First publ. in: Journal of Chemical Physics 100 (1994), 10, pp. 7503-7507

Adiabatic rotation of effective spin. I. New insight into spin-rotational interaction

Ulrich E. Steiner and Yuri A. Serebrennikov
Fakultät für Chemie, Universität Konstanz, D-78434 Konstanz, Germany

The effect of electron spin-rotational (SR) interaction in species with an effective spin $S^{\rm eff}=1/2$ is treated for molecular rotations representing an *adiabatic* perturbation to the electronic system. Based on the adiabatic rotation of effective spin (ARES) concept as well as on the transformation of the Hamiltonian to the rotating molecular frame a useful expression is obtained for the effective spin-Hamiltonian of SR interaction whereby the spin-rotational tensor is represented in terms of a tensor $\hat{\gamma}$ (relating $L+S$ to $S^{\rm eff}$) instead of the g tensor (related to $L+g_eS$). This relation is valid for rotating systems with arbitrary strength of spin–orbit coupling (SOC). An example is provided to demonstrate the dependence of the γ tensor on the SOC parameter. It is shown that only in the case of weak SOC, the traditional representation of the SR Hamiltonian, is equivalent to the more general ARES Hamiltonian. Furthermore, a direct relation between the ARES and the geometrical (topological phase) approach to the problem is pointed out. The ARES spin-Hamiltonian can be represented in terms of a $U(2)$ non-Abelian gauge potential.

I. INTRODUCTION

Spin-rotational interaction is one of the basic mechanisms of spin relaxation.[1–5] In the spin Hamiltonian this interaction is usually represented as

$$H_{\rm sr}=\mathbf{N}\hat{C}\mathbf{S}, \tag{1}$$

where **N** is the operator of rotational angular momentum of the clamped nuclei, **S** is the spin operator, and $\hat{C}$ is the spin-rotational tensor. On the basis of second-order perturbation theory it has been shown[2,6] that

$$\hat{C}=-2\hat{B}\,\delta\hat{g}, \tag{2}$$

where $\hat{B}$ is the rotational constant tensor of the molecule and

$$\delta\hat{g}=\hat{g}-g_e\hat{1} \tag{3}$$

corresponds to the deviation of the g tensor from that of the free electron.

In applying the operator (1) in the theory of spin relaxation of radicals undergoing rotational Brownian motion in solution, the usual approach is the one first applied by Hubbard[1] in the theory of nuclear spin relaxation [i.e., with the nuclear spin operator I in Eq. (1) instead of the electron spin operator S]. Here **N** and $\hat{C}(\Omega)$ (with Ω the set of Euler angles specifying the orientation of the molecule) are considered as independent stochastic variables and the correlation function of their product is approximated by the product of the individual correlation functions of angular momentum and orientation. Although justified in most cases of practical interest, the traditional approach has prevented to note an important fact: as long as the effect of molecular rotation on the spin can be treated as adiabatic—and, as will be shown here, this is the case if the spin Hamiltonian is of the form (1)—the spin state of the molecule is a unique function of the trajectory in orientational configuration space, i.e., it is independent of the particular values of angular velocity realized on this trajectory. Its evolution can be described in purely geometric terms. Thereby an interesting and fruitful view of the problem of spin-rotation interaction emerges.

This view, which occurred to us when dealing with rotational effects on the effective spin in very strongly spin–orbit mixed Kramers doublet species like the Ru(III)-trisbipyridyl complex,[7] will be developed in some detail in this paper. Thereby a general and useful relation will be derived by which the spin-rotational tensor $\hat{C}$ of an electronic spin-1/2 species is readily obtained from the electronic wave functions of its lowest Kramers doublet. Furthermore, the view adopted here will provide the basis for a straightforward stochastic treatment of spin-rotational coupling effects in Kramers doublet species of arbitrary spin–orbit coupling strength, to be presented in a subsequent paper.[8]

II. THE ARES CONCEPT

We consider a molecule with a Kramers doublet as its lowest electronic state noting that, in general, the representation of the electronic wave functions of a Kramers doublet need not be factorizable into orbital and spin part. Let the states $|\tilde{\alpha}\rangle$ and $|\tilde{\beta}\rangle$ form an orthonormal basis of the Kramers doublet (KD), then the Pauli matrices may be used to define the effective spin operators $S_x^{\rm eff}, S_y^{\rm eff}, S_z^{\rm eff}$. (The basis functions may be chosen such that the tensors described below will be diagonal and that z is the main axis of these tensors. Then $|\tilde{\alpha}\rangle$ and $|\tilde{\beta}\rangle$ may be said to represent states corresponding to effective spin quantization along this axis in the molecular frame.)

