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Molecular Kramers Degeneracy and Non-Abelian Adiabatic Phase Factors

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For a molecular system with an odd number of electrons, the electronic Hamiltonian possesses a twofold Kramers degeneracy for all nuclear configurations. It is shown that this leads to a non-Abelian gauge-field term in the effective nuclear Hamiltonian, with permissible gauge transformations belonging to SU(2). This should lead to observable effects analogous to the Berry phase for the nondegenerate case. In particular, an atom in a slowly rotating electric field exhibits changes in its component of angular momentum along the field because of the non-Abelian phase factor.

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The phase factor experienced by an eigenfunction of a parameter-dependent Hamiltonian when the parameters adiabatically traverse a closed path has recently become a topic of considerable interest. Some aspects of the phenomenon have been known for decades,[1,2] but the modern interest stems from the derivation of a general phase factor formula in the context of a molecular Born-Oppenheimer problem[3] followed by its rederivation and recasting in a more general context by Berry[4] and Simon.[5] The generalization to degenerate eigenvalues[6] leads to the replacement of the phase factor by a unitary transformation among the degenerate eigenfunctions that have the properties of a non-Abelian gauge field. This idea has been applied in the context of Born-Oppenheimer treatments of molecular systems to degenerate states of the diatomic molecule,[7] and to a model in which nuclei are constrained to move in a manifold where there is a degeneracy-producing symmetry.[8] Here I wish to point out that Kramers degeneracy in molecular systems furnishes a wide variety of systems in which non-Abelian gauge fields play a role and should lead to many applications in chemical physics and, by analogy, in other fields as well. The only previous treatment of this known to the author[9] dealt only with a special case for which the possibilities were limited. I have tried to formulate this Letter in such a way that it can serve to introduce the chemical physicist to the role of gauge fields in his area, and also be of interest to those looking for simple but nontrivial systems exhibiting gauge behavior.

We consider an electronic Hamiltonian $H(\mathbf{R})$ depending on nuclear coordinates $\mathbf{R}$. We use three-dimensional vector notation for $\mathbf{R}$, but it will be evident that the results are generalizable to any number of dimensions and to any Hamiltonian depending on continuously variable parameters. For each $\mathbf{R}$ we have the eigenvalue equation

$$H(\mathbf{R})\,|j\alpha(\mathbf{R})\rangle\rangle = W_j(\mathbf{R})\,|j\alpha(\mathbf{R})\rangle\rangle, \tag{1}$$

where Latin letters $j, k, \ldots$ are used to denote energy levels, and Greek letters $\alpha, \beta, \ldots$ denote states within a level if there is a degeneracy which holds for all $\mathbf{R}$. Of course, I have principally in mind the case of the twofold Kramers degeneracy.

If $\mathbf{R}$ is displaced continuously along some closed curve C starting at an origin 0, the eigenkets must change continuously in such a way as to satisfy (1) at each point. I describe this by

$$|j\alpha(C)(\mathbf{R})\rangle\rangle = \textstyle\sum_{k,\beta} |k\beta(0)\rangle\rangle\langle k\beta|\,S(C)(\mathbf{R})\,|j\alpha\rangle. \tag{2}$$

For an infinitesimal displacement, we have

$$|j\alpha(C)(\mathbf{R}+d\mathbf{R})\rangle\rangle = \textstyle\sum_{k,\beta} |k\beta(C)(\mathbf{R})\rangle\rangle\langle k\beta|\,1+i\mathbf{G}(\mathbf{R})\cdot d\mathbf{R}\,|j\alpha\rangle, \tag{3}$$

where $G(\mathbf{R})$ is a Hermitean vector operator defined for each $\mathbf{R}$. Combining (2) and (3), we find for the matrix representation of $S(C)(\mathbf{R})$,

$$S(C)(\mathbf{R}+d\mathbf{R}) = S(C)(\mathbf{R})[1+i\mathbf{G}(\mathbf{R})\cdot d\mathbf{R}],$$

which has the formal solution

$$S(C)(\mathbf{R}) = 1 + i\int_0^{\mathbf{R}} \mathbf{G}(\mathbf{R}')\cdot d\mathbf{R}' - \int_0^{\mathbf{R}} \left[\int_0^{\mathbf{R}'} \mathbf{G}(\mathbf{R}'')\cdot d\mathbf{R}''\right]\mathbf{G}(\mathbf{R}')\cdot d\mathbf{R}' + \ldots. \tag{4}$$

