Berry-Phase Calculation of Magnetic Screening and Rotational g Factor in Molecules and Solids

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The orbital magnetic moment due to rotation or pseudorotation in a molecule or a solid and the corresponding rotational g factor are formulated using the Berry-phase technique and standard density functional plane wave methods. Among the simplest molecules, H_2^+, H_2, C_2H_2, CH_4, and CF_4, with known rotational g factors, are used as test cases with excellent results. Alternative, faster localized orbital calculations including the magnetic coupling through heuristic Peierls phase factors are also tested and found to be viable, though less accurate. Application to pseudorotations is exemplified in benzene. It is proposed that these methods will be suited for application to pseudorotations in solids.

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Rotations and pseudorotations in molecules and in solids are cyclic motions where the ionic coordinates execute a closed orbit, thus giving rise, in virtue of their bare charge, to an orbital magnetic moment. Electrons, however, also take part in the motion; and were they to cling infinitely tightly to the ions, they should completely screen—totally cancel—the ionic orbital magnetic moment. In reality, the electrons are tied only softly to the ions, and do not exactly cancel the ionic magnetic moment. The compound result of ion and electron orbital motion is a total rotational g factor tensor g_{ii}^R, $i = 1, 2, 3$ [1], whose components may take real values, ranging from one (no screening) to zero (perfect screening), to negative (overscreening). g_{ii}^R is a basic property, long known for rotation of simple molecules such as H_2 [2,3], but not always quantitatively available, particularly for pseudorotations. The latter may be of special relevance for Jahn-Teller (JT) and pseudo-JT systems in free molecules and in solids. High-accuracy Hartree-Fock and multiconfigurational self-consistent field molecular calculations of rotational g factors are well established in the chemical literature[1,4,5] . Though quite successful, these approaches are not easily extended to solids. On the other hand, the density functional methods that are standard in both solids and molecules could, in principle, be straightforwardly extended to calculate g^R, e.g., through the Berry-phase technique [6–8] introduced in computational physics by King-Smith and Vanderbilt [9] and recently applied to spin waves by Niu *et al.* [9]; but no practical implementation appears to be available.

In this Letter, we introduce practical and accurate density functional Berry-phase plane wave calculations of the rotational g factor of closed-shell electronic systems, molecular or solid. We provide a first demonstration by applying them to rotation and pseudorotation of simple molecules, for some of which accurate g^R values are available, and where a direct physical interpretation of the magnetic screening factor is quite transparent. An alternative density functional local orbital calculation scheme including magnetic field through Peierls phase factors, a heuristic simplification of the more standard phase shifted London basis [4], is benchmarked against the plane wave method, and is shown to be viable and considerably faster, if somewhat less accurate. Application to pseudorotations are finally presented for benzene, laying the ground for future application to pseudorotations in solids.

In the adiabatic approximation, the kinetic energy of ion α with canonical momentum $\mathbf{P}_\alpha$ in an external magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$ is [6–8]

$$T = \frac{1}{2M}[\mathbf{P}_\alpha - \mathbf{A}(\mathbf{R}_\alpha) + \boldsymbol{\chi}_\alpha]^2, \quad (1)$$

where, as usual, $\mathbf{A}$ accounts for the bare Lorentz force, and $\boldsymbol{\chi}_\alpha = i\sum_n^{\mathrm{occ}}\langle\psi_n|\nabla_{\mathbf{R}_\alpha}|\psi_n\rangle$ is the electronic screening correction to the bare Lorentz force, in the form of a Berry connection. The role of this geometric vector potential is to carry the extra field-induced phase factor due to the adiabatic evolution of electrons with wave functions $|\psi_n\rangle$ depending parametrically upon $\mathbf{R}_\alpha$, and is a natural consequence of the requirement that the wave functions be single valued as a function of the nuclear coordinates [6]. Instead of evaluating directly the Berry connection $\boldsymbol{\chi}$, we calculate the discrete Berry-phase γ [8] around a closed orbit in configuration space ($\mathbf{R}_\alpha$), by subdividing the path in a finite number of steps:

$$\gamma = i\oint \boldsymbol{\chi}(\mathbf{R}) \cdot \mathbf{dR} \simeq -\mathrm{Im}\log\ \det\prod_{\xi=0}^{N-1}\langle\psi_\xi|\psi_{\xi+1}\rangle, \quad (2)$$

where index ξ runs on successive atomic configurations in the orbit. This discrete formulation (2) has the crucial advantage of being applicable regardless of the regularity of the phase around the path [8], a quantity uniquely determined by the condition that the highest occupied orbital be separated by a finite gap from the lowest unoccupied at any ξ point of the path. The adiabatic approximation assumed should be fully valid insofar as the rotational excitation energies remain much smaller than that gap. Richer situations could arise for molecular systems with an odd electron number and degeneracy [7]; we shall restrict here to nondegenerate closed-shell cases.

In general, the orbit will either consist of a true molecular rotation, or of a pseudorotation in a molecule or in a solid, where the nuclei undergo concerted small size orbits, generally not circular but closed, around highly symmetric positions. In a pure rotation about some axis, the nuclei are planar rigid rotators and the bare magnetic phase is simply equal to the total flux through the circular orbits of all nuclei, each weighted by its charge. For each nucleus, we used an effective nuclear charge equal to the valence charge only, assuming the core electrons, when present, to be well localized so as to screen completely the corresponding nuclear charge fraction. The Berry-phase summation (2) must generally be carried out explicitly over a suitably fine set of points, covering a finite irreducible arc as dictated by the point symmetry of the molecule or of the crystal cell. The magnetic screening σ is defined as the ratio of the Berry phase over the bare magnetic phase. The rotational g factor, the ratio between the total molecular magnetic moment and the mechanical moment, is

$$g = (\sigma + 1)\frac{\sum_\alpha Z_\alpha r_\alpha^2}{\sum_\alpha m_\alpha r_\alpha^2}, \tag{3}$$

where r_α is the distance of nucleus α from the rotation axis, m_α is its mass in proton units, and Z_α is its valence charge. Calculations were carried out within standard density functional theory (DFT) in the local density approximation, using norm conserving pseudopotentials and plane wave expansions up to 80 Ry. Molecules were placed in a periodically repeated cubic cell, large enough to make interactions between copies irrelevant. We restricted to weak magnetic fields, of the order of laboratory fields (10^4–$10^5 G$), whose effect can be treated as a perturbation—the charge distribution thus unchanged to lowest order. The field was parallel to the rotation axis, taken through the center of mass and perpendicular to the molecular axis in H_2, H_2^+, C_2H_2, along one of the bonds in CH_4 and CF_4, and orthogonal to the molecular plane in benzene. First order corrections to the ground state wave functions were calculated within linear response theory [10] following the prescription of Ref. [11]. The vector potential was chosen in the following form:

$$\mathbf{A_q} = (i\mathbf{q} \times \mathbf{B_q})/(\mathbf{c}\ |\mathbf{q}|^2)\exp[i\mathbf{q} \cdot \mathbf{r}]. \tag{4}$$

This corresponds to a magnetic field $\mathbf{B} = \mathbf{B_q}\exp[i\mathbf{q} \cdot \mathbf{r}]$, modulated with a small wave vector $\mathbf{q} \perp \mathbf{B}$. For practical calculations, we chose $|q| = 0.01\pi/a$, where a is the side of the cubic cell.

If the unperturbed Hamiltonian can be chosen to be real, as is the case for local pseudopotentials, the electronic Berry-phase calculation can be simplified exploiting full rotational symmetry, i.e., iterating to 2π the incremental phase difference between two very close configurations. The summation must instead be done explicitly for nonlocal pseudopotentials where the Hamiltonian is complex, and only the cell symmetry can be used. The same applies to pseudorotations, where the orbit has molecular symmetry and is generally not circular.

