Berry's Phase for Large Spins in External Fields

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It is shown that even for large spins J the fundamental difference between integer and half-integer spins persists. In a quasiclassical description this difference enters via Berry's connection. This general phenomenon is derived and illustrated for large spins confined to a plane by crystal electric fields. Physical realizations are rare-earth nickel borocarbides. Magnetic moments for half-integer spin ($Dy^{3+}, J = 15/2$) and magnetic susceptibilities for integer spin ($Ho^{3+}, J = 8$) are calculated. Experiments are proposed to furnish evidence for the predicted fundamental difference. [S0031-9007(97)05253-8]

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The common belief that large spins are equivalent to classical charged gyroscopes was strikingly undermined by Haldane [1], who indicated that the ground state and low-lying states of magnetic chains consisting of localized spins J are different for integer and half-integer J even if J is large. Here we consider a similar effect for individual large spins placed in external fields such as the crystal electric field (CEF) and the external magnetic field. Its origin can be traced back to a geometric phase occurring on passing from quantum mechanical to quasiclassical spins.

The general Hamiltonian of a localized spin associated with a magnetic moment can be written as a function of its components,

$$H_S = \hat{f}(\vec{J}) - \vec{h}\vec{J}\,, \tag{1}$$

where $\hat{f}(\vec{J})$ is an arbitrary function of $\vec{J}$ satisfying only two requirements. It is a Hermitian operator, and it is an even function of $\vec{J}$: $\hat{f}(\vec{J}) = \hat{f}(-\vec{J})$. The latter requirement is equivalent to time-reversal symmetry [2]. In this paper we will focus on localized moments which are essentially confined to a plane. The confinement is due to the effects of the crystalline electric field. The important degree of freedom is rotation about the normal vector of a certain plane which we choose as z direction. It is then appropriate to introduce the azimuthal angle φ and its conjugate momentum J_z as canonical variables. Setting $\hbar = 1$ we may use

$$J_z = -i\,\frac{\partial}{\partial\varphi}\,, \tag{2a}$$

$$J_x = \sqrt{J(J+1) - J_z^2}\cos\varphi\,, \tag{2b}$$

$$J_y = \sqrt{J(J+1) - J_z^2}\sin\varphi\,. \tag{2c}$$

Equations (2) generally have a symbolical meaning since the operators on the right-hand sides should be ordered to guarantee that $J_x^+ = J_x$, that $J_y^+ = J_y$, and that the canonical permutation relations are satisfied. However, at large J the noncommutativity is small, and we do not need to bother with the symmetrization. Inserting (2) into the Hamiltonian (1), the problem is reduced to the solution of a Schrödinger wave equation with, in general, a complicated differential operator.

So far, no difference between integer and half-integer spins occurred. The difference resides in a different global phase behavior. For large spins J one may pass to a quasiclassical description via the overcomplete set of coherent states $\psi_{\vec{n}}$ with

$$\langle\psi_{\vec{n}}|\vec{J}|\psi_{\vec{n}}\rangle = J\vec{n}\,. \tag{3}$$

Moving the spin induces a certain orbit of the tips of the unit vectors $\vec{n}$ on the unit sphere S^2. If this orbit is closed, there is *no* difference in the purely classical picture between starting point and end point. Because of Berry's connection [3], however, this is not the whole story. In order to be quantitative we first have to fix the phases of the $\psi_{\vec{n}}$ in (3). The natural choice is to fix the phase of $\psi_{\vec{z}}$ and to take [4]

$$\psi_{\vec{n}} = \exp(iJ_z\varphi)\exp(iJ_x\theta)\exp(-iJ_z\varphi)\psi_{\vec{z}}\,, \tag{4}$$

where (φ, θ) are the angles characterizing the unit vector $\vec{n}$ ($\vec{z}$ being the unit vector in z direction). Berry's connection is given for the single, nondegenerate state $\psi_{\vec{n}}$ (Abelian case [3,5,6]) by $\vec{A} = \langle\psi_{\vec{n}}|i\vec{\nabla}|\psi_{\vec{n}}\rangle$. Since $\vec{n}$ is confined to the unit sphere, spherical coordinates are most appropriate and only the A_θ and the A_φ components matter. One finds