Applying this to a closed curve which is an infinitesimal rectangle in the xy plane with sides Δx and Δy, and keeping only leading terms, we easily find

$$S(C) - 1 = \Delta x\,\Delta y \left[i\left(\frac{\partial G_x}{\partial x} - \frac{\partial G_y}{\partial y}\right) - [G_x, G_y] \right]. \tag{5}$$

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It is convenient to divide $\mathbf{G}(\mathbf{R})$ into two parts:

$$\mathbf{G}(\mathbf{R})=\mathbf{f}(\mathbf{R})+\mathbf{g}(\mathbf{R}), \tag{6}$$

where $\mathbf{f}(\mathbf{R})$ is block diagonal with respect to the energy levels, and $\mathbf{g}(\mathbf{R})$ has matrix elements only between states belonging to different levels. The form of $\mathbf{g}(\mathbf{R})$ is determined by the requirement that (1) must be satisfied at all points:

$$\langle k\beta|\mathbf{g}(\mathbf{R})|j\alpha\rangle=i[W_k(\mathbf{R})-W_j(\mathbf{R})]^{-1}\langle k\beta(\mathbf{R})|\nabla H(\mathbf{R})|j\alpha(\mathbf{R})\rangle. \tag{7}$$

There is a freedom of choice of $\mathbf{f}(\mathbf{R})$ corresponding to the freedom of choice in defining degenerate states, but the definitions clearly require that

$$\langle j\beta|\mathbf{f}(\mathbf{R})|j\alpha\rangle=-i\langle j\beta(\mathbf{R})|\nabla j\alpha(\mathbf{R})\rangle. \tag{8}$$

It is easy to show that the right-hand side of (5) is identically block diagonal, as of course it should be, since the closed path must return one to the same energy level. The block-diagonal part depends on the choice of $\mathbf{f}$. If, for example, the eigenkets are required to be single-valued functions of $\mathbf{R}$, we must have $S(C)=1$, implying

$$\frac{\partial}{\partial x}f_y-\frac{\partial}{\partial y}f_x+i[f_x,f_y]=-i[g_x,g_y]_d, \tag{9}$$

where the subscript d stands for the (block-)diagonal part. Equation (9) can be thought of as applying to the entire block-diagonal matrix or separately to each block. On the other hand, if we choose $f=0$ corresponding to adiabatic variation of $\mathbf{R}$ with time,[4] we find

$$S-1=-\Delta x\,\Delta y[g_x,g_y]_d,$$

which, together with (7), gives the appropriate generalization of the Berry formula[3,4] for the nondegenerate case.

We now specialize to the case of interest for this Letter in which $H(\mathbf{R})$ commutes with the time-reversal operator T for all $\mathbf{R}$ and in which the total spin is half-odd integer (odd number of electrons) so that $T^2=-1$. In this case, we have a twofold Kramers degeneracy for each $\mathbf{R}$.[10,11] Specializing to a particular energy level and suppressing the index j, we have two states $|a\rangle$ and $|b\rangle$ for each $\mathbf{R}$, related by

$$T|a\rangle=|b\rangle,\quad T|b\rangle=-|a\rangle. \tag{10}$$

We note from (7) that $\mathbf{g}$ anticommutes with T. With use of this along with (10) and the well-known properties of T, one easily shows that the right-hand side of (9) (restricted to our 2×2 block) is a traceless, Hermitean matrix, but is otherwise arbitrary, depending on details of the Hamiltonian. One also sees from (8) that $\mathbf{f}$ is traceless and Hermitean within the block.

