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Cite as: J. Chem. Phys. 155, 234101 (2021); https://doi.org/10.1063/5.0069637
Submitted: 01 September 2021 • Accepted: 22 November 2021 • Accepted Manuscript Online: 22 November 2021 • Published Online: 15 December 2021


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Cite as: J. Chem. Phys. 155, 234101 (2021); doi: 10.1063/5.0069637
Submitted: 1 September 2021 • Accepted: 22 November 2021 • Published Online: 15 December 2021

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ABSTRACT
In this study, we benchmark density functional theory gauge-including projector-augmented-wave (GIPAW) chemical shieldings against molecular shieldings for which basis set completeness has been achieved [Jensen et al., Phys. Chem. Chem. Phys. 18, 21145 (2016)]. We demonstrate the importance of two-center corrections for GIPAW hydrogen shieldings. For the other nuclei studied, standard GIPAW is sufficiently accurate. We find that GIPAW can be pushed to closely approach the basis set limit. The only source of small inaccuracies lies in the contribution to the shielding that is caused by surface currents, which we estimate comparing GIPAW susceptibilities to converged molecular magnetizabilities.

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I. INTRODUCTION
Solid state NMR is a proven method for structure elucidation and the study of the dynamics of materials.1 Interpretation of the solid state NMR data benefits from a combination of experimental and computational experiments, viz., the calculation of NMR chemical shieldings.2 In particular, the gauge-including projector-augmented-wave (GIPAW)3,4 method has been very successful in calculating chemical shieldings for solid state crystalline systems.3,4,7 Benchmarks against molecular and solid state calculations using various other methods demonstrate its accuracy.3,4,7

The GIPAW method is an extension of the PAW method of Blöchl.8,9 In the PAW method, the orbitals are represented as a sum of smooth pseudo-orbitals and one-center corrections that restore the all-electron (AE) details of the orbitals inside the PAW spheres that are centered on the nuclei. Hence, it yields accurate charge and current densities in the vicinity of the nuclei, albeit with a frozen core. This is crucial for an accurate calculation of nuclear shielding. The PAW method, however, does not yield the correct phase change in the orbitals upon translation in an external magnetic field. The proper phase change is restored by the GIPAW through field-dependent “twists” of the PAW projector functions and partial waves.3,4

In its standard formulation, the GIPAW method only includes all-electron (AE) corrections to the induced current density inside the PAW sphere that encloses the nucleus considered, i.e., it neglects the contributions to nuclear shielding that arise from correction currents in the PAW spheres centered at the other nuclei.3,4 The error caused by the neglect of these two-center contributions has, to our knowledge, never been systematically explored. Here, we study the accuracy attainable in GIPAW shielding calculations by comparing them to basis set converged molecular calculations. These
have recently become available for a set of light element-containing molecules using a multi-wavelet (MW) approach.\textsuperscript{10} We find that the standard GIPAW method is very accurate for all nuclei in the test set, with the exception of $^3$H, for which significant deviations are observed. It is also possible to obtain highly accurate GIPAW shieldings for $^4$He by adding the two-center augmentation corrections introduced in Ref. 11.

Sections II and III provide methodological aspects and technical details. The results are presented in Sec. IV. Section V summarizes the main results and conclusions.

II. METHOD

In its practical implementation, the GIPAW method mimics the NMR experiment: An external magnetic vector potential (describing the uniform applied magnetic field) is applied, and the resulting induced current density is calculated in first-order perturbation theory. This current density $j^{\text{ind}}$ gives rise to an induced magnetic field $B^{\text{ind}}$ at an atomic nucleus $R$ that is calculated with the Biot–Savart law,

$$B^{\text{ind}}(R) = \frac{1}{c} \int j^{\text{ind}}(r) \times \frac{R - r}{|R - r|^3} \, dr.$$  \hspace{1cm} (1)

The shielding tensor is obtained as

$$\sigma_{\alpha\beta}(R) = -\frac{\partial B^{\text{ind}}_\alpha(R)}{\partial B^\beta}.$$  \hspace{1cm} (2)

Here, $B^\alpha$ ($B^{\text{ind}}_\alpha$) denote the Cartesian components of the applied (induced) magnetic field (at nuclear position $R$).

The induced current density is a sum of two contributions: (I) a current density that is calculated from the pseudo-orbitals and represented on the plane wave grid (this current density is present throughout the whole unit cell) and (II) one-center correction currents inside each PAW sphere. These remove the local one-center approximations to the current on the plane wave grid and replace them with the AE one-center currents calculated from the AE partial waves.

