Berry's geometrical phases in ESR in the presence of a stochastic process

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Berry's [Proc. R. Soc. London, Ser. A **392**, 45 (1984)] geometrical phase is discussed in the context of dissipative evolution of an interacting spin system, governed by the stochastic Liouville equation. An analytical treatment is given for a possible ESR experiment on an interacting electron-nucleus system, modulated by two-site jumps. Geometrical phases are shown to be relevant to systems of this type, when their Hamiltonian changes slowly with time. A method for obtaining higher-order corrections to the adiabatic approximation is demonstrated. It is found that if the jumps are slow relative to the rate of change of the Hamiltonian, their effect reduces to familiar line broadening, and the geometrical phases may be observed experimentally. Equations are also set up for a similar ESR experiment on an electron-nucleus system undergoing isotropic rotational diffusion, and a brief discussion of the equations follows.

I. INTRODUCTION

A few years ago it was shown by Berry[1] that when a quantum-mechanical Hamiltonian changes adiabatically, completing a cycle in parameter space, the corresponding physical system will acquire, in general, not only the familiar dynamic phase,[2] but also an additional geometrical phase. This phase is related to the geometry of the circuit traversed by the Hamiltonian in parameter space. The effect has been put in a wider mathematical context by Simon,[3] who showed that Berry's phase can be regarded as the result of parallel transport of the wave function in a bundle with curvature. The existence of geometrical phases in quantum mechanics was discussed in more general mathematical terms by Anandan and Stodolsky[4] and by Garrison and Chiao,[5] among others. It was also found that in classical mechanics there are some adiabatic situations in which one may define "geometrical" angles, analogous to the quantum geometrical phase.[6-10]

For the quantum case, the original treatment has been generalized in various ways. Wilczek and co-workers[11] showed that even for a system with degenerate states, where the adiabatic theorem does not hold, it is possible to define and calculate a geometrical phase, related to a non-Abelian gauge field, unlike Berry's phase, which is related to an Abelian gauge field. Berry[12] developed a method of calculating the relevant phases when the change in the Hamiltonian is not sufficiently slow for the adiabatic approximation to hold. Higher-order adiabatic corrections were also calculated by Sun,[13] and a nonadiabatic process was discussed by Bulgac.[14] An important generalization was made by Aharonov and Anandan.[15] They showed that the geometrical phase is directly related to the cyclic evolution of the wave function, and not to the change in the Hamiltonian. In particular, adiabaticity is not necessary for this phase to appear.

The intensive theoretical work on the subject was accompanied by experiments of several kinds, which verified the theoretical predictions. Optical experiments have been carried out,[16-19] as well as a nuclear quadrupole resonance experiment[20] and nuclear magnetic resonance experiments.[21,22]

In most studies of the geometrical phase, the systems considered were single, noninteracting spins or photons. In one case in which two interacting spins were considered,[22] the consequences of having to use the density matrix instead of the wave function were not explored in detail. In virtually all studies it was also assumed that the evolution of the quantum system was unitary (see, however, the work of Samuel and Bhandari[23]). In most physical situations one is concerned not with single particles, but with a system of interacting particles. Furthermore, in some cases there are complicated processes which influence the behavior of otherwise simple systems in a way that is practically impossible to describe exactly. In many of these cases that influence is taken into account by adding to the Liouville–von Neumann equation of motion for the density matrix a semiclassical term. This term represents the relaxation due to a stochastic process.[24-28] The resulting Redfield-type or stochastic Liouville equations have been used extensively in magnetic resonance, both NMR and ESR, for various spin systems and stochastic processes.[29-34]

The purpose of this paper is to investigate geometrical phases in systems which are described by the stochastic Liouville equation rather than Schrödinger's equation. The general derivation of the relevant equations is developed in Sec. II, concluding with a discussion of the requirements for adiabaticity and the influence of the dissipative process. It is seen that the concept of the geometrical phase remains meaningful in the presence of the stochastic process, and that this phase may be experimentally observed.

In Secs. III and IV these general calculations are illustrated by two examples, in which the conditions necessary for actual experiments are also discussed. The first example is of a hypothetical ESR experiment, similar to an NMR experiment that has already been done.[21] The two new features here are the existence of interactions and the stochastic process. The system considered con-

sists of an electron and a nucleus, with stochastic jumps which modulate their interaction. The calculations proceed in two stages. In the first stage we ignore the jumps, treating the static interacting system. Using Maricq's generalization of average Hamiltonian theory,[35] based on Floquet theory,[36] we calculate systematically the low-order terms for the adiabatic situation, obtaining Berry's phase in the lowest-order term. In the second stage the effect of the stochastic jumps is included approximately, assuming a slow jump rate. This is followed by a discussion of the necessary conditions for observing the calculated effects experimentally.

In the second example the same type of experiment is considered, but for a different electron-nucleus system. The Hamiltonian is assumed to depend on a continuous variable, the molecular orientation with respect to the direction of the static magnetic field. An isotropic rotational diffusion process is present, and as a result of this, the form of the coefficients in the equations is too complicated for an analytical solution. Nevertheless, the significance of the geometrical phases is clear also in this case, and their effect can be calculated. A brief calculation is also presented concerning the possibility of observing geometrical phases in exactly degenerate subspaces[11,14,37] in an ordinary ESR system. A short summary of the main results is given in Sec. V.

II. BERRY'S PHASE IN THE PRESENCE OF A STOCHASTIC PROCESS

Although Berry's phase was originally defined in connection with exact evolution according to Schrödinger's equation, it may still have a meaning when relaxation processes cause a decay of coherence. In the following we shall define and calculate the geometrical (or Berry's) phase for such cases, treating systems which have to be described by a density matrix, which evolves according to a relaxation equation. The basic equation of motion in a high-temperature approximation is then[25-27,30,38-41]

$$\frac{d}{dt}\rho = \frac{i}{\hbar}[\rho(t),H(t)] + \Gamma(\rho(t) - \rho_0(t)) \ . \tag{1}$$

The relaxation term with Γ is constructed so as to lead the decaying ρ to relax to an "instantaneous equilibrium" density matrix ρ_0. The time-dependent Hamiltonian $H(t)$ will now be assumed to change slowly with time, with a corresponding change in its eigenfunctions and eigenvalues,

$$H(t)|n(t)\rangle = E_n(t)|n(t)\rangle \ . \tag{2}$$

From here on, H and E_n will be expressed in angular frequency units. The superoperator Γ operates on Hilbert-space operators as

$$(\Gamma O)_{kl} = \sum_{m,n} \Gamma_{kl,mn} O_{mn} \ . \tag{3}$$

In the basic derivation of Berry's phase, the Hamiltonian is assumed to change slowly in a cycle of period T such that at time T, $H(R(T)) = H(R(0))$ (Ref. 1). Here the components of the vector $R(t)$ are the time-dependent parameters, which fully contain the time

dependence of the Hamiltonian. The number of components of this vector is not important for the basic phenomenon, but in many practical cases (including those which are treated in the present paper) it has three components, e.g., the magnetic field vector for a spin Hamiltonian[1,4,12-15,21] or the wave vector of a photon.[16] For convenience in notation we shall suppress the R dependence of H, writing it just as $H(t)$, from here on. The wave function, assumed initially to be in an eigenstate of $H(0)$, $\Psi(0) = |n(0)\rangle$ evolves adiabatically to

$$\Psi(T) = \exp[i\gamma_n(T)]\exp\left[-i\int_0^T E_n(t')dt'\right]|n(T)\rangle$$

$$= \exp[i\gamma_n(T)]\exp\left[-i\int_0^T E_n(t')dt'\right]|n(0)\rangle \ , \tag{4}$$

in which the geometrical phase is defined by the expression

$$\frac{d}{dt}\gamma_n(t) = i\langle n(R(t))|\nabla|n(R(t))\rangle \frac{d}{dt}R(t) \ , \tag{5}$$

and consequently

$$\gamma_n(T) = i\oint \langle n(R(t))|\nabla|n(R(t))\rangle dR \ . \tag{6}$$

The gradient in both equations is the R gradient. This phase is thus obtained by an integration in parameter space, and an explicit formula was given by Berry for the case of a three-component vector of parameters.[1] Contrary to the traditional treatment of the adiabatic approximation,[2] Berry showed that this phase is nontrivial, and can be observed experimentally. In the work of Aharonov and Anandan[15] this was generalized to the case of a general wave function, not necessarily an eigenfunction of the Hamiltonian. When the quantum system is described by a density matrix, the definition (5) [or (6)] of the phase γ can still be used, but the evolution with time is described differently, even when no dissipative mechanisms are taken into consideration.[20]

In order to see how geometrical phases appear in the "adiabatic" evolution of a quantum system in accordance with Eq. (1), one has to set up equations for appropriate components of the density matrix. The Hamiltonian may still be assumed to change slowly, its time dependence resulting from its dependence on a set of time-dependent parameters. In the cases to be treated explicitly in Secs. III and IV the vector of parameters will be an effective magnetic field in an appropriate frame of reference, but this will not be assumed in the general derivation of the present section.

Using the time-dependent states and energies defined in Eq. (2), the density matrix is expanded as

$$\rho(t) = \sum_{m,n} a_{mn}(t)\exp\left[-i\int_0^t \omega_{mn}(t')dt'\right]|m(t)\rangle\langle n(t)| \ . \tag{7}$$

Here $\omega_{mn}(t') = E_m(t') - E_n(t')$ is the time-dependent transition frequency. The coefficients $a_{mn}(t)$ are matrix elements of $\rho(t)$ in the time-dependent adiabatic basis,

$$a_{mn}(t) = \left\langle m(t) \left| \exp\left[i \int_0^t E_m(t')dt' \right] \rho(t) \exp\left[-i \int_0^t E_n(t')dt' \right] \right| n(t) \right\rangle . \tag{8}$$

Substituting Eq. (7) in Eq. (1), we get the following equation:

$$\exp\left[-i \int_0^t \omega_{kl}(t')dt' \right] \left[\frac{d}{dt} a_{kl}(t) - i\omega_{kl}(t)a_{kl}(t) \right]$$

$$+ \sum_{m,n} \exp\left[-i \int_0^t \omega_{mn}(t')dt' \right] a_{mn}(t) \left[\delta_{n,l} \left\langle k(t) \left| \frac{d}{dt} \right| m(t) \right\rangle + \delta_{k,m} \left\langle \frac{d}{dt} n(t) \left| l(t) \right\rangle \right]$$

$$= -i\omega_{kl}(t)a_{kl}(t)\exp\left[-i \int_0^t \omega_{kl}(t')dt' \right] + \sum_{m,n} \Gamma_{kl,mn} \left[\exp\left[-i \int_0^t \omega_{mn}(t')dt' \right] a_{mn}(t) - a_{mn}^{(0)}(t) \right] . \tag{9}$$