We can define a gauge transformation as an $\mathbf{R}$-dependent unitary transformation $U(\mathbf{R})$ applied to the states $|a\rangle$ and $|b\rangle$:

$$\begin{aligned}|\alpha'(\mathbf{R})\rangle&=U(\mathbf{R})|\alpha(\mathbf{R})\rangle\\&=\textstyle\sum_\beta|\beta(\mathbf{R})\rangle\langle\beta|U(\mathbf{R})|\alpha\rangle,\end{aligned} \tag{11}$$

with α,β taking on the values a and b. If (10) is still to be satisfied by the primed kets, $U(\mathbf{R})$ must belong to the special unitary group SU(2) of unitary operators with unit determinant. The effect of (11) on $\mathbf{F}$ is obtained by the application of (8) to the primed kets,

$$\mathbf{f}'=U^\dagger\mathbf{f}U-iU^\dagger\nabla U, \tag{12}$$

in agreement with the usual formula for a non-Abelian gauge transfermation.

In Born-Oppenheimer approximation, we write a molecular wave function belonging to the given energy level in the form

$$\Psi=\textstyle\sum_\alpha|\alpha(\mathbf{R})\rangle\psi_\alpha(\mathbf{R}).$$

Applying the nuclear gradient operator to this, with use of (8), and ignoring any coupling to other energy levels, we find

$$\nabla\Psi=\sum_\alpha|\alpha\rangle\left\{\nabla\psi_\alpha+i\sum_\beta\langle\alpha|f|\beta\rangle\psi_\beta\right\}.$$

In the effective Hamiltonian for the nuclear wave function $\psi(\mathbf{R})$, therefore, the gradient operator ∇ must be replaced by

$$\nabla+i\mathbf{f}(\mathbf{R}),$$

in which each component of $\mathbf{f}$ is a matrix operating on the two-component column vector $\psi(\mathbf{R})$. The effective Hamiltonian for the motion of the nuclei thus contains a gauge-field term. This is the generalization of the effective vector potential (Abelian gauge field) found in the nondegenerate case.[3,12-15] The presence of such a term is unavoidable if the electronic eigenkets are to be single-valued functions of $\mathbf{R}$, in which case (9) must be satisfied.

It is evident that molecular systems with Kramers degeneracy will furnish many examples of the role of non-Abelian gauge fields and phase factors in chemical physics. The remainder of this Letter is devoted to a particular simple example which is expected to lead to easily observable effects.

Consider an atom with an odd number of electrons, in a level with total angular momentum quantum number $J=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots$. The case $J=\frac{1}{2}$ will prove to be uninteresting, but is included for completeness. The ${}^2P_{3/2}$ ground state of fluorine is an example. If the atom is placed in a uniform electric field $\mathbf{E}$, the degenerate level is split by the Stark Hamiltonian

$$H = A(\mathbf{E}\cdot\mathbf{J})^2, \tag{13}$$

in which A is a constant. The components of $\mathbf{E}$ can here be considered to be continuously variable parameters on which H depends. The Hamiltonian (13) is split into $J+\frac{1}{2}$ Kramers doublets, characterized by the quantum number $|M| - \frac{1}{2}, \frac{3}{2}, \ldots, J$, denoting the absolute value of the component of angular momentum along the field, with energies given by

$$W(|M|) = AE^2|M|^2. \tag{14}$$

Now let $\mathbf{E}$ be initially directed along the z axis, and consider an infinitesimal rotation through an angle $d\phi$, about an axis in the (y,z) plane making an angle θ with the field. The small change in H is given by

$$dH = AE^2 \sin\theta (J_z J_x + J_x J_z) d\phi. \tag{15}$$

If the rotation is carried out adiabatically, the eigenfunctions will follow it according to Eqs. (2)–(3), but with the block-diagonal part $f=0$, so that $\mathbf{G}=\mathbf{g}$. With use of (7), (14), (15), and some elementary angular momentum theory, one finds, for the matrix elements of $\mathbf{g}$,

$$\langle M+1|ig_\phi|M\rangle = -\langle M|ig_\phi|M+1\rangle = [(J+M+1)(J-M)]^{1/2}\sin\theta. \tag{16}$$

Equation (16) holds for elements of g_ϕ linking states belonging to different doublets; if $|M+1| = |M|$, however, which occurs for the doublet with $|M| = \frac{1}{2}$, the matrix element of g_ϕ is zero.

