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

Davide Ceresoli\textsuperscript{1,2} and Erio Tosatti\textsuperscript{1,2,3}

\textsuperscript{1} International School for Advanced Studies (SISSA), Trieste, Italy
\textsuperscript{2} Istituto Nazionale per la Fisica della Materia (INFM), Unità SISSA, Trieste, Italy.
\textsuperscript{3} International Center for Theoretical Physics (ICTP), Trieste, Italy.

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The orbital magnetic moment due to rotation or pseudo-rotation 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\textsubscript{2}, H\textsubscript{2}, C\textsubscript{2}H\textsubscript{2}, CH\textsubscript{4} and CF\textsubscript{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 solvates, to an orbital magnetic moment. Electrons to cling infinitely tightly to the ions, they should completely screen – totally cancel – the ionic orbital magnetic moment. In reality, the electrons are only softly tied 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 $g^R_{ij}$, $i = 1, 2, 3$ [1], whose components may take real values, ranging from one (no screening) to zero (perfect screening), to negative (overscreening). $g^R_{ij}$ is a basic property, long known for rotation of simple molecules such as H\textsubscript{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 Multi Configurational 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 $\alpha$ with canonical momentum $P_\alpha$ in an external magnetic field $B = \nabla \times A$ is [6-8]:

$$T = \frac{1}{2M} (P_\alpha - A(R_\alpha)) + \chi_\alpha^2,$$

where as usual $A$ accounts for the bare Lorentz force, and $\chi_\alpha = i \sum_n \langle \psi_n | \nabla R_\alpha | \psi_n \rangle$ 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 wavefunctions $|\psi_n\rangle$ depending parametrically upon $R_\alpha$, and is a natural consequence of the requirement that the wavefunctions be single-valued as a function of the nuclear coordinates [6]. Instead of evaluating directly the Berry connection $\gamma$ we calculate the discrete Berry phase $\gamma$ around a closed orbit in configuration space ($R_\alpha$), by subdividing the path in a finite number of steps:

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

where index $\xi$ runs on successive atomic configurations in the orbit. This discrete formulation (2) has the crucial
advantage of being applicable regardless of the regular-
ity 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 un-
occupied at any ξ-point of the path. The adiabatic ap-
proximation assumed should be fully valid insofar as the
rotational excitation energies remain much smaller than
that gap. Richer situations could arise for molecular sys-
tems 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 molecu-
lar 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 circu-
lar 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 com-
pletely 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 fi-
nite irreducible arc as dictated by the point symmetry of
the molecule or of the crystal cell. The magnetic screen-
ing σ is defined as the ratio of the Berry phase over the
bare magnetic phase. The rotational g-factor, the ratio
between the total magnetic moment and the mechanical
moment, is:

\[ g = (\sigma + 1) \frac{\sum_{\alpha} Z_{\alpha} r_{\alpha}^2}{\sum_{\alpha} m_{\alpha} r_{\alpha}^2}, \]  

where \( r_{\alpha} \) is the distance of nucleus \( \alpha \) from the rota-
tion axis, \( m_{\alpha} \) is its mass in proton units and \( Z_{\alpha} \) its
valence charge. Calculations were carried out within stan-
dard density functional theory (DFT) in the local density
approximation, using normconserving 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 re-
stricted to weak magnetic fields, of the order of labora-
tory fields (10^4 – 10^6 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 \( \text{H}_2 \), \( \text{H}_2^+ \), \( \text{C}_2\text{H}_2 \), along one
of the bonds in \( \text{CH}_4 \) and \( \text{CF}_4 \), and orthogonal to the
molecular plane in benzene. First order corrections to
the ground state wavefunctions were calculated within
linear response theory [10] following the prescription of
ref. [11]. The vector potential was chosen in the form:

\[ \mathbf{A}_q = (i \mathbf{q} \times \mathbf{B}_q) / (c |\mathbf{q}|^2) \exp[i \mathbf{q} \cdot \mathbf{r}], \]  

This corresponds to a magnetic field \( \mathbf{B} = \mathbf{B}_q \exp[i \mathbf{q} \cdot \mathbf{r}] \), modulated with a small wave vector \( \mathbf{q} \perp \mathbf{r} \).