In this equation we have used the following notation for the "time-dependent (or instantaneous) equilibrium" density matrix[38,39]

$$\rho_0(t) = \sum_{m,n} \delta_{m,n} a_{mn}^{(0)}(t) | m(t) \rangle \langle n(t) | , \tag{10}$$

which is not necessarily the initial state of $\rho(t)$. Assuming *no* degeneracies in the Hamiltonian, it is possible to use the following relations:[2]

$$\left\langle k(t) \left| \frac{d}{dt} m(t) \right\rangle = \frac{\langle k(t) | H' | m(t) \rangle}{\omega_{mk}(t)} \quad (k \neq m) , \tag{11a}$$

$$\left\langle k(t) \left| \frac{d}{dt} k(t) \right\rangle = -i\frac{d}{dt}\gamma k(t) . \tag{11b}$$

For notational convenience, $\partial H / \partial t$ is denoted here by H'. One then obtains from Eq. (9) the following equation of motion for the matrix elements $a_{kl}(t)$:

$$\frac{d}{dt}a_{kl}(t) = ia_{kl}(t)\left[\frac{d}{dt}\gamma_k(t) - \frac{d}{dt}\gamma_l(t) \right] + \exp\left[i \int_0^t \omega_{kl}(t')dt' \right]$$

$$\times \sum_{m,n} \exp\left[-i \int_0^t \omega_{mn}(t')dt' \right] a_{mn}(t) \left[\delta_{l,n}(1-\delta_{k,m})\frac{\langle k(t)|H'|m(t)\rangle}{\omega_{km}(t)} + \delta_{k,m}(1-\delta_{l,n})\frac{\langle n(t)|H'|l(t)\rangle}{\omega_{\ln}(t)} \right]$$

$$+ \exp\left[i \int_0^t \omega_{kl}(t')dt' \right] \sum_{m,n} \Gamma_{kl,mn} \left[a_{mn}(t)\exp\left[-i \int_0^t \omega_{mn}(t')dt' \right] - a_{mn}^{(0)}(t) \right] . \tag{12}$$

It is convenient to decompose the Hamiltonian into a constant part and a time-dependent part, $H = H_0 + H_1(t)$. For a slowly changing Hamiltonian the usual assumptions of the adiabatic approximation[2] are expected to hold,

$$a_{mn}(t) \approx a_{mn}(0) + O\left[\frac{H'}{\omega^2} \right] , \tag{13a}$$

$$\omega_{mn}(t) \approx \omega_{mn}(0) + O(H_1(t)) . \tag{13b}$$

In these equations ω stands for a typical transition frequency of the Hamiltonian. The first equation follows from a calculation of the extent of deviation from the adiabatic approximation,[2] while the second one results from the definition of $\omega_{mn}(t)$. Let us now discuss Eq. (12) first by assuming a simple initial condition, and then generalize to any initial condition. Assuming the simplest initial condition, which is $a_{pq}(0) = 1$ and $a_{kl}(0) = 0$ for

$(kl) \neq (pq)$, there are three (or four) types of equations implied by Eq. (12):

$$\frac{d}{dt}a_{pq}(t) \approx \left[i\left[\frac{d}{dt}\gamma_p(t) - \frac{d}{dt}\gamma_q(t) \right] + \Gamma_{pq,pq} \right] a_{pq}(t) , \tag{14a}$$

$$\frac{d}{dt}a_{pl}(t) \approx \exp\left[i \int_0^t \omega_{ql}(t')dt' \right] \frac{\langle q(t)|H'|l(t)\rangle}{\omega_{lq}(t)}$$

$$+ \exp\left[i \int_0^t \omega_{ql}(t')dt' \right] \Gamma_{pl,pq} \quad (l \neq q) , \tag{14b}$$

$$\frac{d}{dt}a_{kq}(t) \approx \exp\left[i \int_0^t \omega_{kp}(t')dt' \right] \frac{\langle k(t)|H'|p(t)\rangle}{\omega_{kp}(t)}$$

$$+ \exp\left[i \int_0^t \omega_{kp}(t')dt' \right] \Gamma_{kq,pq} \quad (k \neq p) , \tag{14c}$$

$$\frac{d}{dt}a_{kl}(t) \approx \left[\exp\left[i\int_0^t \omega_{kl}(t')dt' \right] \right.$$

$$\left. \times \exp\left[-i\int_0^t \omega_{pq}(t')dt' \right] + C \right] \Gamma_{kl,pq}$$

$$(k\neq p, \ l\neq q) \ . \qquad (14d)$$

The constant C in (14d) is equal to 1 if there is a degeneracy in frequencies, $\omega_{kl}=\omega_{pq}$, and is equal to 0 otherwise. The terms with $a_{pq}^{(0)}(t)$ in Eq. (12) have been omitted here, as they are nonzero only for $p=q$, in which case the geometrical phase difference in Eq. (14a) is zero, so these elements are not relevant for the present discussion. In order to distinguish clearly between the special effects of the stochastic process and the features which result just from using the density matrix instead of a wave function, it is convenient to discuss Eqs. (14) first by ignoring the relaxation part, and then include also the effect of the relaxation. Performing an approximate integration of Eqs. (14b) and (14c) when the relaxation terms are ignored, one gets a rough criterion for adiabaticity,

$$\left| \frac{\langle q(t)|H'|l(t)\rangle}{[\omega_{lq}(t)]^2} \right| \ll 1 \quad (l\neq q) \ . \qquad (15)$$

This is the ordinary requirement for the applicability of the adiabatic approximation.[2] Notice that the only matrix elements $a_{kl}(t)$ that can become nonzero (when $\Gamma=0$) are those that have one energy level in common with the (pq) transition—either $k=p$ or $l=q$. Berry's phases for the individual wave functions result in geometrical phases for all off-diagonal elements of the density matrix, as expressed by Eq. (14a). These geometrical phases cause shifts in the spectral frequencies,[19,20] which can be observed experimentally.

When the elements of the supermatrix Γ are nonzero, three kinds of effects take place. The most obvious one is that the real part of $\Gamma_{pq,pq}$ causes an exponential decay of $a_{pq}(t)$. When the signal is Fourier transformed to the frequency domain, this decay is transformed into a familiar line broadening. In principle there is also a second effect, a frequency shift due to the imaginary part of $\Gamma_{pq,pq}$, but this effect is usually relatively small. Finally, in Eqs. (14b)–(14d) there are elements of the relaxation superma-

trix which contribute to a growth in the magnitude of other elements of the density matrix. Integrating these equations approximately, this contribution is found to change the requirement for the adiabatic approximation to the following one:

$$\left| \frac{\langle q(t)|H'|l(t)\rangle}{[\omega_{lq}(t)]^2} \right| \ll 1 \quad (l\neq q) \qquad (16a)$$

and

$$\left| \frac{\Gamma_{kl,mn}}{\omega_{km}} \right| \ll 1 \quad (k\neq m) \ , \qquad (16b)$$

$$\left| \frac{\Gamma_{kl,mn}}{\omega_{ln}} \right| \ll 1 \quad (l\neq n) \ , \qquad (16c)$$

$$\left| \frac{\Gamma_{kl,mn}}{\omega_{km}-\omega_{ln}} \right| \ll 1 \quad (k\neq m, l\neq n) \ . \qquad (16d)$$

Equations (16b)–(16d) originate in Eqs. (14b)–(14d), respectively. These additional conditions mean that the relaxation process should be slow in comparison with the transition frequencies, since otherwise the whole line shape will be significantly altered by line broadening. It is also necessary that there are no degenerate or nearly degenerate frequencies connected by $\Gamma_{kl,mn}$. As long as this modified criterion for adiabaticity is kept, it is still meaningful to speak about frequency shifts caused by the geometrical phase differences. However, if the matrix elements of Γ are small compared with the transition frequencies, and at the same time they are large compared with the geometrical phase difference, the resulting line broadening is larger than the frequency shift. In this intermediate regime the adiabatic approximation may still be useful to some extent, but not sufficiently accurate to make the observation of Berry's phase feasible. This point will be discussed in some detail in Sec. III.

Now suppose one has a more realistic initial condition, in which several elements of the density matrix are different from zero. Define the set S_I of their index pairs as $S_I=\{(pq)|a_{pq}(0)\neq 0\}$. Then Eq. (14a) would become

$$\frac{d}{dt}a_{pq}(t)=ia_{pq}(t)\left[\frac{d}{dt}\gamma_p(t)-\frac{d}{dt}\gamma_q(t)\right]+\exp\left[i\int_0^t \omega_{pq}(t')dt'\right]$$

$$\times \sum_{(rs)\in S_I}\exp\left[-i\int_0^t \omega_{rs}(t')dt'\right]a_{rs}(t)\left[\delta_{q,s}(1-\delta_{p,r})\frac{\langle p(t)|H'|r(t)\rangle}{\omega_{pr}(t)}+\delta_{p,r}(1-\delta_{q,s})\frac{\langle s(t)|H'|q(t)\rangle}{\omega_{qs}(t)}\right]$$

$$+\exp\left[i\int_0^t \omega_{pq}(t')dt'\right]\sum_{(rs)\in S_I}\Gamma_{pq,rs}\left[a_{rs}(t)\exp\left[-i\int_0^t \omega_{rs}(t')dt'\right]-a_{rs}^0(t)\right]$$

$$(17)$$

and Eqs. (14b)–(14d) would be modified in a similar manner. The equations are now more complicated than with the artificial condition of a single nonzero element in the initial value of the density matrix, but qualitatively the situation is unchanged. In particular, if the relaxation terms are ignored, the rough criterion expressed in (15) for the validity of the adiabatic approximation still applies, and the geometrical phase differences shift the spectral frequencies.

If the full Eq. (17), including the relaxation terms, is considered, the same qualitative situation is encountered as in Eqs. (14). In particular, conditions (16) have to be fulfilled for the adiabatic approximation to apply. It is convenient to arrange the relevant elements of the density matrix, those which belong to the set S_I, in a vector, and the coefficients of these elements in Eq. (17) in a matrix, so that the equation takes the form

$$\frac{d}{dt}\mathbf{a}(t) = \mathbf{X}(t)\mathbf{a}(t) + \mathbf{b}(t) .$$ (18)

The matrix, or rather supermatrix $\mathbf{X}(t)$ contains on the diagonal both the geometrical phase differences and the diagonal elements of the stochastic superoperator. Its off-diagonal elements contain contributions from the two sources of deviation from adiabaticity, viz., the change in the Hamiltonian and the off-diagonal elements of the stochastic superoperator. The vector $\mathbf{b}(t)$ contains the contribution of the equilibrium density matrix to the calculation.