The operator $ig_\phi d\phi$, which generates the adiabatic change in the eigenfunction under the rotation, is *not* the same as the operator for a rotation of the eigenfunction about the axis, the generator of which is

$$-i(J_z\cos\theta + J_y\sin\theta)d\phi. \tag{17}$$

This is easily seen to have the same off-diagonal elements as $ig_\phi d\phi$, but also has a block-diagonal part. The effect of the infinitesimal adiabatic rotation can thus be pictured as a rotation of the eigenfunction following the field according to (17), followed by subtraction of the block-diagonal part. Relative to a coordinate system following the field, therefore, each doublet experiences the infinitesimal transformation

$$1 + dU = 1 + i(J_z\cos\theta + J_{yd}\sin\theta)d\phi, \tag{18}$$

where J_{yd} is the block-diagonal part of J_y.

For doublets with $|M| > \frac{1}{2}$, $J_{yd}=0$, and (18) leads to a phase factor, opposite in sign for the two components of the doublet. This is of some interest, but does not exhibit non-Abelian properties.

Of greater interest to us is the doublet with $|M| = \frac{1}{2}$, for which both terms of (18) contribute. It is convenient to represent J_z and J_{yd} within this block in terms of the Pauli matrices. Elementary angular momentum theory gives the result

$$J_z = \tfrac{1}{2}\sigma_z, \quad J_{yd} = \tfrac{1}{2}(J+\tfrac{1}{2})\sigma_y. \tag{19}$$

For $J=\frac{1}{2}$, we note that (18) simply cancels out the rotation (17), with the result that the angular momentum is simply "left behind." For $J > \frac{1}{2}$, however, this is not possible: No purely block-diagonal operator like (18) corresponds to a rotation.

There are two particularly simple cases in which (18) can be integrated to yield the result of a finite rotation.

(a) Let $\theta=\pi/2$, so that one is rotating about the y axis itself. Integrating (18) and with use of (19), we find

$$\begin{aligned} U(\phi) &= \exp[\tfrac{1}{2}i(J+\tfrac{1}{2})\sigma_y\phi] \\ &= \cos[\tfrac{1}{2}(J+\tfrac{1}{2})\phi] + i\sigma_y\sin[\tfrac{1}{2}(J+\tfrac{1}{2})\phi]. \end{aligned} \tag{20}$$

Equation (20) predicts a reversal of sign of angular momentum component along the field with unit probability at an angle

$$\phi_r = \pi/(J+\tfrac{1}{2}) = \begin{cases} \pi & (J=\frac{1}{2}), \\ \dfrac{\pi}{2} & (J=\frac{3}{2}), \\ \dfrac{\pi}{3} & (J=\frac{5}{2}), \\ \quad\text{etc.} \end{cases}$$

The result for $J=\frac{1}{2}$ just corresponds to the fact that in this case the angular momentum stays put as the field is rotated, with the result that it has reversed direction relative to the field when the field has been rotated through an angle π. The results for other J, however, although easily derivable, are nontrivial and reflect the presence of the non-Abelian gauge field.

(b) Let θ be arbitrary, but rotate through an angle $\phi=2\pi$. In this case, integration of (18) with the aid of (19) gives

$$U(\theta) = \exp\{i\pi[\sigma_z\cos\theta + (J+\tfrac{1}{2})\sigma_y\sin\theta]\} = \cos q + i(\pi/q)[\sigma_z\cos\theta + (J+\tfrac{1}{2})\sigma_y\sin\theta]\sin q, \tag{21}$$

where

$$q = \pi[\cos^2\theta + (J+\tfrac{1}{2})^2\sin^2\theta]^{1/2}. \tag{22}$$

For $J=\frac{1}{2}$, we see from (22) that $q=\pi$, so that (21) just predicts the usual sign change after a rotation through 2π, with no reversal of direction of angular momentum. For other J, though, (21) and (22) predict a finite probability (never equal to unity) for a reversal of angular momentum direction, given by

$$P=q^{-2}[(J+\tfrac{1}{2})\pi\sin\theta\sin q]^2. \tag{23}$$

The angular momentum reversal probability given by (23) is equal to zero for $\theta=0$ or $\pi/2$; in between, it has $J-\frac{1}{2}$ maxima and $J-\frac{3}{2}$ zeros.

The results predicted by (20) and (23) would appear to make possible a relatively simple experimental observation of the non-Abelian phase factor analogous to that already achieved for the Abelian case by observing the rotation of polarization of photons passed through a helically wound optical fiber.[16]

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