These currents give rise, via the Biot–Savart law, to three types of contributions to the induced field at the nuclei:\textsuperscript{12} (1) the field due to the plane wave currents; (2) the field due to the one-center correction current inside the PAW sphere enclosing the nucleus of interest, i.e., for which the shielding is to be obtained; and (3) the field due to the one-center correction currents in all other PAW spheres. The latter are two-center contributions to the field, as they are a sum of pairs involving interactions across two different PAW spheres. This is schematically shown in Fig. 1. Suppose that one wants to calculate the shielding for atom 1. One singles out a unit cell (here cell IV) wherein the shielding for atom 1 (in red) is to be calculated. Contribution (1) is calculated as an integral over whole space (conveniently carried out in reciprocal space). Contribution (2) is an integral over only the PAW sphere enclosing atom 1 in cell IV (in blue). It is crucial for accurate results as it restores the true details of the AE orbitals near the nucleus. Contribution (3) is a sum involving the single atom 1 in cell IV and all other PAW spheres in the infinite crystal (yellow).

Contribution (3) is neglected in the standard GIPAW method. It can be conveniently calculated as described in Ref. 11: The paramagnetic correction current inside the PAW spheres is expanded in multipoles, yielding a set of expansion coefficients. Using these coefficients, smooth augmentation currents are added on the plane wave grid, i.e., a “current augmentation” is carried out. As the augmentation currents have the same multipole expansion by construction and are at distances far from the nucleus at interest (at the center of the blue sphere in Fig. 1), they yield the correct contributions to the shielding. Thus, this contribution is merged into contribution (1) and obtained at negligible computational cost.

III. TECHNICAL DETAILS

Calculations were performed with two sets of potentials: “standard” and “accurate.” The “standard” set consists of standard potentials advised for usage with the Vienna ab initio simulation package (VASP)\textsuperscript{15,14} in most cases (H, Li\textsubscript{sv}, C, N, O, F, Al, P, and S).\textsuperscript{15} The details of the “accurate” potentials are listed in Table I. These also come from the VASP database, except for the third row elements, for which we use “norm-conserving” potentials, as introduced in Ref. 16. Typically, the “accurate potentials” have smaller matching core radii. For Al and P, they also have a smaller frozen core.

In order to be consistent with the calculations of Ref. 10, we cannot directly use the potentials from the VASP database and Ref. 16 as these are scalar relativistic. Hence, all PAW potentials were re-generated as fully non-relativistic potentials. For potentials taken from the VASP database, we did not change any other parameter. We used the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional\textsuperscript{17,18} with potentials consistently generated and un-screened. We always compare to the Perdew–Burke–Ernzerhof
The GIPAW calculations were carried out with the molecular geometries that were used in Ref. 10. These were taken from the supplementary material of Refs. 19 and 20. The GIPAW calculations reported here were carried out with the linear response method of Ref. 4 as implemented in VASP and extended to include, if applicable, the augmentation corrections of Ref. 4. We used a single star of k-points centered on \( \Gamma \). As we compare to molecular shieldings, it makes no sense to include the \( G = 0 \) contribution arising from macroscopic surface currents (Eq. 46 of Ref. 4) in the GIPAW shielding. In Sec. IV B, we separately study the accuracy of the susceptibility that determines the \( G = 0 \) contribution.

For calculations with standard potentials, the default kinetic energy cutoffs were used, i.e., 400 eV for AlF, CO FCN, N\(_2\), N\(_2\)O, O\(_2\), OCS, OF\(_2\), PN, and SO\(_2\); 450 eV for C\(_2\)H\(_2\), C\(_2\)H\(_4\), CH\(_2\)OH, CH\(_3\)F, CH\(_4\), FCCH, H\(_2\)C\(_2\)O, H\(_2\)O, H\(_2\)S, H\(_2\)C\(_2\)O, HCN, HCP, HFCO, HF, HOF, and NH\(_3\); and 599 eV for LiF and LiH. Moreover, many other systems show smaller but clear deviations. As we compare to molecular shieldings, it makes no sense to include the \( G = 0 \) contribution arising from macroscopic surface currents (Eq. 46 of Ref. 4) in the GIPAW shielding. In Sec. IV B, we separately study the accuracy of the susceptibility that determines the \( G = 0 \) contribution.