In general, this set of equations may be solved numerically for specific cases. In order to get some insight into these equations, it is desirable to study some examples analytically, discussing what may be calculated or observed in those cases. This will be done in Secs. III and IV.

III. AN ESR EXPERIMENT ON A SYSTEM WITH TWO-SITE JUMPS

A. General equations

To study the effect of stochastic processes, it is useful to treat two extreme models. One is a model of discrete two-site jumps, and the other is a model of continuous rotational diffusion. In this section we shall consider a possible ESR experiment on an electron-nucleus system in which a simple interaction is modulated by two-site jumps, and in Sec. IV a similar experiment will be discussed for an electron-nucleus system, undergoing rotational diffusion.

It is relatively simple to discuss Berry's phase in the case of a three-dimensional parameter space. In that case the three time-dependent parameters form the components of an ordinary vector, which determines the adiabatic evolution by its influence on the Hamiltonian. In particular, the discussion is simple if the vector moves in a conical circuit in parameter space, precessing around a fixed direction. One way to achieve in practice a situation of this kind in magnetic resonance is to irradiate with one frequency, and to detect the signal relative to a different frequency.[21] We therefore assume such an experimental setting, investigating Berry's effect for the in-

teracting two-spin system, and the influence of the jumps on this effect. This example will also be used for demonstrating how to calculate, in a systematic manner, higher-order corrections to Berry's adiabatic approximation.

Denoting the electronic spin by $\mathbf{S}$ and the nuclear spin by $\mathbf{I}$, it is assumed here that $S = \frac{1}{2}$ and $I = \frac{1}{2}$. The Hamiltonian is taken to be equal to (see Appendix of Ref. 30)

$$H = -\omega_I I_z - \gamma_e \mathbf{B} \cdot \mathbf{S} + D(i)I_z[S_z + \frac{1}{2}(S_+ + S_-)]$$ (19)

in a special reference frame, rotating around the direction of the static magnetic field at the detection frequency ω_{det}. The nuclear Zeeman frequency is ω_I, and the effective magnetic field acting on the electronic spin is

$$\mathbf{B} = \frac{1}{\gamma_e}\{\Delta\hat{\mathbf{z}} + \omega_1[\cos(\delta t)\hat{\mathbf{x}} - \sin(\delta t)\hat{\mathbf{y}}]\} ,$$ (20)

where $\Delta = \omega_0 - \omega_{\text{det}}$ (with ω_0 being the Larmor frequency) is the off-resonance value, and $\delta = \omega_m - \omega_{\text{det}}$ is the difference between the microwave irradiation frequency ω_m and the detection frequency. The electron-nucleus interaction is given in a simplified form by the last term in the Hamiltonian, with

$$D(i) = \begin{cases} +d, & i=1 \\ -d, & i=2 \end{cases}$$ (21)

where the real constant d is taken as positive. These two values of $D(i)$ represent two states of the system, and the stochastic jumps between these two states give rise to the following equation of motion for the density matrix:[42]

$$\frac{d}{dt}\rho^{(i)} = i[\rho^{(i)}, H^{(i)}] - \sum_{i,j} \Gamma_{ij}\rho^{(j)} .$$ (22)

In this equation the full density matrix is a direct sum of the matrices for the two states, because they are coupled only by the stochastic process, for which the matrix Γ is expressed as[30]

$$\Gamma = \frac{1}{\tau}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} .$$ (23)

It is therefore possible to use throughout the calculations a Hilbert space which is a direct sum of the spaces for the two states,[31] and the observed magnetization is obviously an average (with equal weights) over the two states. From here on the two states of the system will be referred to as two sites, to emphasize the similarity of the problem to that of a spin jumping between different sites.

For our purpose it is necessary to work in the time-dependent adiabatic basis of Hilbert space. Ordering the $|S_z I_z\rangle$ basis as $(|\frac{1}{2}\frac{1}{2}\rangle, |-\frac{1}{2}\frac{1}{2}\rangle, |\frac{1}{2}-\frac{1}{2}\rangle, |-\frac{1}{2}-\frac{1}{2}\rangle)$, the Hamiltonian matrix $H^{(i)}$ for site (i) is, in this basis:

$$
\begin{bmatrix}
-\dfrac{\omega_I}{2}-\dfrac{\Delta}{2}+\dfrac{D(i)}{4} & \dfrac{D(i)}{4}-b & 0 & 0 \\[2ex]
\dfrac{D(i)}{4}-b^* & -\dfrac{\omega_I}{2}+\dfrac{\Delta}{2}-\dfrac{D(i)}{4} & 0 & 0 \\[2ex]
0 & 0 & \dfrac{\omega_I}{2}-\dfrac{\Delta}{2}-\dfrac{D(i)}{4} & -\dfrac{D(i)}{4}-b \\[2ex]
0 & 0 & -\dfrac{D(i)}{4}-b^* & \dfrac{\omega_I}{2}+\dfrac{\Delta}{2}+\dfrac{D(i)}{4}
\end{bmatrix}
\tag{24}
$$

with $b=(\omega_1/2)e^{i\delta t}$.

The eigenvalues of this Hamiltonian are found to be

$$
\lambda_{1,2}(i)=-\frac{\omega_I}{2}\pm r_-(i,t), \quad \lambda_{3,4}(i)=\frac{\omega_I}{2}\pm r_+(i,t) ,
\tag{25}
$$

with

$$
2r_\mp(i,t)=\{[\Delta\mp D(i)]^2+[D(i)/2]^2+\omega_1^2\mp D(i)\omega_1\cos(\delta t)\}^{1/2} .
\tag{26}
$$

One may now define an angle $\theta_\mp(i,t)$ by the relations

$$
r_\mp(i,t)\cos[\theta_\mp(i,t)]=\frac{\Delta\mp D(i)}{2} ,
\tag{27a}
$$

$$
r_\mp(i,t)\sin[\theta_\mp(i,t)]=\left|\frac{D(i)}{4}\mp b\right| .
\tag{27b}
$$

It is also convenient to define a time-dependent phase,

$$
\beta_\mp(i,t)=\arg\left[\frac{D(i)}{4}\mp b\right] ,
\tag{28}
$$

which has in general a different value for the two sites. The right eigenvectors corresponding to these eigenvalues are the columns of the following matrix:

$$
\begin{bmatrix}
u_-w_- & u_+w_- & 0 & 0 \\[1ex]
u_+w_-^* & -u_-w_-^* & 0 & 0 \\[1ex]
0 & 0 & v_-w_+ & v_+w_+ \\[1ex]
0 & 0 & v_+w_+^* & -v_-w_+^*
\end{bmatrix} ,
\tag{29}
$$

with the notation

$$
u_\pm=\left[\frac{1\pm\cos(\theta_-)}{2}\right]^{1/2} , \quad v_\pm=\left[\frac{1\pm\cos(\theta_+)}{2}\right]^{1/2} , \quad w_\mp=\exp\left[i\frac{\beta_\mp}{2}\right] .
$$

Note that here both energies and eigenfunctions of the Hamiltonian are time dependent as well as site dependent. In the adiabatic basis one has to solve Eq. (17), which appears here in the form

$$
\begin{aligned}
\frac{d}{dt}a_{pq}^{(i)}(t)=&\,ia_{pq}^{(i)}(t)\left[\frac{d}{dt}\gamma_p^{(i)}(t)-\frac{d}{dt}\gamma_q^{(i)}(t)\right]+\exp\left[i\int_0^t\omega_{pq}^{(i)}(t')dt'\right]\Gamma_{pq,pq}^{(i,i)}\left[a_{pq}^{(i)}(t)\exp\left[-i\int_0^t\omega_{pq}^{(i)}(t')dt'\right]-a_{pq}^{(i)(0)}(t)\right] \\
&+\exp\left[i\int_0^t\omega_{pq}^{(i)}(t')dt'\right]\sum_{(rs)\in S_I}\exp\left[-i\int_0^t\omega_{rs}^{(i)}(t')dt'\right]a_{rs}^{(i)}(t) \\
&\qquad\times\left[\delta_{q,s}(1-\delta_{p,r})\frac{\langle p(t)|H'|r(t)\rangle}{\omega_{pr}(t)}+\delta_{p,r}(1-\delta_{q,s})\frac{\langle s(t)|H'|q(t)\rangle}{\omega_{qs}(t)}\right] \\
&+\exp\left[i\int_0^t\omega_{pq}^{(i)}(t')dt'\right]\Gamma_{pq,pq}^{(i,i')}\left[a_{pq}^{(i')}(t)\exp\left[-i\int_0^t\omega_{pq}^{(i')}(t')dt'\right]-a_{pq}^{(i')(0)}(t)\right] .
\end{aligned}
\tag{30}
$$

Here $i = 1$ or 2 and $i' \neq i$. The time evolution of an element $a_{pq}^{(i)}$ is thus determined by three terms. The first, diagonal term contains a geometrical phase and the diagonal part of the relaxation superoperator. The second term gives the coupling of this matrix element to other density matrix elements related to the same site, as in the ordinary adiabatic situation. The third term gives the coupling of $a_{pq}^{(i)}$ to the corresponding element $a_{pq}^{(i')}$ of the density matrix for the other site, due to the stochastic jump process.

For each site i, the density matrix $\rho(t)$ is made of two 2×2 blocks along the diagonal, since the Hamiltonian commutes with I_z, and each of these blocks is coupled by the jump process only to the corresponding block for the other site. This means that the set of equations (30) is actually divided into two separate sets of equations. One set, involving the $I_z = \frac{1}{2}$ blocks, will be treated here explicitly, and then the trivial modifications $-\omega_I \rightarrow \omega_I$, $D(i) \rightarrow -D(i)$ will give the corresponding results for the $I_z = -\frac{1}{2}$ blocks.

Note that in the absence of the stochastic process the system considered here is similar to the one that was investigated in Tycko's nuclear quadrupole resonance (NQR) experiment,[20] since in both cases there is a four-level system which is divided into two uncoupled two-dimensional systems.