We assume that at $t=0$ the molecule is in a state $\chi_{\rm KD}$ belonging to the lowest Kramers doublet. Consider now a "*sudden*" (i.e., nonadiabatic) rotation of the molecular frame by the angle $d\varphi_\phi$, where ϕ specifies the orientation of the axis of rotation. In this case the electronic wave function $\chi^{(L)}(d\varphi_\phi)_{\rm sudden}$ will *not* follow the motion of the frame, but will remain unchanged in the initial molecular frame (L frame), whereas in a rotated basis of states fixed in the *mov-*

ing molecular frame (M frame), it is described by the following transformation:[9]

$$\chi^{(M)}(d\varphi_\phi)_{\text{sudden}} = [1 + i\ d\varphi_\phi(\mathbf{L}+\mathbf{S})]\chi^{(M)}_{\text{KD}}(0), \tag{4}$$

with **L** and **S** the vector operators of orbital and spin angular momentum, respectively. Unless the Kramers doublet $\{|\tilde{\alpha}\rangle,|\tilde{\beta}\rangle\}$ spans a complete representation of the full rotation double group, which is generally not the case, the state $\chi^{(M)}(d\varphi_\phi)_{\text{sudden}}$ resulting after a sudden rotation $(d\varphi_\phi)_{\text{sudden}}$ will have acquired some contributions of higher electronic states.

On the other hand, in an *adiabatic* rotation which is slow on the time scale $\tau = \hbar/\Delta\epsilon$, where $\Delta\epsilon$ is the energy separation between the ground state and the lowest excited state, the wave function will be completely confined to the lowest KD. Intuitively, in the lab frame in which the molecule was at rest at $t \leqslant 0$ the wave function will change as little as possible, i.e., we may assume that the physical change of the wave function is as close as possible to that expected for a sudden rotation, however with the condition that the resultant state is completely represented within the lowest KD, i.e., through the projection

$$\begin{aligned} \chi^{(M)}_{\text{KD}}(d\varphi_\phi)_{\text{adiabatic}} &= P_{\text{KD}}[1 + i\ d\varphi_\phi(\mathbf{L}+\mathbf{S})]\chi^{(M)}_{\text{KD}}(0) \\ &= [1 + i\ d\varphi_\phi\ P_{\text{KD}}(\mathbf{L}+\mathbf{S})P_{\text{KD}}]\chi^{(M)}_{\text{KD}}(0) \\ &= [1 + i\ d\varphi_\phi\langle(\mathbf{L}+\mathbf{S})\rangle_{\text{KD}}]\chi^{(M)}_{\text{KD}}(0). \end{aligned} \tag{5}$$

Here P_{KD} is the projection operator onto the KD and $\langle(\mathbf{L}+\mathbf{S})\rangle_{\text{KD}}$ denotes the truncated represention of $(\mathbf{L}+\mathbf{S})$ in the Kramers doublet space. Using the vector operator $\mathbf{S}^{\text{eff}}$ of effective spin, the truncated representation of $(\mathbf{L}+\mathbf{S})$ may be expressed in the form

$$\langle \mathbf{L}+\mathbf{S}\rangle_{\text{KD}} \equiv \hat{\gamma}\mathbf{S}^{\text{eff}}, \tag{6}$$

thereby defining a "tensor" $\hat{\gamma}$, similar to the $\hat{g}$ "tensor"[10] which in this formalism is expressed as[12]

$$\langle \mathbf{L}+g_e\mathbf{S}\rangle_{\text{KD}} \equiv \hat{g}\mathbf{S}^{\text{eff}}. \tag{7}$$