$$A_\theta = \langle\psi_{\vec{n}}|i\partial/(\partial\theta)|\psi_{\vec{n}}\rangle = -\langle\psi_{\vec{z}}|J_x|\psi_{\vec{z}}\rangle = 0\,, \tag{5a}$$

$$\begin{aligned} A_\varphi &= \langle\psi_{\vec{n}}|i\sin(\theta)^{-1}\partial/(\partial\varphi)|\psi_{\vec{n}}\rangle \\ &= \sin(\theta)^{-1}\langle\psi_{\vec{z}}|J_z[1-\cos(\theta)] + \sin(\theta)J_y|\psi_{\vec{z}}\rangle \\ &= J[1-\cos(\theta)]/\sin(\theta)\,. \end{aligned} \tag{5b}$$

This connection then gives rise to the geometrical phase $\exp(i\int_\gamma \vec{A}\,d\vec{l})$ along the path γ. Since we are interested in this work in motion in the xy plane only, we have $\theta = \pi/2$ and thus the phase is $\exp(iJ\Delta\varphi)$. As was to be expected from the physical origin of this phase it can

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be put to zero *locally* by an appropriate gauge. Globally, i.e., for complete tours of $\Delta\varphi = 2\pi$, one sees that no effect occurs for integer J but that for half-integer J a factor of -1 applies which cannot be gauged away. One way to account for the phase behavior is to use (2a) and *antiperiodic* boundary condition for half-integer spins and periodic boundary condition for integer spins, respectively. A more elegant way is to stick to the connection $\vec{A}$. This means we use

$$J_z = -i\left(\frac{\partial}{\partial\varphi} - iA_\varphi\right) \tag{6}$$

instead of (2a). Since, however, a change of gauge can alter A_φ by any integer value, one may use (2a) for integer spins. For half-integer spins we use $J_z = -i[\partial/(\partial\varphi) - i/2]$.

Thus, despite the large value of J, the low-lying states of the Hamiltonian (1) for integer and half-integer spins are fundamentally different. In the absence of an external magnetic field all stationary states of a half-integer spin are doubly degenerate (Kramers degeneracy [7]). This means that, in analogy to the linear Stark effect, the ground state may be characterized by a finite magnetic moment. To the contrary, the ground state of an integer spin is nondegenerate for sufficiently low crystalline symmetry. Therefore, the magnetization in the ground state is exactly zero and depends linearly on the magnetic field as long as the field is weak enough.

To be more specific, we consider an important application of these general ideas to the ions of the rare-earth elements Ho^{3+} and Dy^{3+}. The triply charged ions are decisive for the magnetic moments in the compounds $R Ni_2B_2C$ (R stands for a rare-earth element), the properties of which attracted much attention in the last few years [8–11]. The ion Ho^{3+} has 10 electrons in the $4f$ shell. According to Hund's rule, it has the total spin $S = 2$, the orbital moment $L = 6$, and the total moment $J = 8$. The corresponding numbers for Dy^{3+} (9 electrons in the $4f$ shell) are $S = \frac{5}{2}, L = 5, J = \frac{15}{2}$. Thus, both values of J are rather large and close to each other.