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 elec-
tronic Berry phase calculation can be simplified exploit-
ing full rotational symmetry, i.e., iterating to 2π the in-
cremental phase difference between two very close con-
figurations. The summation must instead be done ex-
licitly for nonlocal pseudopotentials where the hamilton-
ian 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 \( \text{H}_2^+ \),
a single electron molecule that can be calculated exactly.
Setting the bond distance at the experimental equilib-
rium value 2.0 a.u., and using for \( \text{H} \) 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 poor screening, reflecting the effective concen-
tration of the electron in the vicinity of the bond center.
Lacking an experimental comparison, this accurate re-
sult, while confirming an earlier variational estimate of
about \(-5\% \) [12], can be used to test the standard self-
consistent pseudopotential electronic structure calcula-
tions to be routinely used later on. Carrying out that
calculation for \( \text{H}_2^+ \) using now a pseudopotential for \( \text{H} \),
and standard self-consistency (as if \( \text{H}_2^+ \) 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 \( \text{H}_2 \) molecule. Using the experimental bond length
of 1.4 a.u., we calculated a g-factor of 0.8755, in excel-
 lent agreement with the experimental value of 0.8787 ob-
tained long ago by Ramsey [2]. Comparison with \( \text{H}_2^+ \)
indicates that the two electrons of \( \text{H}_2 \) just approximately
double to \(-12.45\% \) the single electron screening \(-5.4\% \)
of \( \text{H}_2^+ \), 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 acetyl-
enone (\( \text{C}_2\text{H}_2 \)), methane (\( \text{CH}_4 \)) and carbon tetrachloride
(\( \text{CF}_4 \)). In these molecules the C–H and C–F bonds pos-
sess a partly ionic character, some electron fraction at-
ttracted 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
\( \text{H}_2 \)) a g-factor close to 1 is characteristic of the covalent
bond. The marginally positive g-factor of \( \text{C}_2\text{H}_2 \) confirms
nearly perfect screening of nuclei, whereas the marginally
negative g-factor of \( \text{CF}_4 \) indicates a slight overscreening
(|σ| > 1), due to an important electron fraction that ef-
f ectively orbits beyond the C – F distance. For \( \text{CH}_4 \), 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-CH₃) about C-C bond have been studied. In particular the L = 1 rotational state $\Delta E = \mu H_0 B \Delta m = 7.622 \text{ MHz} g^B \Delta m$, (B in Tesla) has been pursued [13] by NMR in acetyl-acetone ((CH₃CO)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 CH₄, 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 $\nu_{18}$ at 606 cm⁻¹ [14]. Here nuclei move in the molecular plane, the pseudorotation generated by combining the two eigenmodes with a phase factor $u_1 = A(\theta) u_1^{(1)} \cos \theta + u_1^{(2)} \sin \theta$, where $A(\theta)$ is the amplitude. For a general large distortion, $A(\theta)$ should of course be determined for each $\theta$ 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 $\theta$ 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 $\delta \nu_{18} = 5.984 \text{ MHz} (B/\text{Tesla}) \Delta m$. For a field of 10 Tesla the calculated splitting is only a tiny 59.8 MHz, when compared with a reported line width of about 500 GHz even below 50 K [15].

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 wavefunction $\psi_R(r)$ for a non-degenerate level of an atom located at position $R$. Translation in a field is accompanied by a phase factor [16] $\psi_R(r) = \psi_R(r - R) \exp[(ie/c)\Phi(R - r)]$, where $\psi_R(r - R)$ is the atomic wavefunction centered in $R$; and $\Phi(R - r)$ is the integral of the vector potential along the straight line connecting $R$ to $r$. For a very localized state the magnetic phase factor can be included in tight-binding or LCAO form

$$\Psi(r) = \sum_k c_k \exp[(ie/c)\Phi(R_k - r)] \phi_k(r - R_k),$$

where $k$ is the index spanning all the localized basis functions, $R_k$ is center of the $k$-th basis function, and $\Phi(R_k - r)$ is the phase associated with the center $R_k$. In conclusion, the hopping matrix elements of the one-body effective hamiltonian, are renormalized by the so called Peierls factor:

$$H_{kk'} \rightarrow H_{kk'} \exp[(ie/c)\Phi(R_k - R_{k'})].$$

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 equation (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 CF₄ 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 wavefunctions 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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<table>
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<tr>
<th>Molecule</th>
<th>g-factor</th>
<th>Notes</th>
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<tr>
<td>H$_2$</td>
<td>0.9459</td>
<td>PW, EX 80 Ry</td>
</tr>
<tr>
<td>(rotation)</td>
<td>0.9458</td>
<td>PW, EX 120 Ry</td>
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<td></td>
<td>0.9457</td>
<td>PW, EX 160 Ry</td>
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<td>0.9457</td>
<td>PW, EX 200 Ry</td>
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<td></td>
<td>0.9425</td>
<td>PW, DFT 80 Ry</td>
</tr>
<tr>
<td></td>
<td>0.9411</td>
<td>LB, SZ</td>
</tr>
<tr>
<td></td>
<td>0.9115</td>
<td>LB, DZ</td>
</tr>
<tr>
<td></td>
<td>0.9559</td>
<td>LB, DZP</td>
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<tr>
<td>H$_2$</td>
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<td>Expt. [2]</td>
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<tr>
<td>(rotation)</td>
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<td>PW</td>
</tr>
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<td></td>
<td>0.8705</td>
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<td></td>
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<tr>
<td></td>
<td>0.8899</td>
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<td>C$_2$H$_2$</td>
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<tr>
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<td>0.0405</td>
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<td>0.0782</td>
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<td></td>
<td>0.0139</td>
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<tr>
<td></td>
<td>0.0570</td>
<td>MCSCF [5]</td>
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<td>CF$_4$</td>
<td>0.0312</td>
<td>Expt. [3]</td>
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<tr>
<td>(rotation)</td>
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<td>PW</td>
</tr>
<tr>
<td></td>
<td>0.0151</td>
<td>LB, SZ</td>
</tr>
<tr>
<td></td>
<td>+0.0080</td>
<td>LB, DZP</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.2040</td>
<td>PW</td>
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<td>(rotation)</td>
<td>0.219</td>
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<tr>
<td>C$_2$H$_6$</td>
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<td>PW, A = 0.04 Å</td>
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<tr>
<td>(pseudo-rotation $\nu_{18}$)</td>
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<td>LB, SZ, A = 0.02 Å</td>
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<tr>
<td></td>
<td>0.7595</td>
<td>LB, SZ, A = 0.10 Å</td>
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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.

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 $\theta$ of the counterclockwise ion pseudorotation. Full lines: electron accumulation; dashed lines: electron depletion. Interval between isocharge lines: $4 \times 10^{-5}$ (au)$^{-2}$. Carbon displacement amplitude 0.1 Å, here enhanced by a factor 5 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).