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In order to prevent the interaction between the periodic images and obtain the true molecular shieldings, large cubic cells of \( 30 \times 30 \times 30 \text{ Å}^3 \) were used.\(^5\) To attain the basis set limit for the “accurate” potential set, we also carried out calculations with a kinetic energy cutoff on the orbitals of 4000 eV (convergence tests are in Figs. S1 and S2 of the supplementary material). For such a high cutoff, however, the memory burden for the \( 30 \times 30 \times 30 \text{ Å}^3 \) cell is too much. Hence, we approximate the shielding in this large box with 4000 eV cutoff as

\[
\sigma^{\text{iso}}(4000 \text{ eV}, 30 \text{ Å}) \approx \sigma^{\text{iso}}(900 \text{ eV}, 30 \text{ Å}) + \sigma^{\text{iso}}(4000 \text{ eV}, 15 \text{ Å}) - \sigma^{\text{iso}}(900 \text{ eV}, 15 \text{ Å}),
\]

so that calculations with 4000 eV cutoff need only be carried out for \( 15 \times 15 \times 15 \text{ Å}^3 \) cells.

**IV. RESULTS**

**A. Molecular shieldings**

Tables S1 and S2 of the supplementary material list all the calculated GIPAW isotropic shieldings and the MW6 isotropic shieldings from Ref. 10. In the discussion below, the most important results are represented as plots and tables.

Figure 2(a) compares the GIPAW hydrogen shieldings obtained with the standard potentials to the MW6 shieldings. Using standard GIPAW (no current augmentation) deviations can be as large as 2 ppm, which is substantial, given the small shielding range of \(^1\)H. Deviations are particularly large for HCN and HCP, which both have triple bonds. For LiH, the deviation is almost 1 ppm. The two-center augmentation corrections remove these discrepancies to a large extent, reducing the mean absolute error (MAE) from 0.90 to 0.36 ppm (Table II). There remains, however, a substantial scatter. In addition, for some systems, the discrepancies become larger. That is very clear for HOF, which has the most deshielded proton in the whole set of molecules.

The remaining scatter does not come as a surprise: the PAW datasets have large core radii compared to the very small interatomic distances in these molecules. The accurate potentials solve this problem and show a very consistent behavior [Fig. 2(b)]: With standard GIPAW and without two-center corrections, again, there are large deviations for HCN and HCP and somewhat smaller for LiH. Moreover, many other systems show smaller but clear deviations, e.g., H\(_2\)O and H\(_2\)S and the molecules with double bonds C\(_2\)H\(_4\), C\(_3\)H\(_4\) (cyclopropane), HFCO, and CH\(_2\)O. The two-center augmentation corrections consistently remove all these discrepancies, reducing the MAE from 0.75 to 0.10 ppm (Table II). Pushing the plane wave basis set to the limit (4000 eV) reduces the MAE further to 0.04 ppm.

It is difficult to discern a systematic trend in the effect of augmentation corrections. For example, for LiH, the effect is larger than for HF. For HF, however, the interatomic distance is 1.73 a.u., much smaller than 3.01 a.u. of LiH. On the other hand, Li has considerably larger core radii (Table I). The largest shielding deviations are observed for HCN and HCP. Both have triple bonds and have C neighboring H. A similar situation occurs in HCCF, which is also a linear molecule, but here, the augmentation corrections have a very small effect. The GIPAW shielding is already very good without the correction. Evidently, it is difficult to a priori estimate how large its effect will be. For GIPAW calculations of H shieldings in systems with top row elements, it is advisable to always use augmentation corrections and accurate PAW datasets (or, alternatively, very hard norm-conserving datasets).

**TABLE I.** Frozen core configurations and matching core radii \( r_c \) for \( s, p, d, \) and \( f \) partial waves in atomic units for the “accurate” PAW datasets. The number of projectors for each quantum number \( l \) is given in parentheses. "*" indicates that this is taken as local potential.