All the compounds ($R = \mathrm{Y, La, Ho, Dy, Tm, Tb, Er, Yb}$) crystallize as perovskites with the rare-earth ions forming a tetragonal centered lattice [9]. The magnetic moments of the Ho and Dy compounds are confined presumably in the ab plane thus realizing the situation discussed above. The simplest CEF Hamiltonian H_{CEF} displaying tetragonal symmetry reads

$$H_{\mathrm{CEF}} = \frac{a}{2} J_z^2 - 2b(J_x^4 + J_y^4), \tag{7}$$

with $a, b > 0$. Quartic (and higher) terms in J_z are neglected since we assume $J_z \ll J_x, J_y$. For the same reason one can introduce the coordinate φ in a slightly simplified way [compared to (2)]: $J_x = J\cos\varphi, J_y = J\sin\varphi$, and $J_z = -i\partial/(\partial\varphi) + A_\varphi$ with $A_\varphi = 0$ for integer J and $A_\varphi = 1/2$ for half-integer J. Together with the magnetic field contribution, the total Hamiltonian becomes

$$H = -\frac{a}{2}\left(\frac{\partial}{\partial\varphi} - iA_\varphi\right)^2 - \frac{b}{2} J^4[3 + \cos(4\varphi)] - hJ\cos(\varphi - \varphi_h), \tag{8}$$

where φ_h is the angle the magnetic field forms with the x axis. The effective field h is the magnetic field times $g\mu_{\mathrm{B}}$. The Hamiltonian (8) was found in a previous work [12] in which it was also analyzed for integer J.

It will be shown later that the CEF constants a and bJ^2 are of the same order of magnitude. Because of the large value of J the potential energy has very deep minima near the points $\varphi = \varphi_l = l\pi/2, l \in \{0, 1, 2, 3\}$. Let us denote the oscillatory states localized near each value of φ_l as $|l\rangle$. To be more specific, each $|l\rangle$ is the ground state [13] of $H_l = -(a/2)\partial^2/(\partial\varphi^2) + U_l(\varphi)$ with

$$U_l(\varphi) = \begin{cases} -\frac{bJ^4}{2}[3 + \cos(4\varphi)], & \text{for } |\varphi - l\frac{\pi}{2}| \le \frac{\pi}{4}, \\ -bJ^4, & \text{otherwise.} \end{cases} \tag{9}$$

Without loss of generality we assume that the corresponding eigenenergy is zero. Neglecting the overlap between different $|l\rangle$, we find that the energy level is fourfold degenerate. The overlap lifts partly the degeneracy even in the absence of magnetic field. In complete analogy to the derivation of the dispersion of a tight-binding model [14] we define the hopping matrix element

$$w = -\langle l|H - H_{l+1}|l + 1\rangle > 0. \tag{10}$$

The hopping part of effective Hamiltonian is

$$H_w = -w[C(\alpha) + C^+(\alpha)], \tag{11}$$

where C is the unitary rotation operator which induces $|l\rangle \to |l + 1 \bmod 4\rangle \exp(i\alpha)$. For integer spin we have $\alpha = 0$; for half-integer spin we use $\alpha = \pi/4$ resulting from

$$\exp(i\alpha) = \exp\left(i\int_{l\pi/2}^{(l+1)\pi/2} A_\varphi\, d\varphi\right). \tag{12}$$

This is the direct effect of the connection A_φ in absolute analogy to the Peierls phase in tight-binding models in magnetic fields. For what follows it is important to note that w is exponentially small if the wells at φ_l are deep enough such that the ground states $|l\rangle$ are well, i.e., exponentially, localized. To estimate w we use the ansatz $|l\rangle \propto \exp(-|\int_{l\pi/2}^{\varphi}\sqrt{2[U_l(\varphi) - U_{\min}]/a}\, d\varphi|)$ which is motivated by the ground state energy close to the minima and its natural extension in a WKB-type approach. The main contribution to the φ integral for w comes from the vicinity of $\varphi = \pi/4$ for $l = 0$ and leads to

$$w \propto \exp\left(-\sqrt{\frac{2bJ^4}{a}}\right). \tag{13}$$

The eigenstates and eigenvalues of (11) are easily read off since we deal with a translationally invariant, $d = 1$, four-site tight-binding model. Thus the eigenstates are characterized by some momentum $k \in \{0, \pm\pi/2, \pi\}$

$$\psi_k = \frac{1}{2} \sum_{l=0}^{3} \exp(ikl)\, |l\rangle . \qquad (14)$$

The corresponding eigenenergies are

$$E_k = -2w \cos(k + \alpha) . \qquad (15)$$

Thus for integer J ($\alpha = 0$) there is a nondegenerate ground state ($k = 0, E_k = -2w$), two degenerate excited states ($k = \pm\pi/2, E_k = 0$), and the highest excited state ($k = \pi, E_k = 2w$). For half-integer J ($\alpha = \pi/4$) both the ground state and the excited state are doubly degenerate with ($k = 0, -\pi/2, E_k = -\sqrt{2}\,w$) and ($k = \pi/2, \pi, E_k = \sqrt{2}\,w$).