In Sec. II it was explicitly shown how the initial condition of the density matrix determines the set of matrix elements which are relevent during adiabatic evolution. In magnetic resonance experiments the initial condition is usually easy to express in terms of the components of the relevant angular momentum operator, which is $\mathbf{S}$ in the present case. Its components in the adiabatic basis are

$$S_x = \begin{bmatrix} \frac{1}{2}\sin(\theta)\cos(\beta) & \frac{1}{2}\cos(\theta)\cos(\beta) + \frac{i}{2}\sin(\beta) \\[2mm] \frac{1}{2}\cos(\theta)\cos(\beta) - \frac{i}{2}\sin(\beta) & -\frac{1}{2}\sin(\theta)\cos(\beta) \end{bmatrix} , \tag{31}$$

$$S_y = \begin{bmatrix} -\frac{1}{2}\sin(\theta)\sin(\beta) & \frac{1}{2}\cos(\theta)\sin(\beta) + \frac{i}{2}\cos(\beta) \\[2mm] -\frac{1}{2}\cos(\theta)\sin(\beta) - \frac{i}{2}\cos(\beta) & \frac{1}{2}\sin(\theta)\sin(\beta) \end{bmatrix} , \tag{32}$$

$$S_z = \begin{bmatrix} -\frac{1}{2}\cos(\theta) & \frac{1}{2}\sin(\theta) \\[2mm] \frac{1}{2}\sin(\theta) & \frac{1}{2}\cos(\theta) \end{bmatrix} . \tag{33}$$

It is thus clear that if one starts with a conventional initial condition, as $\rho = S_z$ or $\rho = S_x$, all elements of the density matrix are relevant. It is therefore assumed here that all matrix elements are relevant to the behavior of the system. Working in the $I_z = \frac{1}{2}$ subspace, the equations form the set

$$\frac{d}{dt}\mathbf{a} = \mathbf{X}\mathbf{a} + \mathbf{b} . \tag{34}$$

The density matrix elements are arranged in the vector $\mathbf{a}$ in the order

$$\mathbf{a} = \begin{bmatrix} a_{11}^{(1)} \\ a_{12}^{(1)} \\ a_{21}^{(1)} \\ a_{22}^{(1)} \\ a_{11}^{(2)} \\ a_{12}^{(2)} \\ a_{21}^{(2)} \\ a_{22}^{(2)} \end{bmatrix} , \tag{35}$$

while the matrix $\mathbf{X}$ is

$$
\begin{vmatrix}
-\dfrac{1}{\tau} & \epsilon^{(1)*} & \epsilon^{(1)} & 0 & \dfrac{1}{\tau} & 0 & 0 & 0 \\[2ex]
\epsilon^{(1)} & i\gamma'^{(1)}-\dfrac{1}{\tau} & 0 & \epsilon^{(1)} & 0 & \dfrac{1}{\tau}\epsilon^{(1,2)} & 0 & 0 \\[2ex]
\epsilon^{(1)*} & 0 & -i\gamma'^{(1)}-\dfrac{1}{\tau} & \epsilon^{(1)*} & 0 & 0 & \dfrac{1}{\tau}\epsilon^{(1,2)*} & 0 \\[2ex]
0 & \epsilon^{(1)*} & \epsilon^{(1)} & -\dfrac{1}{\tau} & 0 & 0 & 0 & \dfrac{1}{\tau} \\[2ex]
\dfrac{1}{\tau} & 0 & 0 & 0 & -\dfrac{1}{\tau} & \epsilon^{(2)*} & \epsilon^{(2)} & 0 \\[2ex]
0 & \dfrac{1}{\tau}\epsilon^{(1,2)*} & 0 & 0 & \epsilon^{(2)} & i\gamma'^{(2)}-\dfrac{1}{\tau} & 0 & \epsilon^{(2)} \\[2ex]
0 & 0 & \dfrac{1}{\tau}\epsilon^{(1,2)} & 0 & \epsilon^{(2)*} & 0 & -i\gamma'^{(2)}-\dfrac{1}{\tau} & \epsilon^{(2)*} \\[2ex]
0 & 0 & 0 & \dfrac{1}{\tau} & 0 & \epsilon^{(2)*} & \epsilon^{(2)} & -\dfrac{1}{\tau}
\end{vmatrix}. \tag{36}
$$

In this matrix the following definitions have been used, omitting everywhere the minus subscript [see Eqs. (26)–(28)]:

$$\gamma'^{(1)} = \frac{d}{dt}[\gamma_1^{(1)}(t) - \gamma_2^{(1)}(t)] , \tag{37a}$$

$$\gamma'^{(2)} = \frac{d}{dt}[\gamma_1^{(2)}(t) - \gamma_2^{(2)}(t)] , \tag{37b}$$

$$\epsilon^{(1)} = \frac{-i\omega_1\delta}{4r(1,t)}\{\cos[\delta t - \beta(1,t)]$$

$$-i\cos[\theta(1,t)]\sin[\delta t - \beta(1,t)]\}$$

$$\times \exp\left[2i\int_0^t r(1,t')dt'\right] , \tag{38}$$

$$\epsilon^{(2)} = \frac{-i\omega_1\delta}{4r(2,t)}\{\cos[\delta t - \beta(2,t)]$$

$$-i\cos[\theta(2,t)]\sin[\delta t - \beta(2,t)]\}$$

$$\times \exp\left[2i\int_0^t r(2,t')dt'\right] , \tag{39}$$

$$\epsilon^{(1,2)} = \exp\left[2i\int_0^t [r(1,t') - r(2,t')]dt'\right] . \tag{40}$$

Finally, the vector **b** has elements of the form

$$\frac{1}{\tau}a_{kl}^{(i)(0)}(t)\left[\exp\left[i\int_0^t \omega_{kl}^{(i)}(t')dt'\right] - \exp\left[i\int_0^t \omega_{kl}^{(i')}(t')dt'\right]\right] \tag{41}$$

using the fact that at equilibrium the density matrix has equal elements for the two sites.

The exact time dependence of the elements of **X** is very complicated. The functions $\epsilon^{(1)}$ and $\epsilon^{(2)}$ are differences of products of three terms, each term having a different behavior. In each product, the first term oscillates at the frequency δ, the second term oscillates at the same frequency but with an extra time-dependent phase β, and the last term is the exponent, for which elliptic integrals have to be evaluated. In the adiabatic approximation one would normally set δ equal to zero in each of these terms, because it is small compared with $r(i,t)$ [see Eq. (13)]. This would leave basically only one time-independent frequency (in the third term). In fact, exactly the same simplification can be obtained without invoking the adiabatic approximation at this point, by considering the special effect which is studied here. For Berry's phase one is interested in complete cycles of evolution of the quantum system, or of the Hamiltonian. It is therefore required that the signal be measured not at any arbitrary instant t, but at regular intervals,

$$t = nT = n\frac{2\pi}{\delta} \quad (n = 1,2,3,\ldots) . \tag{42}$$

It is easy to show that T, the period of adiabatic evolution, is also the period of most quantities in the matrix **X**,

$$\beta(i, t+T) = \beta(i,t) , \tag{43a}$$

$$r(i, t+T) = r(i,t) , \tag{43b}$$

$$\cos[\delta(t+T) - \beta(i, t+T)] = \cos[\delta t - \beta(i,t)] , \tag{43c}$$

$$\sin[\delta(t+T) - \beta(i, t+T)] = \sin[\delta t - \beta(i,t)] . \tag{43d}$$

As for the geometrical phase, in each cycle it accumulates the same additional value

$$\gamma_1^{(i)}(t) - \gamma_2^{(i)}(t) = \gamma_1^{(i)}(nT) - \gamma_2^{(i)}(nT)$$

$$= n[\gamma_1^{(i)}(T) - \gamma_2^{(i)}(T)]$$

$$= \frac{t}{T}[\gamma_1^{(i)}(T) - \gamma_2^{(i)}(T)] , \tag{44}$$

so that the quantity appearing in the matrix is simply a constant,

$$\gamma'^{(i)} = \frac{1}{T}[\gamma_1^{(i)}(T) - \gamma_2^{(i)}(T)] = -\delta\{1 - \cos[\theta(i,t)]\} . \tag{45}$$

In this equation we have used the well-known value of Berry's phase for the case of motion in a conical circuit in parameter space.[1,21] Considering now only times $t = nT$, n being any positive integer, and using the equalities in Eq. (43), the time dependence of X becomes very simple,

$$\beta(i,nT) = \arg\left[\frac{D(i)}{2} - \frac{\omega_1}{2}\right] = \begin{cases} 0 & [\text{if } D(i) > \omega_1] \\ \pi & [\text{if } D(i) < \omega_1] \end{cases}, \quad (46a)$$

$$\cos[\delta nT - \beta(i,nT)] = \cos[\beta(i,nT)]$$
$$= \begin{cases} 1 & [\text{if } D(i) > \omega_1] \\ -1 & [\text{if } D(i) < \omega_1] \end{cases}, \quad (46b)$$

$$\sin[\delta nT - \beta(i,nT)] = 0 , \quad (46c)$$

$$\epsilon^{(i)}(t) = -i\frac{\omega_1\delta\cos[\beta(i,nT)]}{4r(i,nT)}\exp[2inT\,r(i,nT)]$$
$$\equiv -i\alpha(i)\exp[i\omega(i)t] . \quad (46d)$$

Substituting these expressions in the set of equations

The matrix χ is defined as

$$\begin{bmatrix} 0 & -\alpha\exp(-i\omega t) & \alpha\exp(i\omega t) & 0 \\ \alpha\exp(i\omega t) & -\gamma' & 0 & \alpha\exp(i\omega t) \\ -\alpha\exp(-i\omega t) & 0 & \gamma' & -\alpha\exp(-i\omega t) \\ 0 & -\alpha\exp(-i\omega t) & \alpha\exp(i\omega t) & 0 \end{bmatrix} , \quad (48)$$

while the vector f is

$$f = \begin{bmatrix} a_{11}(t) \\ a_{12}(t) \\ a_{21}(t) \\ a_{22}(t) \end{bmatrix} . \quad (49)$$

Equation (47) has been deliberately presented here in a form similar to Schrödinger's equation in Shirley's[36] or Maricq's work.[35] The reason is that Floquet analysis, on which their formalisms were based, is also natural to use here, and it is convenient to use the same notation. One has to keep in mind that the Liouville-space vector $f(t)$ is not a wave function, and the Liouville-space matrix $\chi(t)$, playing in this equation a role analogous to that of the Hamiltonian, is not Hermitian.[41] Nevertheless, Floquet's theorem[43] can still be used, since it does not require hermiticity of the matrix (see, e.g., Ref. 30).

Using ordinary Floquet theory as in Shirley's paper[36] one obtains in the present case an infinite-dimensional matrix with eleven nonzero diagonals, which is not simpler to treat than the original problem of Eq. (47). On the other hand, the time dependence can be averaged over with average Hamiltonian theory (AHT),[44,40] because ω, the oscillation frequency, is of the same order of magnitude as ω_1, and thus (in the adiabatic case) much

(34), the coefficients are either constant in time, or oscillating at one of three frequencies. In the upper-diagonal block the frequency is $\omega^{(1)}$, in the lower-diagonal block $\omega^{(2)}$ and in the off-diagonal blocks the difference of these two frequencies. Even so this set of differential equations is too difficult for a direct solution, so the work will proceed in two stages. In the first stage the time-dependent problem will be solved for a single site, using a Floquet-type method to obtain higher-order corrections to the usual adiabatic approximation. In the second stage an approximation will be used for the domain of slow jump rates, in order to get an explicit analytical result for the case of stochastic jumps.