As the first test case, we studied the rotation of H_2^+, a single electron molecule that can be calculated exactly. Setting the bond distance at the experimental equilibrium value 2.0 a.u., and using for H the bare proton Coulomb potential (not the pseudopotential), we obtained an electron screening of -5.4%, and thus a g factor of 0.946 (see Table I for convergence details). This, we note, is a very

TABLE I. Plane wave (PW), localized-basis (LB), and exact (EX) result: DFT stands for pseudopotential self-consistent local density functional calculation; unless otherwise indicated, the PW calculations are DFT with a PW cutoff energy of 80 Ry. SZ, DZ, and DZP are basis sets used for the LCAO expansion.

Molecule	g factor	Notes
H_2^+	0.9459	PW, EX 80 Ry
(rotation)	0.9458	PW, EX 120 Ry
	0.9457	PW, EX 160 Ry
	0.9457	PW, EX 200 Ry
	0.9425	PW, DFT 80 Ry
	0.9411	LB, SZ
	0.9115	LB, DZ
	0.9359	LB, DZP
H_2	0.8787	Experiment [2]
(rotation)	0.8755	PW
	0.8765	LB, SZ
	0.8258	LB, DZ
	0.8694	LB, DZP
	0.8899	MCSCF [5]
C_2H_2	0.0490	Experiment [3]
(rotation)	0.0405	PW
	0.0782	LB, SZ
	0.0139	LB, DZP
	0.0570	MCSCF [5]
CF_4	−0.0312	Experiment [3]
(rotation)	−0.0445	PW
	−0.0151	LB, SZ
	+0.0080	LB, DZP
CH_4	0.2040	PW
(rotation)	0.219	LB, SZ
C_6H_6	0.7851	PW, $A = 0.04$ Å
(pseudorotation ν_{18})	0.7934	PW, $A = 0.10$ Å
	0.7596	LB, SZ, $A = 0.02$ Å
	0.7593	LB, SZ, $A = 0.04$ Å
	0.7595	LB, SZ, $A = 0.10$ Å

poor screening, reflecting the effective concentration of the electron in the vicinity of the bond center. Lacking an experimental comparison, this accurate result, while confirming an earlier variational estimate of about -5% [12], can be used to test the standard self-consistent pseudopotential electronic structure calculations to be routinely used later on. Carrying out that calculation for H_2^+ using now a pseudopotential for H, and standard self-consistency (as if H_2^+ were a many-electron system), we found a g factor of 0.9425, in close agreement with the exact result 0.946. Satisfied by this check, we moved on to calculate the rotational g factor of the H_2 molecule. Using the experimental bond length of 1.4 a.u., we calculated a g factor of 0.8755, in excellent agreement with the experimental value of 0.8787 obtained long ago by Ramsey [2]. Comparison with H_2^+ indicates that the two electrons of H_2 just approximately double to -12.45% the single electron screening -5.4% of H_2^+, irrespective of a factor 1.42 in the H—H distance.

In order to further benchmark the accuracy of our method, we considered next three molecules with large magnetic screening and small g factors [3], namely, acetylene (C_2H_2), methane (CH_4), and carbon tetrafluoride (CF_4). In these molecules, the C—H and C—F bonds possess a partly ionic character, some electron fraction attracted to a larger distance from the center, and thus likely to screen more effectively the nuclei. Our results (Table I) confirm a large screening and agree very closely with experiment where available. The small g factor is thus an indicator of ionicity, whereas (as exemplified by H_2) a g factor close to 1 is characteristic of the covalent bond. The marginally positive g factor of C_2H_2 confirms nearly perfect screening of nuclei, whereas the marginally negative g factor of CF_4 indicates a slight overscreening ($|\sigma| > 1$), due to an important electron fraction that effectively orbits beyond the C—F distance. For CH_4, we calculated a rotational g factor of 0.20, but found no data in literature for comparison. However, constrained rotations of methyl end groups (—C—CH_3) about the C—C bond have been studied. In particular, the $L = 1$ rotational state $\Delta E = \mu_N g^R B \Delta m =$ (7.622 MHz) $g^R B \Delta m$ (B in tesla) has been pursued [13] by NMR in acetylacetone [$(CH_3CO)_2$], showing a splitting of about 38 kHz for a field of 0.05 T, corresponding to a methyl group g factor of about 0.1. This screening level is somewhat larger than that calculated for CH_4, most likely reflecting a slight increase in ionicity of the methyl C—H bonds, compensating the decrease in the C—C bond. This underlines an exquisite sensitivity of the rotational g factor to even delicate changes of the chemical circumstances.