The main difference between integer and half-integer spins resides here in a different degeneracy of the ground states. Physically this difference becomes manifest, for instance, when a magnetic field h is applied. We first consider an in-plane field as in (8). For well-localized states $|l\rangle$ such a magnetic field is site diagonal with matrix elements

$$H_h = hJ \cos(l\pi/4 - \varphi_h) . \qquad (16)$$

The eigenvalues of $H_w + H_h$ can be given analytically. For integer spins and half-integer spins one finds, respectively,

$$E_{\rm int} = \pm\sqrt{2w^2 + \frac{\bar h^2}{2} \pm \sqrt{\left(2w^2 + \frac{\bar h^2}{2}\right)^2 - \bar h_x^2 \bar h_y^2}} , \qquad (17a)$$

$$E_{\rm hint} = \pm\sqrt{2w^2 + \frac{\bar h^2}{2} \pm \bar h\sqrt{2w^2 + \frac{\bar h^2}{4} - \frac{\bar h_x^2 \bar h_y^2}{\bar h^2}}} , \qquad (17b)$$

where we used $\bar h$ as a shorthand for hJ. From (17) one obtains for the ground-state energies in the limit of small magnetic fields

$$E_{\rm int} \approx -2w - h^2J^2/(4w) , \qquad (18a)$$

$$E_{\rm hint} \approx -\sqrt{2}\,w - hJ/2 . \qquad (18b)$$

As expected, the correction is quadratic in the nondegenerate, integer J case, but linear in the degenerate, half-integer J case (as in the linear Stark effect). So we have for integer J a finite $T = 0$ susceptibility

$$\chi_{\rm plane} = -g^2\mu_{\rm B}^2 (\partial E)^2/(\partial h^2) = g^2\mu_{\rm B}^2 J^2/(2w) . \qquad (19)$$

For half-integer J the system shows a finite magnetic momentum

$$\mu = -g\mu_{\rm B}\partial E/(\partial h) = g\mu_{\rm B} J/2 , \qquad (20)$$

leading to a Curie susceptibility diverging for $T \to 0$. This constitutes an essential difference between integer and half-integer spin. For large magnetic fields, however, the difference vanishes since w becomes unimportant. Asymptotically one obtains for $hJ \gg w$

$$E \approx \pm hJ \cos(\varphi_h); \qquad \pm hJ \sin(\varphi_h) , \qquad (21)$$

irrespective of whether J is integer or half-integer. This equation implies that the corresponding magnetic moments at saturation are directed along one of the four easy axes. This intermediate asymptotic is valid in the range $w \ll hJ \ll bJ^4$ where our tight-binding treatment stays valid. At significantly larger h the saturation magnetic moment is directed parallel to the magnetic field. Comparing (20) and (21), we find that the finite magnetic moment at low magnetic field for half-integer J is precisely half of its saturation value ($9.8\mu_{\rm B}$ for Dy^{3+}; cf. $10\mu_{\rm B}$ for Ho^{3+} with integer J).

