number operator and the operator S_Z. The resulting representation is as given in table 1. For an aribitrary spin S, the representative matrix is as shown in table 2. S_x has been expressed in terms of the shift operators S^+ and S^- which impose stringent selection rules (Slichter 1963).

An examination of the matrix tables indicates clearly the zero-field splitting at $H_0 = 0$. By putting $H_0 = 0$ one can see immediately that the energies of $S_z = 1/2$ and $-1/2$ are the same. This value is different from the equal energies of $S_z = 3/2$ and $-3/2$ by an amount $2D$. This is the effect of crystal field splitting.

The transition rates $W_{(n, S_z \to m, S'_z)}$ corresponding to an off-diagonal element $\langle n, S_z | \gamma\hbar\mu(\xi^\dagger + \xi) S_x | m, S'_z \rangle$ in table 1 is given by (Yariv 1967)

$$W_{(n, S_z \to m, S'_z)} = \frac{2\pi}{\hbar} |\langle n, S_z | \gamma\hbar\mu(\xi^\dagger + \xi) S_x | m, S'_z \rangle|^2 \times \delta[(m-n)\hbar\omega + \gamma\hbar H_0 (S'_z - S_z)] \tag{3}$$

Eq. (3) implies that we would have non-zero transition rates only when

$$(m-n)\hbar\omega + \gamma\hbar H_0 (S'_z - S_z) = 0$$

i.e., when

$$(m-n)\hbar\omega = -\gamma\hbar H_0 (S'_z - S_z). \tag{4}$$

It is obvious from equation (4) that if $m > n$ then $S'_z < S_z$. In other words, for the excitation of the oscillator field the spin system has to undergo a transition to a lower energy state (and vice versa). This is to be expected since the total energy of the spin-oscillator system will have to be conserved. This means that the off-diagonal elements which are five steps away from the principal diagonal will not lead to any physically permissible transitions while those which are three steps away will do so.

It can be seen that this formalism can be easily extended to interpret the usual semi-classical method involving coordinate transformations. In the case of spin 3/2, to have an evolution of the density matrix which would depend on a time-independent Hamiltonian, one has to carry out a transformation through an operator (Goldman 1970)

$$U = \exp(iAt) \quad \text{where} \quad A = (\tfrac{1}{2})\omega [S_z^2 - \tfrac{1}{3} S(S+1]. \tag{5}$$

The new coordinate system is still referred to as a 'rotating' frame. This

Table 1. Matrix elements of the Hamiltonian (1) for spin 3/2.

		(n−1)				(n)				(n+1)			
		$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
(n−1)	$\frac{3}{2}$	$(n-\frac{1}{2})\hbar\omega+\frac{3}{2}\gamma\hbar H_0+D$					$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n}$						
	$\frac{1}{2}$		$(n-\frac{1}{2})\hbar\omega+\frac{1}{2}\gamma\hbar H_0-D$			$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n}$		$\hbar\gamma\mu\sqrt{n}$					
	$-\frac{1}{2}$			$(n-\frac{1}{2})\hbar\omega-\frac{1}{2}\gamma\hbar H_0-D$			$\hbar\gamma\mu\sqrt{n}$		$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n}$				
	$-\frac{3}{2}$				$(n-\frac{1}{2})\hbar\omega-\frac{3}{2}\gamma\hbar H_0+D$			$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n}$					
(n)	$\frac{3}{2}$		$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n}$			$(n+\frac{1}{2})\hbar\omega+\frac{3}{2}\gamma\hbar H_0+D$					$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n+1}$		
	$\frac{1}{2}$	$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n}$		$\hbar\gamma\mu\sqrt{n}$			$(n+\frac{1}{2})\hbar\omega+\frac{1}{2}\gamma\hbar H_0-D$			$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n+1}$		$\hbar\gamma\mu\sqrt{n+1}$	
	$-\frac{1}{2}$		$\hbar\gamma\mu\sqrt{n}$		$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n}$			$(n+\frac{1}{2})\hbar\omega-\frac{1}{2}\gamma\hbar H_0-D$			$\hbar\gamma\mu\sqrt{n+1}$		$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n+1}$
	$-\frac{3}{2}$			$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n}$					$(n+\frac{1}{2})\hbar\omega-\frac{3}{2}\gamma\hbar H_0+D$			$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n+1}$	
(n+1)	$\frac{3}{2}$						$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n+1}$			$(n+\frac{3}{2})\hbar\omega+\frac{3}{2}\gamma\hbar H_0+D$			
	$\frac{1}{2}$					$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n+1}$		$\hbar\gamma\mu\sqrt{n+1}$			$(n+\frac{3}{2})\hbar\omega+\frac{1}{2}\gamma\hbar H_0-D$		
	$-\frac{1}{2}$						$\hbar\gamma\mu\sqrt{n+1}$		$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n+1}$			$(n+\frac{3}{2})\hbar\omega-\frac{1}{2}\gamma\hbar H_0-D$	
	$-\frac{3}{2}$							$\sqrt{\frac{3}{2}}\hbar\gamma\mu\sqrt{n+1}$					$(n+\frac{3}{2})\hbar\omega-\frac{3}{2}\gamma\hbar H_0+D$