<table>
<thead>
<tr>
<th>Frozen core</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)_h</td>
<td>0.80(2)</td>
<td>0.80(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(_{sv})*</td>
<td>1.40(1), 1.70(1)</td>
<td>1.40(1)</td>
<td>1.40(1)</td>
<td></td>
</tr>
<tr>
<td>C(_2)_h</td>
<td>[He] 1.10(2)</td>
<td>1.10(2)</td>
<td>1.10(1)</td>
<td></td>
</tr>
<tr>
<td>N(_2)_h</td>
<td>[He] 1.10(2)</td>
<td>1.10(1)</td>
<td>1.10(1)</td>
<td></td>
</tr>
<tr>
<td>O(_2)_h</td>
<td>[He] 1.10(2)</td>
<td>1.10(2)</td>
<td>1.10(1)</td>
<td></td>
</tr>
<tr>
<td>F(_2)_h</td>
<td>[He] 0.85(2)</td>
<td>1.10(2)</td>
<td>1.10(1)</td>
<td></td>
</tr>
<tr>
<td>Al(_{sv})<em>GW(</em>{nc}) [He]</td>
<td>1.75(3)</td>
<td>2.00(3)</td>
<td>1.80(2)</td>
<td>2.00(1)</td>
</tr>
<tr>
<td>P(_{sv})<em>GW(</em>{nc}) [He]</td>
<td>1.70(3)</td>
<td>1.95(3)</td>
<td>1.70(2)</td>
<td>2.00(1)</td>
</tr>
<tr>
<td>S(_{GW})_nc [He]</td>
<td>1.23(2)</td>
<td>1.34(2)</td>
<td>1.70(2)</td>
<td>1.80(1)</td>
</tr>
</tbody>
</table>

*aSame as the standard PAW dataset.

(PBE) “MW6” results of Ref. 10, i.e., those for a multiwavelet basis at precision \( e = 10^{-6} \).
Next, we consider the shieldings of the second row nuclei C, N, O, and F. Figures 3(a)–3(d) show the difference of the MW6 and GIPAW shieldings, 

\[ \Delta \sigma_{iso} = \sigma_{iso}^{MW6} - \sigma_{iso}^{GIPAW}, \] 

as a function of the MW6 shielding and calculated with the standard PAW potentials. In all cases, \( \Delta \sigma_{iso} \) is small compared to the shielding range of the element. The augmentation corrections have little

| TABLE II. Mean absolute errors in ppm for several nuclei comparing GIPAW and MW6 PBE isotropic shieldings (shielding constants), from the data in Table S2 of the supplementary material. GIPAW shieldings calculated with both accurate and standard PAW datasets without or with (AUG) current augmentation and using various kinetic energy cutoffs \( E_{\text{cut}} \). Molecular geometries taken from the supplementary material of Refs. 19 and 20. MW6: multiwavelet basis at precision \( \epsilon = 10^{-6} \) from Table 8 of Ref. 10. |
|---|---|---|---|---|
| Accurate | Standard | | | |
| | AUG | | | |
| | | 900 | 900 | 4000 | AUG |
| H | 0.75 | 0.10 | 0.04 | 0.90 | 0.36 |
| Li | 0.74 | 0.66 | 0.70 | 0.59 | 0.57 |
| C | 0.47 | 0.50 | 0.11 | 1.14 | 1.26 |
| N | 1.03 | 0.95 | 0.31 | 9.35 | 10.06 |
| O | 1.83 | 1.70 | 0.62 | 6.41 | 6.03 |
| F | 1.69 | 1.62 | 0.52 | 6.09 | 5.29 |
| Al | 0.55 | 0.05 | 0.01 | 2.84 | 2.50 |
| P | 1.89 | 1.97 | 1.97 | 4.64 | 3.16 |
| S | 5.64 | 6.31 | 6.26 | 6.62 | 6.15 |

effect and do not yield a systematic improvement. This is also evident from the MAE (Table II). For C and N, they even produce a slight increase from 1.14 to 1.26 ppm and from 9.35 to 10.06 ppm, respectively.

Looking a bit more in detail, for C with just the standard PAW potentials [Fig. 3(a)], we observe some scatter in \( \Delta \sigma_{iso} \). Outliers are seen for CO, OCS, FCN, and HCN (indicated with bold font in Table III). For these molecules, featuring double and triple bonds, the standard PAW datasets are not sufficiently accurate anyway. For similar cases, HCP and FCCH, the standard datasets do not yield outliers. This is probably fortuitous. The augmentation corrections reduce the scatter but do not remove the outliers (for CO, etc.). For N, C, and F, the augmentation corrections yield hardly any improvement with the standard potentials [Figs. 3(b)–3(d)].

The situation is markedly different for the accurate potentials. Figures 3(a-2)–3(d-2) show that for all four nuclei, the augmentation corrections substantially reduce the scatter. Moreover, if we also push the plane wave basis to the limit (4000 eV cutoff), \( \Delta \sigma_{iso} \) is systematically reduced. All this is also evident from the MAE in Table II.