Equation (5) can be integrated to describe the adiabatic transformation of a state within the Kramers doublet during a general trajectory T of molecular rotation:

$$\chi^{(M)}_{\text{KD}\ \text{ARES}}(T) = P\left\{\exp\left(i\int_T d\varphi_\phi\ \hat{\gamma}\mathbf{S}^{\text{eff}}\right)\right\}\chi^{(M)}_{\text{KD}}(0), \tag{8}$$

where P denotes a path-ordered product and the subscript ARES stands for "adiabatic rotation of effective spin." On the other hand, taking the time derivative of Eq. (5) and using the definition of angular velocity

$$\boldsymbol{\omega} = d\varphi_\phi/dt \tag{9}$$

we can write

$$\dot{\chi}^{(M)}_{\text{KD,ARES}} = i[\boldsymbol{\omega}\hat{\gamma}\mathbf{S}^{\text{eff}}]\chi^{(M)}_{\text{KD,ARES}}, \tag{10}$$

which will be termed the ARES equation of motion of the system in the rotating molecular frame. Equation (10) defines the corresponding Hamiltonian:

$$H^{(M)}_{\text{ARES}} = -\boldsymbol{\omega}\hat{\gamma}\mathbf{S}^{\text{eff}} \tag{11}$$

and, according to Eq. (8), the evolution operator can be represented as

$$U^{(M)}_{\text{ARES}}(t) = P\left\{\exp\left(-i\int_0^t H^{(M)}_{\text{ARES}}(t')dt'\right\}\right.. \tag{12}$$

Here and in the following $\hbar = 1$ will be used.

III. DERIVATION OF THE SPIN-ROTATIONAL TENSOR USING THE ARES FORMALISM

In principle, both Hamiltonians, the spin-rotational operator H_{sr}, Eq. (1), and the ARES operator, Eq. (11), describe the effect of molecular rotation on the effective spin. Note that to second order of perturbation theory as applied in deriving Eq. (2) the effective spin is not distinct from real spin. Therefore, in the pertinent literature, the distinction is usually not made very clearly. However, the two spin Hamiltonians cannot yet be directly compared because the ARES Hamiltonian, Eq. (11), refers to the spin in the rotating molecular frame, whereas in case of the spin-rotational Hamiltonian, Eq. (1), the spin is considered in the laboratory (L) frame. To relate both Hamiltionians to each other, we will rewrite Eq. (10) in the L frame. For this purpose we have to perform a reverse rotation of the coordinate system compensating for the rotation of the molecule. This may be written as

$$\begin{aligned} \dot{\chi}^{(L)}_{\text{KD,ARES}} &= (i\boldsymbol{\omega}\hat{\gamma}\mathbf{S}^{\text{eff}} - i\boldsymbol{\omega}\mathbf{S}^{\text{eff}})\chi^{(L)}_{\text{KD,ARES}} \\ &= i\boldsymbol{\omega}(\hat{\gamma} - \hat{1})\mathbf{S}^{\text{eff}}\chi^{(L)}_{\text{KD,ARES}}. \end{aligned} \tag{13}$$

Thus, formally, χ_{KD} is subject to two rotations with angular velocities $\boldsymbol{\omega}$ and $-\boldsymbol{\omega}$, however only the first one is associated with a physical change of the state, whereas the second one is a usual coordinate transformation. Thus the ARES Hamiltonian for the effective spin in the L frame is

$$H^{(L)}_{\text{ARES}} = -\boldsymbol{\omega}(\hat{\gamma} - \hat{1})\mathbf{S}^{\text{eff}} \equiv -\boldsymbol{\omega}\delta\hat{\gamma}\mathbf{S}^{\text{eff}}. \tag{14}$$

To compare it with the spin-rotational Hamiltonian, Eq. (1), we write

$$\mathbf{N} = \tfrac{1}{2}\boldsymbol{\omega}\hat{B}^{-1} \tag{15}$$

or

$$H_{\text{sr}} = \tfrac{1}{2}\boldsymbol{\omega}\hat{B}^{-1}\hat{C}\mathbf{S}. \tag{16}$$

Comparison of Eqs. (14) and (16) yields the relation between the spin-rotational tensor and the γ tensor if the spin in Eq. (1) is interpreted as effective spin:

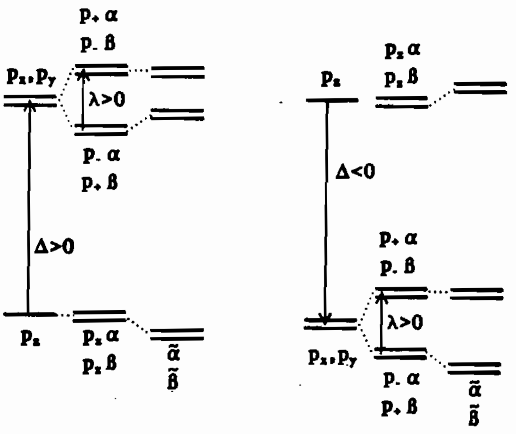
$$\hat{C} = -2\hat{B}\delta\hat{\gamma}. \tag{17}$$

To compare this result with the traditional one, Eq. (2), we have to investigate the relation between the tensors $\delta\hat{\gamma}$ and $\delta\hat{g}$. Using their definitions one has

$$\begin{aligned} (\hat{g} - g_e\hat{1})\mathbf{S}^{\text{eff}} &\equiv \langle \mathbf{L} + g_e\mathbf{S}\rangle_{\text{KD}} - g_e\mathbf{S}^{\text{eff}} \\ &= \langle \mathbf{L}\rangle_{\text{KD}} + g_e(\langle \mathbf{S}\rangle_{\text{KD}} - \mathbf{S}^{\text{eff}}), \end{aligned} \tag{18}$$

$$(\hat{\gamma} - \hat{1})\mathbf{S}^{\text{eff}} \equiv \langle \mathbf{L}+\mathbf{S}\rangle_{\text{KD}} - \mathbf{S}^{\text{eff}} = \langle \mathbf{L}\rangle_{\text{KD}} + (\langle \mathbf{S}\rangle_{\text{KD}} - \mathbf{S}^{\text{eff}}). \tag{19}$$

Thus it is seen that $\delta\hat{\gamma}$ and $\delta\hat{g}$ differ only to the extent that the projection of the real spin onto the KD differs from ef-



(a) **(b)**

FIG. 1. Level scheme of an electron in an atomic p shell under the effect of spin–orbit coupling and axial electric field splitting. (a) Case of $\Delta>0$; (b) case of $\Delta<0$.

fective spin. This difference is zero to first order in spin–orbit coupling.[12] Therefore, in the case of weak spin–orbit coupling, as applies to most organic radicals, the traditional result and the ARES result are equivalent. However, for strongly spin–orbit coupled Kramers doublets, as, e.g., in the case of some transition metal complexes,[7,13] the difference becomes significant and the correct result is given by Eq. (17) involving the $\hat\gamma$ tensor, whereby it is to be understood that the spin operator in Eq. (16) represents the effective spin.

As an example of a γ tensor calculation let us consider the case of an ion or atom with a $(np)^1$ valence electron configuration in an axially symmetric ligand field. Let the spin–orbit coupling constant be λ (>0) and the axial field splitting parameter Δ (defined >0, if the nondegenerate orbital state p_z is lowest in energy). In this case the lowest KD is given by

$$|\tilde\alpha\rangle=\cos(x)|p_z\alpha\rangle+\sin(x)|p_+\beta\rangle, \tag{20}$$

$$|\tilde\beta\rangle=\cos(x)|p_z\beta\rangle+\sin(x)|p_-\alpha\rangle, \tag{21}$$

where

$$p_+=-\frac{1}{\sqrt{2}}(p_x+ip_y),\quad p_-=\frac{1}{\sqrt{2}}(p_x-ip_y), \tag{22}$$

and

$$\tan(x)=\frac{\sqrt{2}\lambda}{\lambda/2-\Delta-\sqrt{(\lambda/2-\Delta)^2+2\lambda^2}} \tag{23}$$

with $-(\pi/2)\leqslant x\leqslant(\pi/2)$.

The ordering of the various spin–orbit states resulting from the p^1 configuration under the effect of an axial ligand field and of spin–orbit coupling is shown in Fig. 1. Applying Eqs. (6), (20), and (21) the components of the γ tensor are obtained as

$$\gamma_\parallel=1;\quad \gamma_\perp=\cos^2(x)+2\sqrt{2}\sin(x)\cos(x). \tag{24}$$

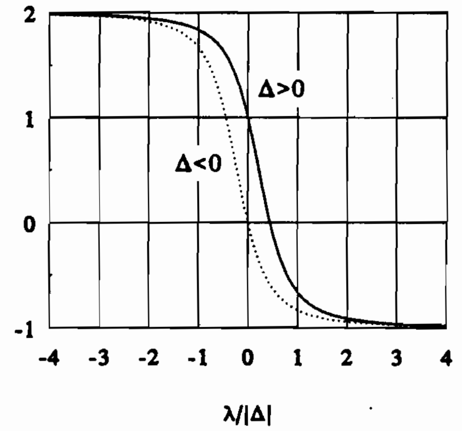


FIG. 2. Dependence of $\gamma_\perp$ on the relative strength of spin–orbit coupling and electric field splitting.