B. One-site problem

Substituting Eqs. (46) in Eq. (34) for the case of a single site, and multiplying by i, the equation of motion for the density matrix elements becomes

$$i\frac{d}{dt}f(t) = \chi(t)f(t) , \quad (47)$$

larger than δ, which determines the intervals between detection points. However, the AHT approach will not only average out many details of the time dependence, it will also require $t = m2\pi/\omega$, where m is an integer, whereas the observation of Berry's phase requires $t = nT$. These two conditions may not be compatible, and when we go back to the original two-site problem, in which there are two different values for ω, we shall have three simultaneous requirements, which will in general be incompatible. It is therefore necessary to choose an intermediate approach, keeping some of the time dependence in χ and eliminating the need of having a special relationship between ω and δ. Maricq's generalization of AHT, based on Floquet theory, is indeed appropriate for this purpose.[35] The original derivation was done for a Hermitian χ, but this is not essential for the method.

In Maricq's formalism, Eq. (47) is solved by

$$f(t) = P(t)\exp(-i\hat{H}t)f(0) , \quad (50)$$

where $f(0)$ is the initial condition, and

$$P(t) = \sum_n P_n(t), \quad \hat{H} = \sum_n \hat{H}_n , \quad (51)$$

in which $P_n(t + 2\pi/\omega) = P_n(t)$. The first terms in these series are $P_0(t) = 1$ and $\hat{H}_0 = 0$. The general terms for $n > 0$ are defined as

$$P_n(t) = -i \int_0^t \left[\chi(t')P_{n-1}(t') - \sum_{k=1}^{n-1} P_k(t')\hat{H}_{n-k} - \hat{H}_n \right] dt' \ , \quad (52a)$$

$$\hat{H}_n = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \left[\chi(t')P_{n-1}(t') - \sum_{k=1}^{n-1} P_k(t')\hat{H}_{n-k} \right] dt' \ . \quad (52b)$$

It was shown by Maricq that for any $n > 0$, $\hat{H}_n = \overline{H}_{n-1}$, where $\overline{H}_{n-1}$ is the $(n-1)$ term in the Magnus expansion used by ordinary AHT. A convenient form for $P_n(t)$ and $\hat{H}_n$ may be obtained by expanding $P_n(t)$ and the original

"Hamiltonian" (in our case the Liouville-space matrix χ) in a Fourier series,

$$\chi(t) = \sum_\mu \chi_\mu e^{i\mu\omega t}, \quad P_n(t) = \sum_\mu P_{n,\mu} e^{i\mu\omega t} \ , \quad (53)$$

from which one gets the expressions

$$\hat{H}_n = \sum_\nu \chi_{-\nu} P_{n-1,\nu} - \sum_{k=1}^{n-1} P_{k,0}\hat{H}_{n-k} \ , \quad (54a)$$

$$P_n(t) = \sum_{\mu \neq -\nu} \chi_\mu P_{n-1,\nu} \frac{1-\exp[i(\mu+\nu)\omega t]}{(\mu+\nu)\omega}$$
$$- \sum_{k=1}^{n-1} \sum_{\nu \neq 0} P_{k,\nu}\hat{H}_{n-k} \frac{1-\exp(i\nu\omega t)}{\nu\omega} \quad (54b)$$

The first few terms are then given by

$$\hat{H}_1 = \chi_0 \ , \quad (55a)$$

$$P_1(t) = \sum_{\mu \neq 0} \chi_\mu \frac{1-\exp(i\mu\omega t)}{\mu\omega} \ , \quad (55b)$$

$$\hat{H}_2 = \sum_{\mu=1}^\infty \frac{1}{\mu\omega}([\chi_\mu,\chi_{-\mu}] + [\chi_0,\chi_\mu] - [\chi_0,\chi_{-\mu}]) \ , \quad (55c)$$

$$P_2(t) = \sum_{\mu=1}^\infty \frac{-1}{(\mu\omega)^2}[\chi_\mu\chi_{-\mu}(1-e^{i\mu\omega t}) + \chi_{-\mu}\chi_\mu(1-e^{-i\mu\omega t})]$$
$$+ \sum_{\mu \neq 0}\sum_{\nu \neq 0} \chi_\mu\chi_\nu(1-\delta_{\nu,-\mu})\frac{1}{\nu\omega}\left[\frac{1-\exp(i\mu\omega t)}{\mu\omega} - \frac{1-\exp[i(\mu+\nu)\omega t]}{(\mu+\nu)\omega}\right] \ , \quad (55d)$$

$$\hat{H}_3 = \sum_{\nu \neq 0} \chi_{-\nu}\left[\frac{\chi_\nu\chi_{-\nu}}{(\nu\omega)^2} + \sum_{\nu' \neq 0}(1-\delta_{\nu',\nu})\frac{\chi_{\nu'}\chi_{\nu-\nu'}}{(\nu\omega)(\nu'\omega)} - \sum_{\nu' \neq 0}(1-\delta_{\nu',-\nu})\frac{\chi_\nu\chi_{\nu'}}{(\nu\omega)(\nu'\omega)}\right]$$
$$- \sum_{\mu \neq 0}\frac{\chi_\mu}{\mu\omega}\sum_{\nu=1}^\infty \frac{1}{\nu\omega}([\chi_\nu,\chi_{-\nu}] + [\chi_0,\chi_\nu] - [\chi_0,\chi_{-\nu}]) \ . \quad (55e)$$

Using these formulas one can calculate the matrices for the present case. The results are given in the Appendix. In these matrices the quantities α and γ' are of the same order of magnitude as δ, while ω is similar in magnitude to the irradiation strength ω_1. It is therefore clear that in Eq. (51) the two series converge rapidly in the adiabatic regime. It will be shown below that by taking just two terms in each expansion we reproduce Berry's version of the adiabatic approximation plus a small correction. By taking into account a sufficient number of terms in the expansions, it is possible to get higher order adiabatic corrections.

Assuming an adiabatic situation, the series expansion for the average Liouville space "Hamiltonian" will be approximated by

$$\hat{\mathbf{H}} \approx \hat{H}_1 + \hat{H}_2 \equiv A \quad (56)$$

where the matrix A is defined by

$$A = \begin{bmatrix} 0 & b & -b & 0 \\ -b & -a & 0 & -b \\ b & 0 & a & b \\ 0 & b & -b & 0 \end{bmatrix} \ , \quad (57)$$

with $a = \gamma' + 2\alpha^2/\omega, b = \gamma'\alpha/\omega$ $(a \gg b)$. The series for $\mathbf{P}(t)$ will be truncated as

$$\mathbf{P}(t) \approx P_0(t) + P_1(t) = \begin{bmatrix} 1 & p^* & p & 0 \\ p & 1 & 0 & p \\ p^* & 0 & 1 & p^* \\ 0 & p^* & p & 1 \end{bmatrix} \ , \quad (58)$$

with $p = (\alpha/\omega)(1-e^{i\omega t})$.

For the computation of the exponent $\exp(-i\hat{H}t)$ in Eq. (50) it is desirable to transform $\hat{\mathbf{H}}$, or rather its approximation A, to a canonical form,

$$T^{-1}AT = \Lambda \tag{59}$$

so that the exponent will be computed as

$$\exp(-i\hat{H}t) \approx \exp(-iAt) = T\exp(-i\Lambda t)T^{-1} . \tag{60}$$

Like the original Liouville space "Hamiltonian" χ [Eq. (48)], the matrix A is not only nonhermitian, it is also not a "normal matrix," i.e., it does not commute with its Hermitian adjoint,[45] $AA^{\dagger} - A^{\dagger}A \neq 0$. As a consequence of this, the matrix A is diagonalized by a nonunitary transformation, and its (right) eigenvectors do not in themselves form a complete orthogonal set. In fact, its right and left eigenvectors are a biorthogonal set, for which certain symmetries may be relevant.[41] Carrying out the diagonalization procedure for A, the eigenvalues are found to be

$$\lambda_1 = \lambda_2 = 0, \quad \lambda_3 = -\lambda_4 = a(1-4c^2)^{1/2} \equiv ar , \tag{61}$$

with $c \equiv b/a$, and the corresponding eigenvectors are the columns of the matrix T,

$$T = \begin{vmatrix} \dfrac{1}{\sqrt{2}} & -d & c & c \\ 0 & 2cd & g_+ & g_- \\ 0 & 2cd & g_- & g_+ \\ \dfrac{1}{\sqrt{2}} & -d & c & c \end{vmatrix} , \tag{62}$$

with $d = [2(1+4c^2)]^{-1/2}$ and $g_{\pm} = -2c^2/(1\pm r)$. Using Eq. (60) the exponent is approximately given by (see Appendix)

$$\exp(-i\hat{H}t) \approx \exp(-iAt)$$

$$\approx \begin{vmatrix} 1-\phi_2 & c-\phi_1 & -\phi_1^* & -\phi_2 \\ \phi_1 & \phi_0^* & \phi_2-2c^2 & \phi_1 \\ \phi_1^* & \phi_2-2c^2 & \phi_0 & \phi_1^* \\ -\phi_2 & -c-\phi_1 & -\phi_1^* & 1-\phi_2 \end{vmatrix} , \tag{63}$$

using the definitions

$$\phi_0 = e^{-i\lambda_3 t} - 2c^2 \approx e^{-i\gamma't} , \tag{64a}$$

$$\phi_1 = c(e^{i\lambda_3 t} - 1) \approx \frac{\alpha}{\omega}(e^{i\gamma't}-1) , \tag{64b}$$

$$\phi_2 = c^2 2\cos(\lambda_3 t) \approx \left[\frac{\alpha}{\omega}\right]^2 (e^{i\gamma't}+e^{-i\gamma't}) . \tag{64c}$$

Combining this result with Eq. (58) the approximate solution for Eq. (47) is calculated with

$$\mathbf{F}(t) \equiv \mathbf{P}(t)\exp(-i\hat{H}t)$$

$$\approx \begin{vmatrix} 1+F_{14} & F_{12} & F_{12}^*-c & F_{14} \\ F_{21} & F_{22} & F_{23} & F_{21} \\ F_{21}^* & F_{23}^* & F_{22}^* & F_{21}^* \\ F_{14} & F_{12}-2c & F_{12}^*-c & 1+F_{14} \end{vmatrix} , \tag{65}$$

where the matrix elements F_{ij} are

$$F_{14} = 2q^2\{\cos(\omega t)-1-\cos[(\omega-\gamma')t]\} ,$$

$$F_{12} = q(2-e^{-i(\omega-\gamma')t}) ,$$

$$F_{21} = q(e^{i\gamma't}-e^{i\omega t}) , \tag{66}$$

$$F_{22} = (1-2q^2)e^{i\gamma't}+2q^2(e^{i(\omega+\gamma')t}-e^{i\omega t}) ,$$

$$F_{23} = 2iq^2\sin(\gamma't)+2q^2(e^{i(\omega-\gamma')t}-e^{i\omega t}) ,$$

with $q \equiv \alpha/\omega \ll 1$.