Let us consider now the action of magnetic field along the z axis. To do so we rewrite

$$\frac{a}{2} J_z^2 - hJ_z = \frac{a}{2}\left(J_z - \frac{h}{a}\right)^2 - \frac{h^2}{2a} = \frac{a}{2}\left(-\frac{i\partial}{\partial\varphi} + A_\varphi - \frac{h}{a}\right)^2 - \frac{h^2}{2a} . \qquad (22)$$

From this we infer that the z-axis magnetic field adds a constant to the Hamiltonian and acts as if the connection A_φ is changed in the manner $A'_\varphi = A_\varphi - h/a$. Inserting A'_φ in (12) shows that the Peierls phase α in (11) is changed like $\alpha \to \alpha - \pi h/(2a)$. The effect of the Peierls phase change on the eigenenergies and on the ground-state energy, in particular, is easily found in (15). So, for integer J, we have $E = -2w \cos[\pi h/(2a)] - h^2/(2a)$ and from this $\chi_{\rm axis} = a^{-1} - \pi^2 w/(2a^2)$. Because of the exponential smallness of w [see (13)] the second term is negligible compared to the first one, and we find $\chi_{\rm axis} = a^{-1}$ for integer J. Note that $\chi_{\rm axis}$ is exponentially small compared to $\chi_{\rm plane}$ in (19) which proves the consistency of our treatment for which we assumed that the moments are essentially confined to the plane. For half-integer spin we consider $E = -2w \cos[\pi h/(2a) - \pi/4] - h^2/(2a)$ and derive $\mu = -g\mu_{\rm B}\partial E/(\partial h) = g\mu_{\rm B} w/(\sqrt{2}\,a)$ for the local moment in z direction. We obtain again a moment in z direction which is exponentially small compared to the one in the plane (20) consistent with the outset of our theory. We observe that the difference between integer and half-integer J is also visible in the magnetic properties perpendicular to the easy plane.

The quasiclassical treatment implying the splitting of each oscillatory level into a quadruplet is valid provided that the level spacing between the localized oscillatory levels ω is much larger than w. It is certainly incorrect for energies E close to the maximum potential energy $U_{\rm max} = 2bJ^2$. One should have a rough idea of how many quadruplets our treatment can be expected to apply to. In the cases of interest $J = 15/2$, 8 the total number of states is 16 or 17. Thus one can expect that one or two quadruplets are well described by the effective four-site tight-binding model. This conclusion is confirmed by direct diagonalization of the 17×17 matrix in a model crystal field [15]. In order to have an estimate for the ratio b/a we compare the total number of states $2J + 1$ with the number of levels N in the four wells of the potential $U(\varphi) = -(bJ^4/2)[3 + \cos(4\varphi)]$ in the quasiclassical approach

$$N = \frac{8}{\pi\hbar}\int_0^{\pi/4}\sqrt{2m[U_{\max} - U(\varphi)]}\,d\varphi = \sqrt{\frac{32bJ^4}{\pi^2 a}}\,. \tag{23}$$

The area in phase space of the maximum classical orbit is divided by $2\pi\hbar$ to obtain an estimate for the number of states. Here $\hbar^2/m$ is set to a. The upper boundary for N is $2J + 1 \approx 2J$, we find $bJ^2/a \leq \pi^2/8 \approx 1.23$.

Let us discuss the experimental consequences of the difference between integer and half-integer J described above. The clearest manifestations would occur in dilute alloys of the type $R_{1-x}R'_x\mathrm{Ni_2B_2C}$, where $R =$ La, Lu, Y, and $R' =$ Dy, Ho. All three triply charged ions R have zero magnetic moment. The direct check of our prediction would be the measurement of EPR spectra for these alloys at low temperature $T < w$ (at about 2 K according to the estimate in [15]). We expect that the lowest four levels are split as described above into singlet, doublet, and singlet for Ho. The resonance frequency will not depend much on the magnetic field as long as $hJ \ll w$. In the case of Dy alloys, however, the EPR resonance frequency is proportional to the magnetic field as long as this is small due to the finite magnetic moment. One can also check the nonlinear dependence of energies (17a) and (17b) on the magnetic field.

Another option is to measure the magnetic field at a nucleus by NMR. The magnetic field at a nucleus must be essentially zero for Ho alloys and nonzero for Dy alloys.