The dependence of $\gamma_\perp$ on the spin–orbit coupling parameter λ is shown in Fig. 2. It is different for positive and negative values of Δ because the character of the lowest KD changes accordingly [cf. Fig. 1, note that the square root term in Eq. (23) does not change its sign with Δ]. If $\Delta>0$, $\gamma_\perp$ approaches 1 for $\lambda/|\Delta|\rightarrow0$, i.e., the Kramers doublet becomes a normal spin doublet [$p_z\alpha,p_z\beta$, because $\cos(x)\rightarrow1$] and the spin is completely decoupled from the rotation of the molecular frame. If $\Delta<0$ and $\lambda/|\Delta|\rightarrow0$,[15] then $\gamma_\perp\rightarrow0$, which means that the effective spin, once it has been oriented along the molecular axis, will rigidly follow the rotations of this axis. Such a situation may also be reached in the case $\Delta>0$, namely if $\lambda/\Delta=4/9$. In this case the effect of pure spin rotation, mixing $p_z\alpha$ with $p_z\beta$ [being represented by the $\cos^2(x)$ term in Eq. (24)] is just opposite to the effect of orbital rotation, mixing p_+ with p_z and p_z with p_- [being represented by the $\sin(x)\cos(x)$ term in Eq. (24)].

It is of interest to note that the values of $\gamma_\perp$ may fall outside the region $0\leqslant\gamma_\perp\leqslant1$. Having $\gamma_\perp<0$ means that the effective spin rotates faster than the molecular frame, whereas for $\gamma_\perp>1$ the effective spin rotates in a direction opposite to that of the molecular frame.

For a d^5 (or d^1) electron configuration in a trigonally distorted octahedral ligand field the γ tensor was given previously.[7] In applying that result or the analogous one obtained here for p^1 (which, with reversed sign of the spin–orbit coupling constant, is also valid for p^5) one should take care that the assigned representation of the KD basis be used, because the γ tensor components depend on the definition of the basis of states.

IV. ALTERNATIVE DERIVATION OF THE ARES HAMILTONIAN

In Sec. II the starting point for the derivation of the effective Hamiltonian of the rotating Kramers doublet was the time dependence of the wave function in the molecular frame. This time dependence was intuitively anticipated by adopting a "principle of least motion in the lab frame" for the electronic system. Here we will show that the ARES

Hamiltonian can also be derived in a more straightforward manner by following the approach pointed out by Wick.[16]

Let $H_0^{(M)}$ represent the full electronic Hamiltionian (including SOC) for the situation when the molecule is at rest. If the molecular framework and the coordinate system attached to it rotate with an angular velocity $\boldsymbol{\omega}$, the electronic Hamiltonian becomes time-dependent, its representation $H_R^{(L)}(t)$ in the L frame being given by

$$H_R^{(L)}(t)=R(t)H_0^{(M)}R^{-1}(t) \tag{25}$$

with the rotational operator $R(t)$ given by[9]

$$R(t)=\exp\{-i\boldsymbol{\omega}(\mathbf{L}+\mathbf{S})t\}. \tag{26}$$

The motion of the electronic system described by the wave function $\psi(t)$ in the L frame is given by the time-dependent Schrödinger equation:

$$\dot{\psi}(t)=-iH_R^{(L)}(t)\psi(t). \tag{27}$$

This motion may be represented in the rotating M frame by substituting $\psi(t)=R(t)\Phi^{(M)}(t)$ into Eq. (27), which yields

$$\dot{\Phi}^{(M)}(t)=-i\{H_0-\boldsymbol{\omega}(\mathbf{L}+\mathbf{S})\}\Phi^{(M)}(t). \tag{28}$$