Taking a very common initial condition for such an experiment, $\rho(0) = S_z$, the solution for the density matrix is

$$\mathbf{f}(t) = \begin{vmatrix} -C+Sq\{3-2\cos[(\omega-\gamma')t]\} \\ S\{e^{i\gamma't}+2q^2[2e^{i\omega t}\cos(\gamma't)-\cos(\gamma't)-2e^{i\omega t}]\} \\ S\{e^{-i\gamma't}+2q^2[2e^{-i\omega t}\cos(\gamma't)-\cos(\gamma't)-2e^{-i\omega t}]\} \\ C+Sq\{1-2\cos[(\omega-\gamma')t]\} \end{vmatrix} , \tag{67}$$

with $C \equiv \frac{1}{2}\cos[\theta(0)]$ and $S \equiv \frac{1}{2}\sin[\theta(0)]$. Measuring S_x, for example, the observed magnetization is

$$\mathrm{Tr}(S_x\rho) = [a_{11}(t)-a_{22}(t)]\tfrac{1}{2}\sin(\theta)\cos(\beta)$$

$$- [a_{12}(t)+a_{21}(t)]\tfrac{1}{2}\cos(\theta)\sin(\beta)$$

$$+ [a_{21}(t)-a_{12}(t)]\frac{i}{2}\cos(\beta) , \tag{68}$$

with a similar result for S_y. The leading term in the amplitude of the signal has Berry's phase shift, and the other terms are, in the adiabatic case, relatively small corrections to the main term. In fact, by including in Eq. (51) also higher-order terms in each expansion, one may generate in a systematic manner higher-order corrections to the adiabatic approximation. The use of Maricq's formalism for the time-dependent single-site problem thus provides us not only with a way to calculate the geometrical phases analogous to Berry's phase, but also with a method for deriving corrections to this version of the adiabatic approximation.

C. Two-site problem

It is now possible to return to the original two-site problem. In the general case, having the solution of the one-site problem does not make the situation simpler, but if the rate of stochastic jumps is sufficiently slow, i.e., $1/\tau \ll \|\chi(t)\|$, an approximation can be made. Equation (34) separates into the two equations

$$\frac{d}{dt}\mathbf{a}^{(1)}(t) = \left[-i\chi^{(1)}(t) - \frac{1}{\tau}\mathbf{1}\right]\mathbf{a}^{(1)}(t) + \mathbf{b}^{(1)} , \qquad (69a)$$

$$\frac{d}{dt}\mathbf{a}^{(2)}(t) = \left[-i\chi^{(2)}(t) - \frac{1}{\tau}\mathbf{1}\right]\mathbf{a}^{(2)}(t) + \mathbf{b}^{(2)} , \qquad (69b)$$

where 1 is the unit matrix. The equations are immediately solved by

$$\mathbf{a}^{(1)}(t) = e^{-t/\tau}\mathbf{f}^{(1)}(t) + \mathbf{F}^{(1)}(t)\int_0^t [\mathbf{F}^{(1)}(t')]^{-1}\mathbf{b}^{(1)}(t')dt' ,$$

$$(70a)$$

$$\mathbf{a}^{(2)}(t) = e^{-t/\tau}\mathbf{f}^{(2)}(t) + \mathbf{F}^{(2)}(t)\int_0^t [\mathbf{F}^{(2)}(t')]^{-1}\mathbf{b}^{(2)}(t')dt' ,$$

$$(70b)$$

where $\mathbf{f}^{(1)}(t)$ and $\mathbf{f}^{(2)}(t)$ solve Eqs. (69) when there is no stochastic process (formally, when $1/\tau=0$). Calculating the matrices $G^{(i)} \equiv [\mathbf{F}^{(i)}(t')]^{-1}$ one finds (see Appendix) the lowest order elements, in terms of powers of α/ω, to be the diagonal elements. The first and fourth elements are unimportant, because they multiply in Eq. (70) the first and fourth elements of $\mathbf{b}$, which are equal to zero. The relevant elements are $G_{22}^{(i)} \approx e^{-i\gamma't}$ and $G_{33}^{(i)} \approx e^{i\gamma't}$. These elements multiply in Eq. (70) the second and third elements of $\mathbf{b}$, respectively, which oscillate with high frequencies. Therefore the integrals in Eq. (70) are relatively small corrections to the first term on the right-hand side of this equation. As a result of this, the main influence of the stochastic process is, as usual, just to multiply the nontrivial part of the density matrix (the part which is not proportional to the unit operator) by decaying exponents. Fourier transforming to the frequency domain, one gets a characteristic broadening of the signal (the small frequency shift due to the jumps is neglected in this approximation). The calculation of the geometrical phases is not affected, in this approximation.

The condition for observing a geometrical phase in the slow jump rate domain is to have a significant frequency shift because of the geometrical phase, without a comparable broadening by the jump mechanism. As noted above, the geometrical phases are associated with frequency shifts that are roughly equal to γ', so their magnitude is similar to δ. These shifts occur relative to the transition frequency of $2r(i,t)$ [see Eqs. (38) and (39)], which is similar in magnitude to ω_1. Since in the adiabatic case δ/ω_1 is small, the shifts are correspondingly small. On the other hand, this ratio should not be very small, because then the whole effect will be too small to observe.[21] The shift will not be noticed if the broadening exceeds γ' by a sufficient amount, so the condition for observing the shift is

$$\frac{1}{\tau} \ll \gamma' \sim \delta . \qquad (71)$$

This means that in the present context there are three, not two, relevant dynamic regimes. For $1/\tau > \omega_1$ the dissipative mechanism is too fast to allow any adiabatic evolution. For $\omega_1 > 1/\tau > \delta$ the adiabatic approximation may be useful, although it is not very accurate. In this case the jump process is not fast enough to cause significant line broadening that will change the basic structure of the spectrum. It is fast enough, however, to broaden the lines to such a degree as to hide the frequency shifts originating from the geometrical phases. Only when $1/\tau \ll \delta$ or at least $1/\tau < \delta$ the adiabatic approximation is sufficiently good, so that also Berry's phase can be observed.

The situation described here, in which motions that are too slow to influence the general line shape may still be fast enough to modify the effect of the geometrical phases in the spectrum, can be used for studying very slow motions. The slow time scale, determined by δ—the rate of change of the Hamiltonian—makes Berry's effect more sensitive to such motions than the general structure of the spectrum. To study such slow diffusion processes one may do a "forced precession" experiment, measuring the magnetization during the irradiation of the system. The chief requirements are detecting at a frequency which may be different from the irradiation frequency, and measuring stroboscopically at $t = nT$, $n = 1,2,3,\ldots$. The experiment has to be repeated for several values of δ, including $\delta=0$, to check the linear relationship which should exist between the frequency shift and δ. The frequency domain spectrum is concentrated in a very narrow region, of width δ, with high-frequency resolution. Very slow motion will somewhat broaden the line, as predicted by Eqs. (69) and (70). When the rate of motion is comparable to δ one may have to include higher order terms in the solution of Eq. (34), because then also the higher-order frequency shift caused by the motion becomes important.

Alternatively, it is possible to irradiate with a strong pulse, and then detect the free-induction decay. In this case the measured signal oscillates at its ordinary unshifted frequency, and the only mark left by the geometrical phase is a constant phase factor in the amplitude of the signal. One therefore needs to measure the ratio $\langle S_y \rangle / \langle S_x \rangle$ at a particular moment, preferably immediately after the pulse, or after an additional echo pulse, to avoid dead-time problems. This ratio should depend on the value of δ. A measurement of this kind would require very accurate phasing in the detector, and the relation between the measured quantity and the frequency δ would not be as simple as in the previous type of experiment. An additional difficulty here would involve the length of the pulse. The duration of the pulse should be $t_p = nT \geq T = 2\pi/\delta$ so that at least one cycle of adiabatic evolution will be completed. The pulse would then have a very large tipping angle,

$$\omega_1 t_p \geq 2\pi\frac{\omega_1}{\delta} \gg 2\pi , \qquad (72)$$

in addition to being strong, to achieve a significant rota-

tion of the magnetization.

Finally, it is necessary to compare the effects described above for the two spectral lines, related to $I_z = \frac{1}{2}$ and $I_z = -\frac{1}{2}$ manifolds. It is obvious from the definition of $r(i,t)$ above that if the hyperfine coupling is relatively large, an appropriate choice of off-resonance value Δ would result in very different transition frequencies for the $I_z = \frac{1}{2}$ and $I_z = -\frac{1}{2}$ subspaces. It should be noted that from the definition of $\cos[\theta(i,t)]$ [Eq. (27)] and the formula for γ' [Eq. (45)], an appropriate choice of Δ could also make one of the phase shifts $\gamma(i)'$ much larger than the other. Then the geometrical phases would selectively shift mainly one of the two spectral lines, leaving the other one almost unaffected. If the smaller shift is not too small to be unobservable in practice, the difference in size between the two frequency shifts would make a further distinction between time scales in the very slow diffusion regime. Also here, if the motion is not very slow, one may need to consider higher order terms in the solution of the relevant equations in order to include the motional frequency shift in the calculation.