Considering the case of C, with the accurate potentials, we again observe an outlier for CO but not for OCS and FCN and HCN (Table III). Instead, there are outliers for HFCO and one of the FCCH carbons [black dots in Fig. 3(a-2)]. All these outliers are removed by the augmentation corrections (red circles). At 900 eV, there is a consistent deviation of about 0.5 ppm, with substantially smaller scatter. Increasing the cutoff to 4000 eV significantly reduces the deviation without affecting the scatter (green dots). The MAE is 0.11 ppm. Obviously, increasing the cutoff does not bring a real gain: when comparing to experimental chemical shifts, only shielding differences matter and these are nearly equally well calculated with a 900 eV cutoff. Moreover, there is a nearly linear
dependence of the small error on the shielding (see Fig. S5 of the supplementary material). Hence, this error could, in principle, be corrected for.

For N, we observe similar behavior, albeit less pronounced. Without any corrections, the range of $\Delta \sigma_{\text{iso}}$ is about 4 ppm, and with augmentation corrections, it is about 1 ppm [Fig. 3(b-2)]. Similar behavior is clearly observed for O and F [Figs. 3(c-2) and 3(d-2)].

The other nuclei (Li, Al, P, and S) only occur a few times in the set of molecules, making it hardly possible to discern trends. We discuss them briefly. Li occurs only in LiH and LiF. Both yield very similar shieldings. The GIPAW shieldings are similar for accurate and standard potentials and appear hardly affected by augmentation corrections. The latter appears reasonable: both the H and F anions have a simple electronic structure, with no or very deep 1s core electrons. On the contrary, the Li augmentations do affect the H and F shieldings. This is probably due to polarization of the relatively shallow Li core that is not frozen in the PAW potential. Our best Li shieldings still have an MAE of 0.7 ppm. This shows that there is room for improvement, i.e., a harder PAW potential with smaller core radii. This is difficult to realize if the PAW datasets have to be made without a frozen core. For Al, we only have a single data point (AlF). The effect of the augmentation current is modest (0.5 ppm for the accurate PAW potentials). The most accurate GIPAW number (542.91 ppm) is practically on top of the MW6 shielding (542.90 ppm). For P and S, there are two and three different shieldings to compare, respectively (see Tables S1 and S2 of the supplementary material). Our best numbers show deviations of 1–2 ppm, except for SO$_2$. Such deviations are quite reasonable. One needs more material to make a systematic comparison. For SO$_2$, our best calculation gives $\Delta \sigma_{\text{iso}} = 16$ ppm. This is in the deshielded...
limit, which is typically the most difficult to get accurate. Improving this result probably requires unfreezing the 2s/2p semicore. The accurate S PAW dataset is the only one with a [Ne] frozen core; see Table I.

**B. Molecular magnetizabilities**

Above, we benchmarked on molecular shieldings. In a crystalline environment, however, there is an additional contribution to the shielding due to the induced surface currents flowing on the crystallite’s surface. Such a contribution is absent in molecular shieldings. The surface currents are a macroscopic quantity and are determined by the bulk magnetic susceptibility of the crystal. In Eqs. 47 and 48 of Ref. 4, the susceptibility tensor used for shielding calculations is approximated as

\[ \chi_0 = \lim_{q \to 0} \frac{F_\delta(q) - 2F_\delta(0) + F_\delta(-q)}{q^2} \]

with

\[ F_\delta(q) = (2 - \delta_q)Q_\delta(q) \]

and

\[ \Delta \sigma_{\text{iso}} = \frac{1}{e^2 N_b V c} \sum_{i=x,y,z} \sum_{\nu,\delta,\kappa,\lambda} \text{Re} \left\{ \langle \hat{u}_\nu^{(i)} | \hat{v}_\nu^{\delta \kappa \lambda} \hat{G}_{\nu \nu} | \epsilon_{\nu \delta \kappa \lambda} \rangle \hat{u}_\nu^{(i)} \hat{v}_\nu^{\delta \kappa \lambda} \hat{G}_{\nu \nu} | \epsilon_{\nu \delta \kappa \lambda} \rangle \} \]

where the LHS of the matrix element is constructed as the complex conjugate of the RHS. Both expressions reproduce the correct AE limit of the susceptibility of Ref. 26. Neither expression is a 100% true PAW expression.26,27