Thereby the electronic Hamiltonian in the rotating molecular frame is obtained, viz.,

$$H^{(M)}=H_0^{(M)}-\boldsymbol{\omega}(\mathbf{L}+\mathbf{S}). \tag{29}$$

If $\|H_0^{(M)}\|$ and $\|\boldsymbol{\omega}(\mathbf{L}+\mathbf{S})\|$ are of largely different order of magnitude as is usually the case for molecules undergoing thermal rotation, a perturbational treatment is appropriate. The eigenvectors of $H_0^{(M)}$ define the basis of states with possible (e.g., Kramers) degeneracies. To lowest order, the perturbational part $-\boldsymbol{\omega}(\mathbf{L}+\mathbf{S})$ will only affect the motion of the electronic system within the degenerate subspaces of eigenstates of $H_0^{(M)}$ and the effective Hamiltonian in such a reduced space is given by the corresponding projection, e.g.,

$$H_{\text{ARES}}^{(M)}=\langle H^{(M)}\rangle_{\text{KD}}=-\boldsymbol{\omega}\hat{\gamma}\mathbf{S}^{\text{eff}}, \tag{30}$$

as obtained in Sec. II, Eq. (11).

V. ARES AND NON-ABELIAN GAUGE STRUCTURE OF SPIN-ROTATIONAL INTERACTION

In recent years the problem of the evolution of a quantum system under a slowly varying Hamiltonian has received considerable attention (see, e.g., Ref. 17). This interest was stimulated by Berry's remarkable discovery of a geometrical phase in the adiabatic cyclic evolution of a nondegenerate energy state.[18] It was immediately realized[19] that Berry's phase may be interpreted as being generated by a corresponding gauge potential. In particular, it has been shown by Wilczek and Zee[19] that if a set of n quantum states of the parameter-dependent Hamiltonian remains degenerate as the Hamiltonian varies adiabatically, a non-Abelian gauge potential emerges, and the relevant gauge group is $U(n)$. Note that gauge potentials, which figure prominently in modern theories of fundamental interactions, appear here in ordinary quantum-mechanical problems, whose initial formulation has no apparent relationship to gauge fields.

The effect of a non-Abelian gauge potential on the ^{35}Cl NQR spectrum of a single crystal of sodium chlorate has been demonstrated in a recent interesting experiment.[20] A nonzero magnetization of the sample was prepared by a radiofrequency pulse and its time evolution was monitored as the crystal underwent a double rotor trajectory. The effective spin Hamiltonian of the system (nuclear spin $I=3/2$) is given by[21,22]

$$H_Q=\omega_Q\exp[-i\alpha(t)I_z^{\times}]\exp[-i\beta(t)I_y^{\times}]I_z^2, \tag{31}$$

where $I_i^{\times}I_j\equiv[I_i,I_j]$, ω_Q is the strength of the quadrupolar interaction and I_i $(i=x,y,z)$ is the ith component of the nuclear spin operator in the electric field gradient principal axis system. The spherical angles $\alpha(t)$ and $\beta(t)$ describe the orientation of the crystal in the laboratory frame. The components $\dot{\alpha}(t)$ and $\dot{\beta}(t)$ of the angular velocity of the crystal rotation were much smaller than ω_Q, i.e., the quadrupolar spin Hamiltonian was changed adiabatically.

It has been shown by Zee[22] that in such a case the geometric part of the evolution of this system is governed by the following propagator:

$$U=P\exp\left\{-\int[A_\beta\,d\beta+A_\alpha\,d\alpha]\right\}. \tag{32}$$

Here $\mathbf{A}$ is a $U(2)$ gauge potential, which in the subspace of the lowest KD, i.e., for the $m,m'=\pm\frac{1}{2}$ pair has a non-Abelian structure:

$$A_\beta=-i\kappa\,\frac{\sigma_y}{2};\quad A_\alpha=-i\left[\cos\beta\,\frac{\sigma_z}{2}-\kappa\sin\beta\,\frac{\sigma_x}{2}\right], \tag{33}$$

where the σ_i are the corresponding Pauli matrices. In the case under consideration, $\kappa=I+\frac{1}{2}=2$.