IV. ELECTRON-NUCLEUS SYSTEM WITH AN ANGLE DEPENDENT HAMILTONIAN

A. Isotropic rotational diffusion of an electron-nucleus system

As in the previous example the system to be considered consists of an electron with spin $S = \frac{1}{2}$ and a nucleus with spin $I = \frac{1}{2}$, but this time with a different, perhaps more realistic model for the Hamiltonian and for the stochastic process. In principle it is possible to treat a general case, with a g tensor that has no axial symmetry and with hyperfine coupling in which the pseudosecular terms are not negligible. However, such generality will complicate the calculations without changing the basic result, so that the physics of the problem will be obscured. We therefore restrict the discussion to the case of an axially symmetric g tensor and include only the secular term of the hyperfine coupling. Using the reference frame which rotates at ω_{det} around the static magnetic field, the Hamiltonian is assumed to be[30]

$$H = -\omega_I I_z - \gamma_e \mathbf{B} \cdot \mathbf{S} + D(\Omega) I_z S_z , \tag{73}$$

The effective magnetic field $\mathbf{B}$ is equal to

$$\mathbf{B} = \frac{1}{\gamma_e} \{ [\Delta + g(\Omega)]\hat{z} + \omega_1[\cos(\delta t)\hat{x} - \sin(\delta t)\hat{y}] \} . \tag{74}$$

In this expression $\Delta = \omega_0 - \omega_{det}$ includes the isotropic part of the g tensor, while the axially symmetric g tensor is defined as

$$g(\Omega) = gD_{00}^2(\Omega) = g\frac{1}{2}(3\cos^2\beta - 1) . \tag{75}$$

The Euler angles $\Omega = (\alpha,\beta,\gamma)$ specify the molecular orientation with respect to the direction of the static magnetic field. The oscillation frequency δ is again $\omega_m - \omega_{det}$, and the orientation-dependent hyperfine coupling is

$$D(\Omega) = DD_{00}^2(\Omega) , \tag{76}$$

where D is a constant. The stochastic process is assumed to be isotropic rotational diffusion, for which the relaxation operator is

$$\Gamma = R \nabla_\Omega^2 , \tag{77}$$

where the constant R characterizes the rate of the motion. The eigenfunctions of this operator are Wigner's functions $D_{KM}^L(\Omega)$, with eigenvalues $RL(L+1)$. The equation of motion of the density matrix is now[30]

$$\frac{\partial}{\partial t}\rho(\Omega,t) = i[\rho(\Omega,t),H(\Omega,t)] - \Gamma_\Omega[\rho(\Omega,t) - \rho_0(\Omega,t)] . \tag{78}$$

In order to solve this equation it is convenient, on the one hand, to expand the density matrix in terms of the eigenfunctions of the stochastic super operator, to be denoted for simplicity as $f_m(\Omega)$, where the index m stands for the set of indices (L,K,M). The corresponding eigenvalues will be denoted as r_m. On the other hand, in order to follow the adiabatic behavior of the system, one has to use an adiabatic basis in spin space.

The Hamiltonian has the following matrix in the $|S_z I_z\rangle$ basis:

$$\begin{bmatrix} -\dfrac{\omega_I}{2} - \dfrac{\omega_z}{2} + \dfrac{D(\Omega)}{4} & -b & 0 & 0 \\[2mm] -b^* & -\dfrac{\omega_I}{2} + \dfrac{\omega_z}{2} - \dfrac{D(\Omega)}{4} & 0 & 0 \\[2mm] 0 & 0 & \dfrac{\omega_I}{2} - \dfrac{\omega_z}{2} - \dfrac{D(\Omega)}{4} & -b \\[2mm] 0 & 0 & -b^* & \dfrac{\omega_I}{2} + \dfrac{\omega_z}{2} + \dfrac{D(\Omega)}{4} \end{bmatrix} , \tag{79}$$

with b as in Eq. (24) and $\omega_z/2 \equiv \Delta + g(\Omega)/2$. Since both the Hamiltonian and the diffusion process do not couple the subspaces of $I_z = \frac{1}{2}$ and $I_z = -\frac{1}{2}$, it is again possible to do the calculation just for one of the subspaces. The eigenvalues of $H(t)$ are

$$\lambda_{1,2} = -\frac{\omega_I}{2} \pm r_-, \quad \lambda_{3,4} = \frac{\omega_I}{2} \pm r_+ , \tag{80}$$

where

$$2r_\pm = \{[\Delta + g(\Omega) \pm D(\Omega)/2]^2 + \omega_1^2\}^{1/2} . \tag{81}$$

Using the definitions

$$2r_\pm \cos(\theta_\pm) = \Delta + g(\Omega) \pm \frac{D(\Omega)}{2} , \tag{82a}$$

$$2r_\pm \sin(\theta_\pm) = \omega_1 , \tag{82b}$$

the corresponding eigenvectors are the columns of the following matrix:

$$\begin{bmatrix} u_- w & u_+ w & 0 & 0 \\ -u_+ w^* & u_- w^* & 0 & 0 \\ 0 & 0 & v_- w & v_+ w \\ 0 & 0 & -v_+ w^* & v_- w^* \end{bmatrix} , \tag{83}$$

with the definitions $u_\pm = \sqrt{[1 \pm \cos(\theta_-)]/2}$, $v_\pm = \sqrt{[1 \pm \cos(\theta_+)]/2}$, and $w = e^{i\delta t/2}$. In the present example, only the eigenfunctions of H are time dependent, while the energies are constant.

It is now possible to transform to the adiabatic basis the components of the angular momentum vector **S**, and using the same arguments as in the previous example, all matrix elements of the density matrix are found to be relevant in the sense of Eq. (18).

Since the adiabatic states are angle dependent as well as time dependent, they can be expanded in terms of Wigner's functions, the "coefficients" being time-dependent vectors in spin space. We shall use here the notation **v** for a column vector, and $\mathbf{v}^\dagger$ for the corresponding complex conjugate row vector. Therefore in the expression for ρ in Eq. (7) the following relation holds:

$$|k(t)\rangle\langle l(t)| = \sum_{m,n} \mathbf{v}_m^{(k)}(t)\mathbf{v}_n^{(l)\dagger}(t)f_m(\Omega)f_n^*(\Omega) . \tag{84}$$

This relation makes it possible to calculate the relaxation term in Eq. (78), and this calculation will now be outlined. The eigenvectors of H found above are either of the form

$$|k(t)\rangle = \begin{bmatrix} wu_1(\Omega) \\ w^* u_2(\Omega) \\ 0 \\ 0 \end{bmatrix} \tag{85}$$

or of the form

$$|k(t)\rangle = \begin{bmatrix} 0 \\ 0 \\ wv_1(\Omega) \\ w^* v_2(\Omega) \end{bmatrix} . \tag{86}$$

The angle-dependent functions are those that were defined following Eq. (83); in all of them, the angle dependence is contained in expressions of the type $[aD_{00}^0(\Omega) + bD_{00}^2(\Omega)]^{1/2}$. When such an expression is expanded in the functions $D_{KM}^L(\Omega)$, the coefficients are obtained by multiplying each expression by $D_{KM}^{L*}(\Omega)$ and integrating over $d\Omega$. Nonzero coefficients can be obtained only for $K = M = 0$, so that the relevant functions are just $d_{00}^L(\beta)$, which are Legendre polynomials in $\cos(\beta)$. Taking into account the parity of the integrand, it is clear that only even values of L will have nonzero coefficients, their magnitude is found to decrease for large L roughly as $1/L$. It is thus possible in practice to truncate the infinite summation over even values of L at some high value of L. Operating with Γ_Ω on the density matrix, one has to operate on products of two functions [see Eq. (84)]. Each such product can be expressed in terms of the eigenfunctions of $\Gamma_\Omega, f_m(\Omega)$ by means of standard formulas.[46] In the present simple case the $f_m(\Omega)$ are just the normalized $d_{00}^J(\beta)$, for which one has

$$d_{00}^{J'}(\beta)d_{00}^{J''}(\beta) = \sum_J (2J+1) \begin{bmatrix} J' & J'' & J \\ 0 & 0 & 0 \end{bmatrix}^2 d_{00}^J(\beta) . \tag{87}$$

Substituting in Eq. (17) the results obtained here, the equations of motion for $a_{kl}(t)$, contain in the relaxation part a double summation over even L values. In this summation, an element of Γ has the form

$$\Gamma_{pq,rs} = \mathrm{Tr}(|q(t)\rangle\langle p(t)|\Gamma|r(t)\rangle\langle s(t)|) . \tag{88}$$

The resulting element of the relaxation superoperator is a sum over functions of Ω. Premultiplying the equations of motion by $D_{00}^{0*}(\Omega)$ and integrating them over $d\Omega$ one obtains equations which do not contain any angle dependence.

In order to carry out the procedure described above, one needs to find the coefficients of Wigner's functions in the eigenstates of $H(t)$, in principle for all even values of L, and in practice for some finite number of them. In a similar problem, involving equations for all even L values which are coupled among them, it was also found that truncation for some value of L is possible.[30] In that case four L values were found to be sufficient for $\|H\|/R \leq 10$ and seven L values to be sufficient for $\|H\|/R \approx 100$. This gives only a rough estimate for the present case, because here an expansion over L values is involved, rather than coupling of algebraic equations, and also the Hamiltonian considered here is not exactly the same as the one for which the quoted numbers were found. Nevertheless, it seems that also here the number of relevant L values should be of a similar order of magnitude.

The set of equations to be solved has the same general structure as in Eqs. (34) except that here the matrix **X** consists of a single 4×4 submatrix instead of two such submatrices. The complexity of the present case lies in

the calculations that are needed to get a reasonable approximation for the values of the matrix elements of $\mathbf{X}$, before applying the procedures of Sec. III to get an actual solution.

It is clear that the set of equations obtained here can only be solved numerically, and it is difficult to get analytical estimates for the geometrical phases and for the influence of the stochastic process on these phases. Nevertheless, comparing the structure of these equations to those contained in Eqs. (34) it seems that the geometrical phases should still have an observable effect, with the diffusion process resulting in an overall line broadening, as long as only the slow motion domain is examined. It therefore seems that the same types of experiments mentioned in Sec. III C would also be useful here. In particular, the "forced precession" experiment could be used as explained above both to study the influence of diffusion on Berry's phase, and to study very slow motions by their influence on that phase.

As shown in Sec. III, the interesting domain for the geometrical phases is that of slow diffusion, in which $R \leq \delta \ll \|H\|$. It was mentioned there that in practice it is inconvenient to use a very small δ, and in fact it was found in an actual case that $4\delta \approx \|H\|$ is sufficient to achieve an adiabatic situation in which Berry's phase is relevant.[21] It therefore seems that, within the slow diffusion domain, a large dynamic range may be covered by coupling just several L values. In the present case, however, the situation is complicated by inhomogeneous broadening, due to the presence of molecules at all orientations. This broadening is similar in magnitude to the irradiation strength ω_1, and in order to reduce it one has to irradiate only a specific spin packet by using a relatively weak ω_1. This would make $\sin(\theta)$ in Eq. (82) very small, and according to Eq. (45) Berry's frequency shift

would become much smaller than δ. The shift could then be observed only if the motion is very slow, satisfying the rough inequality

$$\frac{1}{\tau} < \delta \frac{\omega_1}{D} \ll D \ . \tag{89}$$

This restriction to slower motions would necessitate the use of more terms in the expansion over L values, in addition to the fact that the observation of the effect would require greater accuracy.