Table 2. Matrix elements of the Hamiltonian (1) for arbitrary spin S.

		n−1				n				n+1			
		S	S-1	−(S−1)	−S	S	(S−1)	−(S−1)	−S	S	(S−1)	−(S−1)	−S
	S	$(n-\frac{1}{2})\hbar\omega + \gamma\hbar H_0 S + D[S^2 - \frac{1}{3}S(S+1)]$					$\frac{1}{2}\gamma\hbar\mu\sqrt{2ns}$						
	S-1		$(n-\frac{1}{2})\hbar\omega + \gamma\hbar H_0(S-1) + D[(S-1)^2 - \frac{1}{3}S(S+1)]$			$\frac{1}{2}\gamma\hbar\mu\sqrt{2ns}$							
	−(S−1)			$(n-\frac{1}{2})\hbar\omega + \gamma\hbar H_0(S-1) + D[(S-1)^2 - \frac{1}{3}S(S+1)]$					$\frac{1}{2}\gamma\hbar\mu\sqrt{2ns}$				
	−S				$(n-\frac{1}{2})\hbar\omega - \gamma\hbar H_0 S + D[S^2 - \frac{1}{3}S(S+1)]$			$\frac{1}{2}\gamma\hbar\mu\sqrt{2ns}$					
	S		$\frac{1}{2}\gamma\hbar\mu\sqrt{2ns}$			$(n+\frac{1}{2})\hbar\omega + \gamma\hbar H_0 S + D[S^2 - \frac{1}{3}S(S+1)]$					$\frac{1}{2}\gamma\hbar\mu\sqrt{2S(n+1)}$		
	S-1	$\frac{1}{2}\gamma\hbar\mu\sqrt{2ns}$					$(n+\frac{1}{2})\hbar\omega + \gamma\hbar H_0(S-1) + D[(S-1)^2 - \frac{1}{3}S(S+1)]$			$\frac{1}{2}\gamma\hbar\mu\sqrt{2S(n+1)}$			
	−(S−1)			$\frac{1}{2}\gamma\hbar\mu\sqrt{2ns}$				$(n+\frac{1}{2})\hbar\omega - \gamma\hbar H_0(S-1) + D[(S-1)^2 - \frac{1}{3}S(S+1)]$					$\frac{1}{2}\gamma\hbar\mu\sqrt{2S(n+1)}$
	−S			$\frac{1}{2}\gamma\hbar\mu\sqrt{2ns}$					$(n+\frac{1}{2})\hbar\omega - \gamma\hbar H_0 S + D[S^2 - \frac{1}{3}S(S+1)]$			$\frac{1}{2}\gamma\hbar\mu\sqrt{2S(n+1)}$	
	S						$\frac{1}{2}\gamma\hbar\mu\sqrt{2S(n+1)}$			$(n+\frac{3}{2})\hbar\omega + \gamma\hbar H_0 S + D[S^2 - \frac{1}{3}S(S+1)]$			
	(S−1)					$\frac{1}{2}\gamma\hbar\mu\sqrt{2S(n+1)}$					$(n+\frac{1}{2})\hbar\omega + \gamma\hbar H_0(S-1) + D[(S-1)^2 - \frac{1}{3}S(S+1)]$		
	−(S−1)							$\frac{1}{2}\gamma\hbar\mu\sqrt{2S(n+1)}$				$(n+\frac{1}{2})\hbar\omega - \gamma\hbar H_0(S-1) + D[(S-1)^2 - \frac{1}{3}S(S+1)]$	
	−S						$\frac{1}{2}\gamma\hbar\mu\sqrt{2S(n+1)}$						$(n+\frac{3}{2})\hbar\omega - \gamma\hbar H_0 S + D[S^2 - \frac{1}{3}S(S+1)]$

term is, of course, a misnomer. It would be interesting to see the effect of the above coordinate transformation on the matrix form. If $|\psi\rangle$ was the state vector in the old representation before the rotation of axes is carried out, then the Schrödinger equation in the new representation becomes

$$i\hbar \frac{\partial}{\partial t} U^\dagger |\psi\rangle = [U^\dagger H U - i\hbar U^\dagger \dot{U}] U^\dagger |\psi\rangle \tag{6}$$