Zee[22] noted that a non-Abelian gauge potential of the same structure had been obtained by Moody *et al.*[23] in an analysis of Λ doubling in diatomic molecules $(\Lambda=\pm\frac{1}{2})$, the main difference occuring in the definition of the parameter κ, which in the latter case takes the form

$$\kappa=2\langle+\tfrac{1}{2}|L_y+S_y|-\tfrac{1}{2}\rangle. \tag{34}$$

It is well-known that measurements of the splitting between the components $\Lambda=\frac{1}{2}$ and $\Lambda=-\frac{1}{2}$ in a rotating molecule allow one to obtain information about the spin-rotational interaction in the system (see, e.g., Ref. 24). Although the original physical problems involved in the NQR experiments with a doubly rotated monocrystal[20] and in microwave gas phase spectroscopy of diatomics[24] are very different, the algebra leading to the determination of the corresponding non-Abelian gauge potential is the same, since, as has been mentioned by Zee[22] "the rotationally invariant connection on the sphere is essentially unique."

Given this short excursus into a field of high current interest of both theoreticians and experimentalists, we may easily establish the relationship between the representation of spin-rotational interaction in terms of the ARES Hamiltonian [Eq. (11)] and its non-Abelian gauge structure. In order to do this we should rewrite Eq. (11) using expression (35) for the projections of the angular velocity $\boldsymbol{\omega}$ of a linear rotator on the main axes of the molecular tensor of inertia:

$$\omega_x=-\dot{\alpha}\sin\beta;\quad \omega_y=\dot{\beta},\quad \omega_z=\dot{\alpha}\cos\beta. \tag{35}$$

As a result we obtain

$$H^{(M)}_{\mathrm{ARES}} = -\{\dot{\beta}\gamma_{\perp} S^{\mathrm{eff}}_{y} + \dot{\alpha}[-\sin\beta\gamma_{\perp} S^{\mathrm{eff}}_{x} + \cos\beta\gamma_{\|} S^{\mathrm{eff}}_{z}]\}. \tag{36}$$

It is easy to see from Eqs. (33) and (36) that for diatomics ($\gamma_{\perp}=\kappa$, $\gamma_{\|}=1$, see Sec. III):

$$H^{(M)}_{\mathrm{ARES}} = -i\{A_{\beta}\dot{\beta} + A_{\alpha}\dot{\alpha}\} \tag{37}$$

and thus $U^{(M)}_{\mathrm{ARES}}$ [Eq. (12)] equal U defined by Eq. (32). Equation (37) shows that spin-rotational interaction can also be viewed as the effect of a non-Abelian gauge potential **A**, defined by Eq. (33).

VI. CONCLUSIONS

In this paper we have considered the effect of adiabatic molecular rotation on systems with effective spin, $S^{\mathrm{eff}}=1/2$. We have shown that, because it is of spin-*orbit* nature, the *effective* spin follows the reorientation of the molecular axes in a prescribed way, which is characterized as adiabatic rotation of effective spin (ARES). While we have used this concept to derive the spin-rotational Hamiltonian and to determine the spin-rotational tensor, it seems important to emphasize that reciprocal conclusion is also true. Actually, starting with the traditional form of the spin-rotational Hamiltonian [Eq. (1)] as a phenomenological basis and time integrating the spin motion over any classical trajectory of molecular rotation we arrive to the conclusion that the effect of spin-rotational interaction, i.e., the trajectory of effective spin orientations (the sequence of states adopted in the 2×2 spin space of the Kramers doublet) is a unique function of the sequence of positions adopted in the orientational space of the molecular axes, irrespective of the values of angular velocity at which the molecule passes this trajectory. Qualitatively this is easy to see, since $H_{\mathrm{sr}}\,dt$, a differential *action* of H_{sr}, is proportional to $\omega\,dt=d\varphi$, i.e., the *distance* in angular space. Whether this distance is covered at low angular velocity ω in a long time interval dt or at fast ω in short dt does not matter, as long as the molecular rotation represents an adiabatic perturbation to the electronic system, or—equivalently—as long as the spin-rotational tensor is constant. Under such conditions the time evolution of effective spin can be described in purely geometric terms as an action of a $U(2)$ non-Abelian gauge potential.

ACKNOWLEDGMENTS

Financial support of this work by the Deutsche Forschungsgemeinschaft and the grant of an Alexander von Humboldt fellowship to Y. A. S. is gratefully acknowledged.

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