B. Possibility of degeneracy in the rigid limit

In Sec. IV A the effect of rotational motion on Berry's phase was examined. In the rigid limit, i.e., when the diffusion rate is zero, one may in principle investigate another interesting manifestation of Berry's phase. This is related to non-Abelian gauge fields, appearing when the Hamiltonian has an exact degeneracy that is not broken by the time-dependence.[11,14,37]

Suppose the angle-dependent Hamiltonian used above includes also a pseudosecular term in the hyperfine interaction,

$$H = -\omega_I I_z - \gamma_e \mathbf{B} \cdot \mathbf{S}$$

$$+ D(\Omega) I_z S_z + [D'(\Omega) I_+ + D'^*(\Omega) I_-] S_z \ , \tag{90}$$

where $\mathbf{B}$ is defined as in Eqs. (72) and (73), and $D(\Omega)$ is given by Eq. (74). The pseudosecular hyperfine constant is equal to[30]

$$D'(\Omega) = -\sqrt{3/8} D D_{01}^2(\Omega) \ . \tag{91}$$

In the $|S_z I_z\rangle$ basis the Hamiltonian is thus represented by

$$\begin{bmatrix} -\dfrac{\omega_I}{2} - \dfrac{\omega_z}{2} + \dfrac{D(\Omega)}{4} & -b & c & 0 \\[2mm] -b^* & -\dfrac{\omega_I}{2} + \dfrac{\omega_z}{2} - \dfrac{D(\Omega)}{4} & 0 & -c \\[2mm] c^* & 0 & \dfrac{\omega_I}{2} - \dfrac{\omega_z}{2} - \dfrac{D(\Omega)}{4} & -b \\[2mm] 0 & -c^* & -b^* & \dfrac{\omega_I}{2} + \dfrac{\omega_z}{2} + \dfrac{D(\Omega)}{4} \end{bmatrix} \ , \tag{92}$$

with $c = D'(\Omega)/2$.

In general this Hamiltonian has four different eigenvalues, and the subspaces of $I_z = \frac{1}{2}$ and $I_z = -\frac{1}{2}$ are coupled. Suppose now the sample is not a powder but a single crystal, with a specific orientation Ω with respect to the static magnetic field. If the orientation is chosen so that the polar angle is equal to the "magic angle," i.e., $\beta = \arccos(1/\sqrt{3})$ then $D_{00}^2(\Omega) = 0$. One may also choose conveniently $\omega_0 = \omega_{\text{det}}$ so that the Hamiltonian matrix becomes

$$\begin{bmatrix} -a & -b & c & 0 \\ -b^* & -a & 0 & -c \\ c^* & 0 & a & -b \\ 0 & -c^* & -b^* & a \end{bmatrix} \ , \tag{93}$$

with $a = \omega_I/2$.

This Hamiltonian has a degeneracy either when $c = 0$, which is simply the case treated in Sec. IV A, or when $a = 0$. In the first case the $I_z = \frac{1}{2}$ and $I_z = -\frac{1}{2}$ subspaces

are uncoupled, but in the second case all four spin states are coupled by H. To achieve $a = 0$ one has to irradiate the nuclei continuously at their resonance frequency, in addition to irradiating the electrons, and work in a rotating frame with respect to the nuclei. The element c then becomes time dependent, being multiplied by the factor $\exp(-i\omega_I t)$. The eigenvalues of H are then

$$\lambda_1 = \lambda_2 = \left[\left[\frac{\omega_1}{2}\right]^2 + \left|\frac{D'(\Omega)}{2}\right|^2\right]^{1/2},$$

$$\lambda_3 = \lambda_4 = -\lambda_1 . \tag{94}$$

In each of the two degenerate subspaces occurring here one may observe geometrical phases that are related to a non-Abelian gauge field.[11] This means that if the system is initially in one eigenstate of the Hamiltonian, it will evolve into a linear combination of all eigenstates with the same energy. The transformation involved can be calculated using the method of Ref. 11. This effect, which is more general than the ordinary effect of Berry's phase in a nondegenerate case, would be especially interesting to study, as it has not been observed experimentally so far. In practice, however, two obstacles should be overcome before such an experiment becomes feasible. First, with ordinary instrumentation the orientation of the single crystal with respect to the static magnetic field can be determined up to a precision of roughly 1°. Having such an error in the angle, the secular dipolar term and the g tensor will not vanish exactly, and the degeneracies will be split. Moreover, irradiating the nuclei effectively at their resonance frequency while the electrons are irradiated close to their resonance value, requires very high power in order to cover a significant part of the spectrum. Therefore one could investigate the general case of nonabelian gauge fields only after solving these practical problems.

V. SUMMARY

Berry's version of the adiabatic approximation was studied for interacting quantum systems which are described by a density matrix, evolving in a semiclassical manner according to the stochastic Liouville equation. Starting with a general equation, it was shown that in spite of the loss of coherence caused by the stochastic process, it is still possible to calculate and observe the geometrical phase shifts, provided one remains in the domain of slow motions. A distinction was made between motions which are slow relative to the rate of change of the Hamiltonian, for which Berry's phase is observable, and less slow motions, which are still slow compared with the transition frequencies of the Hamiltonian. In the latter case the line broadening resulting from the stochastic process is sufficiently large to mask the frequency shifts caused by the geometrical phases, although the line broadening is still too small to change significantly the structure of the spectrum.

The general discussion was followed by a detailed treatment of two electron-nucleus systems, studied by ESR experiments. First we considered a model of an electron and a nucleus with a simple interaction term, modulated by two-site jumps. The calculations were done at first for a single site, using Maricq's generalization of average Hamiltonian theory to calculate systematically higher-order corrections to the adiabatic approximation. Then an approximate result was obtained for the two-site problem, demonstrating the general conclusions mentioned above. The basic requirements for a possible ESR experiment, testing these predictions, were also discussed. The second example was of an electron and a nucleus with a secular hyperfine interaction, modulated by isotropic rotational diffusion. The equations were set up, showing the same basic features as in the first example. A complete analysis was not done, due to the complexity of the equations, which requires a numerical solution, but the possibility of doing relevant experiments was briefly discussed. Also the conditions for observing geometrical phases in a degenerate subspace of an ESR system were considered.

In conclusion, from the theoretical calculations done here it seems that an ESR experiment may be done to examine the influence of a stochastic process on Berry's phase. Such an experiment may also be useful for studying very slow motions, since it should have high resolution in the frequency domain.

ACKNOWLEDGMENTS

APPENDIX

In this appendix the explicit formulas will be given for several matrices that were used in the Floquet analysis of the single-site problem discussed in Sec. III. Using Eqs. (55), the following matrices are obtained:

$$\hat{H}_1 = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & -\gamma' & 0 & 0 \\ 0 & 0 & \gamma' & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}, \tag{A1}$$

$$P_1(t) = \frac{\alpha}{\omega} \begin{bmatrix} 0 & 1-e^{-i\omega t} & 1-e^{i\omega t} & 0 \\ 1-e^{i\omega t} & 0 & 0 & 1-e^{i\omega t} \\ 1-e^{-i\omega t} & 0 & 0 & 1-e^{-i\omega t} \\ 0 & 1-e^{-i\omega t} & 1-e^{i\omega t} & 0 \end{bmatrix}, \tag{A2}$$

$$\hat{H}_2 = \frac{\alpha}{\omega} \begin{bmatrix} 0 & \gamma' & -\gamma' & 0 \\ -\gamma' & -2\alpha & 0 & -\gamma' \\ \gamma' & 0 & 2\alpha & \gamma' \\ 0 & \gamma' & -\gamma' & 0 \end{bmatrix}, \tag{A3}$$

$$P_2(t) = \left[\frac{\alpha}{\omega}\right]^2 \begin{bmatrix} p_0 & 0 & 0 & p_0 \\ 0 & -2p_1 & 2p_1 - p_2 & 0 \\ 0 & 2p_1^* - p_2^* & -2p_1^* & 0 \\ p_0 & 0 & 0 & p_0 \end{bmatrix}, \tag{A4}$$

$$\hat{H}_3 = \left[\frac{\alpha}{\omega}\right]^2 \begin{bmatrix} 0 & 2\alpha & -2\alpha & 0 \\ -2\alpha & -2\gamma' & 2\gamma' & -2\alpha \\ 2\alpha & -2\gamma' & 2\gamma' & 2\alpha \\ 0 & 2\alpha & -2\alpha & 0 \end{bmatrix} . \qquad (A5)$$

In Eq. (A4), $p_0 \equiv 2\cos(\omega t) - 2$, $p_1 \equiv (1 - e^{i\omega t})$, and $p_2 \equiv 1 - e^{2i\omega t}$.

It is clear that if the change in the actual spin Hamiltonian is slow relative to the frequencies typical to this Hamiltonian, both expansions converge quickly. For the average Liouville space "Hamiltonian" related to χ the matrices (A1) and (A3) combine to give the lowest-order nontrivial approximation, which is the matrix A [see Eq. (56)]. Diagonalizing A, the eigenvectors are the columns of the transformation matrix T, which is approximately given by [see paragraph which follows Eq. (61)]

$$T \approx \begin{bmatrix} \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & c & c \\ 0 & \sqrt{2}c & -c^2 & -1 \\ 0 & \sqrt{2}c & -1 & -c^2 \\ -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & c & c \end{bmatrix} . \qquad (A6)$$

Since this is not a unitary matrix, its inverse has to be computed using standard procedures for inverting a general matrix. The inverse matrix T^{-1} is approximately equal to

$$T^{-1} \approx \begin{bmatrix} \dfrac{1}{\sqrt{2}} & \sqrt{2}c & \sqrt{2}c^3 & -\dfrac{1}{\sqrt{2}} \\ -\dfrac{1}{\sqrt{2}} & -\sqrt{2}c & -\sqrt{2}c & -\dfrac{1}{\sqrt{2}} \\ -c & -c^2 & -1 & -c \\ -c & -1 & -c^2 & -c \end{bmatrix} . \qquad (A7)$$

Substituting these matrices in Eq. (60), Eq. (63) is obtained.

In order to invert $\mathbf{F}$ it is convenient to write

$$\mathbf{F}^{-1} = \exp(i\hat{\mathbf{H}}t)\mathbf{P}^{-1} \approx [\exp(-iAt)]^*\mathbf{P}^{-1} , \qquad (A8)$$

since A is a real matrix. In the resulting matrix $G \equiv \mathbf{F}^{-1}$ the elements G_{12}, G_{13}, G_{21}, G_{24}, G_{31}, G_{34}, G_{42}, and G_{43} are found to be of the same order of magnitude as q, and the elements G_{14}, G_{41}, G_{23} and G_{32} are $\sim q^2$. The elements G_{11} and G_{44} are approximately equal to 1, $G_{22} \approx e^{-i\gamma't}$ and $G_{33} \approx e^{i\gamma't}$.

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