Finally, one can also measure the spin magnetic susceptibility of the alloys at low temperatures. At temperatures $T > w$, the in-plane magnetic susceptibilities for both Ho and Dy compounds almost coincide and are equal to $(g\mu_B J)^2/(2k_B T) \approx 50\mu_B^2/(k_B T)$ per ion. At low temperatures $T < w$, the magnetic susceptibility of the Ho compounds saturates at the value $(g\mu_B J)^2/(2w)$, whereas the Dy compounds display the Curie susceptibility with half as much coefficient $(g\mu_B J)^2/(4k_B T) \approx 25\mu_B^2/(k_B T)$ per ion. The Curie susceptibility in Dy alloy will persist down to $T \approx 0.1$ K at $x = 0.01$.

In an interesting paper [16] Loss *et al.* considered a simpler version of the crystal field symmetry, creating twofold degenerate level for a large spin. In this case the Kramers degeneracy ensures the suppression of the tunneling for half-integer spins. We have shown that such a full suppression is a specific feature of this low-symmetry situation and does not take place for higher symmetries.

Berry's connection must be taken into account for many-body problems as well. For example, for the quantum XY-model Berry's connection $A_\phi = 0, 1/2$ leads to a fundamental difference in the nature of the ground state for integer and half-integer spins. It will be described in a future publication. An analysis of Berry's phase modification for soliton dynamics in 1D Ising ferromagnet has been done in [17].

In conclusion, we have shown that the well-known difference between the magnetic properties of ions of integer or half-integer total magnetic moments J due to the absence or presence of Kramers degeneracy is captured in the quasiclassical limit of large J by a Berry phase. In the tetragonal environment studied here, integer spins display no finite magnetic moment in the ground state, whereas the half-integer spins display a finite magnetic moment of half their saturation value. The difference is due to Kramers degeneracy [7] necessarily associated with half-integer spins. Any quasiclassical approach has to take the geometric Berry phase into account in order to capture the essential difference between integer and half-integer spins. The difference should be manifest in the spectrum of EPR, in NMR, and in the magnetic susceptibility of diluting the alloys $\mathrm{Lu_{1-x}Ho_xNi_2B_2C}$ and $\mathrm{Lu_{1-x}Dy_xNi_2B_2C}$.

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[1] F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983); Phys. Lett. **93A**, 464 (1983); Bull. Am. Phys. Soc. **27**, 181 (1982).

[2] D. J. Newman, Adv. Phys. **20**, 197 (1971).

[3] M. V. Berry, Proc. R. Soc. London A **392**, 45 (1984).

[4] J. Moody, A. Shapere, and F. Wilczek, Phys. Rev. Lett. **56**, 893 (1986).

[5] F. Wilczek and A. Zee, Phys. Rev. Lett. **52**, 2111 (1984).

[6] A. Shapere and F. Wilczek, *Geometric Phases in Physics* (World Scientific, Singapore, 1989).

[7] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970), p. 647.

[8] R. J. Cava *et al.*, Nature (London) **376**, 146 (1994); R. Nagaranjan *et al.*, Phys. Rev. Lett. **72**, 274 (1994).

[9] T. Siegrist *et al.*, Nature (London) **367**, 254 (1994).

[10] M. Xu *et al.*, Physica (Amsterdam) **227C**, 381 (1994).

[11] K. D. D. Rathnayaka *et al.*, Phys. Rev. B **53**, 5688 (1996).

[12] V. A. Kalatsky and V. L. Pokrovsky, Report No. cond-mat 9511135; Phys. Rev. B (to be published).

[13] One can also discuss any of the excited states as long as these are well localized in the minima.

[14] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976).

[15] B. K. Cho, B. N. Harmon, D. C. Johnston, and P. C. Canfield, Phys. Rev. B **53**, 2217 (1996).

[16] D. Loss, D. DiVincenzo, and G. Grinstein, Phys. Rev. Lett. **69**, 3233 (1992).

[17] H. B. Braun and D. Loss, Phys. Rev. B **53**, 3237 (1996).