Besides rotations, the present technique can be directly applied to calculate g factors for pseudorotations. They appear in molecules and in solids as suitably degenerate vibrational modes. As the simplest prototype, we chose the lowest E_2 mode of benzene C_6H_6, of frequency ν_{18} at 606 cm^{-1} [14]. Here, nuclei move in the molecular plane, the pseudorotation generated by combining the two eigenmodes with a phase factor $\mathbf{u_i} = \mathbf{A}(\theta)[\mathbf{u_i}^{(1)} \cos\theta + \mathbf{u_i}^{(2)} \sin\theta]$, where $A(\theta)$ is the amplitude. For a general large distortion, $A(\theta)$ should, of course, be determined for each θ in such a way to minimize the total energy, giving a noncircular pseudorotation orbit; in the present case of a small vibration, $A(\theta)$ was chosen constant. A pseudorotation in benzene is expected to trigger orbital currents encircling the large molecular radius, and that might lead to unusually large magnetic screenings. The calculated g factor of benzene (Table I) indicates instead for this pseudorotational mode a surprisingly modest 20% screening by the orbital electron currents. To understand that, we display in Fig. 1 frames showing the evolution with θ of the electron charge density difference relative to undistorted benzene. Atoms pseudorotate counterclockwise, their small orbit causing large orbital electron currents with a complex pattern. The electron imbalance forms a sort of dipole—from the C—H bonds to the carbon ring—that rotates clockwise, while shifting phase, until at $\theta = \pi$ its sign has reversed—from the carbon ring to the C—H bonds. Moreover, from $\theta = \pi$ until $\theta = 2\pi$, the charge motion occurs in reverse. The nearly exact balance of positive and negative currents explains the globally small magnetic screening in benzene. According to our calculated g factor, a magnetic field should theoretically lead to a splitting of this E_2 mode $\delta\nu_{18} = 5.984$ MHz $(B/\text{tesla})\ \Delta m$. For a field of 10 T, the calculated splitting is only a tiny 59.8 MHz, when compared with a reported linewidth of about 500 GHz even below 50 K [15].

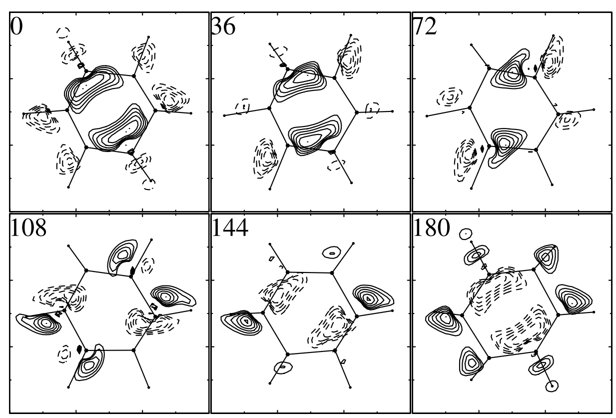

FIG. 1. Illustration of orbital current caused by a pseudorotation in benzene. Plot shows the difference between distorted and undistorted electron density in the molecular plane at increasing values of the phase θ of the counterclockwise ion pseudorotation. Full lines: electron accumulation; dashed lines: electron depletion. Interval between isocharge lines: 4×10^{-5} (au)$^{-2}$. Carbon displacement amplitude 0.1 Å, here enhanced by a factor for clarity. Note the clockwise motion of electron accumulation, and its phase shift into a depletion at $\theta = \pi$. The current is basically reversed from $\theta = \pi$ to $\theta = 2\pi$, explaining a relatively small magnetic screening (see text).