Therefore

$$H' = U^\dagger H U - i\hbar U^\dagger \dot{U} \tag{7}$$

Hence

$$\langle n, S_z | U H' U^\dagger | m, S'_z \rangle = \langle n, S_z | H | m, S'_z \rangle\rangle + (\tfrac{1}{2} S_z^2 - \tfrac{5}{8}) \hbar\omega \delta_{mn} \delta S_z S'_z. \tag{8}$$

The matrix representation of the Hamiltonian operator (eq. 1) in the transformed representation is as shown in table 3. This representation has been obtained by using the results of eq. (8). On inspecting eq. (8), as also from the comparison of table 1 with table 3, it is clear that transition probabilities are not affected by this transformation. A somewhat similar suggestion has been made by Daniels (1974) while discussing the case of spin 1/2.

It has been observed earlier (Allegrini and Arimondo 1971) that in some cases, the results of quantum field theoretical methods and the semi-classical methods are equivalent. From the point of view of the principle of uncertainty, the reason for this has been traced back to the exceedingly large number of photons present in the r.f. field. However, the differences in the classical and quantum approaches will show up when factors such as those involved in the case of periodic oscillation, of the occupation probability of one of the Zeeman levels in the presence of an r.f. field (Mystre *et al* 1974), etc. are also to be considered; *i.e.*, when the consideration of merely the matrix elements of the Hamiltonian operator is inadequate. On the basis of our results, the prima facie equivalence of the quantum field theoretic and the semi-classical methods can be attributed to the fact that the classical coordinate transformations do not lead to any substantial change in the matrix elements of the Hamiltonian operator.

4. Conclusions

It can be concluded from the above that by using the quantum method, not only can one get over the inadequacies of the classical methods, but one also has the advantage of having a theoretical basis, as against the arbitrariness involved in the semi-empirical classical methods. One finds that the present quantal method contains the classical one, because the results of the two do not differ significantly. It is implicit in the formalism that the present approach is equally applicable to nuclear magnetic resonance and the electron spin resonance phenomena. It is possible to extend this approach very conveniently to tackle more difficult problems, such as those involving time-evolution of the states and their interactions with the spin systems, etc. Further work on these lines is in progress.

Table 3. Matrix elements of the transformed Hamiltonian (8) for spin 3/2.

		$(n-1)$				(n)				$(n+1)$			
		$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
	$\frac{3}{2}$	$n\hbar\omega + \frac{3}{2}\gamma\hbar H_0 + D$					$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n}$						
$(n-1)$	$\frac{1}{2}$		$(n-1)\hbar\omega + \frac{1}{2}\gamma\hbar H_0 - D$			$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n}$		$\hbar\gamma\mu\sqrt{n}$					
	$-\frac{1}{2}$			$(n-1)\hbar\omega - \frac{1}{2}\gamma\hbar H_0 - D$			$\hbar\gamma\mu\sqrt{n}$		$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n}$				
	$-\frac{3}{2}$				$n\hbar\omega - \frac{3}{2}\gamma\hbar H_0 + D$			$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n}$					
(n)	$\frac{3}{2}$		$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n}$			$(n+1)\hbar\omega + \frac{3}{2}\gamma\hbar H_0 + D$					$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n+1}$		
	$\frac{1}{2}$	$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n}$		$\hbar\gamma\mu\sqrt{n}$			$n\hbar\omega + \frac{1}{2}\gamma\hbar H_0 - D$			$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n+1}$		$\hbar\gamma\mu\sqrt{n+1}$	
	$-\frac{1}{2}$		$\hbar\gamma\mu\sqrt{n}$		$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n}$			$n\hbar\omega - \frac{1}{2}\gamma\hbar H_0 - D$			$\hbar\gamma\mu\sqrt{n+1}$		$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n+1}$
	$-\frac{3}{2}$			$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n}$					$(n+1)\hbar\omega - \frac{3}{2}\gamma\hbar H_0 + D$			$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n+1}$	
$(n+1)$	$\frac{3}{2}$						$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n+1}$			$(n+2)\hbar\omega + \frac{3}{2}\gamma\hbar H_0 + D$			
	$\frac{1}{2}$					$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n+1}$		$\hbar\gamma\mu\sqrt{n+1}$			$(n+1)\hbar\omega + \frac{1}{2}\gamma\hbar H_0 - D$		
	$-\frac{1}{2}$						$\hbar\gamma\mu\sqrt{n+1}$		$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n+1}$			$(n+1)\hbar\omega - \frac{1}{2}\gamma\hbar H_0 - D$	
	$-\frac{3}{2}$							$\frac{\sqrt{3}}{2}\hbar\gamma\mu\sqrt{n+1}$					$(n+2)\hbar\omega - \frac{3}{2}\gamma\hbar H_0 + D$

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