In addition to the accurate plane wave calculations just demonstrated, it seemed desirable to develop an even simpler scheme for a faster approximate evaluation of rotational and pseudorotational g factors. We explored a parallel formulation based on a localized-basis set, applicable both to isolated molecules and to periodic systems. Consider a wave function $\psi_{\mathbf{R}}(\mathbf{r})$ for a nondegenerate level of an atom located at position $\mathbf{R}$. Translation in a field is accompanied by a phase factor [16] $\psi_{\mathbf{R}}(\mathbf{r}) = \psi_0(\mathbf{r} - \mathbf{R}) \exp[(ie/c)\Phi(\mathbf{R} \rightarrow \mathbf{r})]$, where $\psi_0(\mathbf{r} - \mathbf{R})$ is the atomic wave function centered in $\mathbf{R}$; and $\Phi(\mathbf{R} \rightarrow \mathbf{r})$ is the integral of the vector potential along the straight line connecting $\mathbf{R}$ to $\mathbf{r}$. For a very localized state, the magnetic phase factor can be included in the tight-binding or LCAO form,

$$\Psi(\mathbf{r}) = \sum_{\mathbf{k}} \mathbf{c}_{\mathbf{k}} \exp[(ie/c)\Phi(\mathbf{R}_{\mathbf{k}} \rightarrow \mathbf{r})]\phi_{\mathbf{k}}(\mathbf{r} - \mathbf{R}_{\mathbf{k}}), \quad (5)$$

where k is the index spanning all the localized-basis functions, $\mathbf{R}_{\mathbf{k}}$ is center of the kth basis function, and $\Phi(\mathbf{R}_{\mathbf{k}} \rightarrow \mathbf{r})$ is the phase associated with the center $\mathbf{R}_{\mathbf{k}}$. In conclusion, the hopping matrix elements of the one-body effective Hamiltonian, are renormalized by the so-called Peierls factor:

$$H_{kk'} \rightarrow H_{kk'} \exp[(ie/c)\Phi(\mathbf{R}_{\mathbf{k}} \rightarrow \mathbf{R}_{\mathbf{k}'})]. \quad (6)$$

This Peierls phase approximation is valid for slowly varying magnetic field relative to atomic distances. It should become equivalent to the exact London shifted basis [4] in the limit of infinitely localized-basis functions, and is thus affected by an error proportional to the amount of delocalization. Within this formalism, there is no need to perform a linear response calculation, but only standard matrix diagonalizations. We employed the fully self-consistent DFT code SIESTA [17], based upon an expansion of the wave functions on atom-centered basis orbitals, and the same pseudopotentials as described earlier. The charge density was expanded up to a kinetic energy of 320 Ry. We used three sets of basis functions: the minimal basis (single-ξ, SZ); the SZ basis set plus the first excited states (double-ξ, DZ); the DZ basis plus d orbitals (DZP). Following the same procedure as in the plane wave case, we diagonalized the Hamiltonian for different atomic configurations and calculated the Berry phase with Eq. (2). We repeated calculations for all molecules considered earlier, and obtained the rotational g factors summarized in Table I. Though clearly less accurate, the agreement with experiment and with the plane wave calculations is still quite good. Interestingly, the simplest minimal basis set SZ calculations, including just one function per angular momentum channel, gives the best results. In particular, in CF_4 where the g factor is marginally negative, the bigger DZP calculation fails to reproduce the overscreening but the SZ gets it. When using larger basis sets, the excited states are more diffuse and the Peierls approximation is evidently worse. Altogether the localized-basis calculations require much less computational effort than the plane wave ones. In our case, the CPU time required was 4 to 5 times smaller; and for bigger molecules the ratio is expected to increase. Moreover, the memory requirements are far smaller, since the wave functions do not need to be memorized. This advantage should make that method preferable for larger size problems where the plane wave approach becomes impractical.

We stress in closing that, formulated as they are on a periodic lattice, both methods described here are automatically suited to calculate magnetic screening for rotations and pseudorotations in insulating solids. We are actively working along that direction, and will be reporting results in the near future.

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