| TABLE III. $\Delta\sigma_{\text{iso}}$ (ppm) for C for various GIPAW calculations from the data in Table S2 of the supplementary material. Outliers (see the main text) are in boldface. “AUG” denotes current augmentation. |
|-----------------|--------------|---------------|---------------|---------------|
| $E_{\text{cut}}$ (eV) | $\sigma_{\text{iso}}$ (MW6) (ppm) | 900 | 900 | 4000 | AUG |
| CH$_3$O | -29.56 | 0.32 | 0.53 | -0.27 | 0.28 | 1.32 |
| H$_2$CO | -20.46 | 0.23 | 0.57 | -0.19 | 1.27 | 1.39 |
| CO | -17.58 | -1.14 | 0.52 | -0.14 | -4.44 | -3.82 |
| HCP | 11.67 | -0.30 | 0.55 | -0.15 | 1.21 | 1.36 |
| HFCO | 19.49 | -0.86 | 0.53 | -0.16 | -0.03 | 1.09 |
| OCS | 20.99 | -0.14 | 0.70 | 0.04 | -2.76 | -2.59 |
| C$_2$H$_4$ | 46.12 | -0.23 | 0.43 | -0.24 | 0.12 | 0.74 |
| C$_2$H$_6$ | 60.95 | 0.59 | 0.46 | -0.17 | 0.95 | 0.75 |
| FCN | 67.29 | 0.53 | 0.52 | -0.04 | -1.00 | -1.61 |
| HCN | 69.02 | 0.97 | 0.56 | -0.02 | 2.61 | 1.64 |
| FCCH | 81.17 | 0.25 | 0.69 | 0.11 | 1.21 | 1.38 |
| CH$_3$F | 104.27 | 0.69 | 0.64 | 0.14 | 1.45 | 1.28 |
| H$_2$C$_2$O | 136.81 | 0.33 | 0.44 | -0.01 | 0.77 | 0.81 |
| FCCH | 169.60 | -0.63 | 0.42 | 0.04 | -0.10 | 0.76 |
| C$_3$H$_4$ | 176.35 | 0.07 | 0.33 | -0.01 | -0.05 | 0.30 |
| H$_2$C$_2$O | 184.88 | 0.22 | 0.27 | -0.08 | 0.47 | 0.27 |
| CH$_4$ | 189.93 | 0.46 | 0.40 | 0.07 | 0.58 | 0.31 |

To assess the accuracy of these expressions with molecular calculations, we compare the GIPAW susceptibilities to the MW6 magnetizabilities. The results are summarized in Table IV.4 A more general account is provided in Figs. S4 and S5. The $vGv$ expression performs better than $pGv$ for both the standard and the accurate PAW datasets. Also the accurate datasets outperform the standard datasets, where the best results ($R^2 = 0.982$) are obtained with $vGv$ and the accurate potentials. For these, $R^2 = 0.982$ and the MAE is 11 J/T² (the molecular magnetizabilities span a range of ~800 J/T²). The sulfur-containing molecules and O$_3$ exhibit clear deviations. For the shieldings, we observed already that the accurate S potential does not perform optimally. Paramagnetic ozone exhibits the largest deviation by far of the order of 50%. Hence, we performed another calculation for O$_3$ with a special very accurate PAW dataset.4 That gave 187.1 J/T² with $pGv$ and 184.3 J/T² with $vGv$. The MW6 number is 184.17 J/T².4 This confirms the validity of the above expressions. The dataset, however, is already close to the AE limit as the $pGv$ result is also very good. These findings suggest that improvements on the $vGv$ expression should be possible with a faster convergence with the completeness/quality of the PAW dataset. As the product of Green’s function and augmented velocity operator

| TABLE IV. $R^2$ values and mean absolute errors of PBE magnetizability calculated with the $pGv$ and $vGv$ expressions for standard and accurate PAW datasets compared to MW6 magnetizabilities (Table 6 of Ref. 10). |
|-----------------|--------------|---------------|---------------|
| PAW dataset | $R^2$ | MAE (10$^{-30}$ J/T²) |
| $pGv$ | Standard | 0.869 | 40 |
| $vGv$ | Standard | 0.908 | 25 |
| $pGv$ | Accurate | 0.947 | 29 |
| $vGv$ | Accurate | 0.982 | 11 |
working on the occupied subspace is already available in the shielding calculation, \( vGv \) is probably the optimum for computational efficiency.

How inaccuracies in the molecular susceptibilities affect the calculated shieldings is difficult to say, as these, contrary to the susceptibilities, depend on the density. When comparing calculated shieldings for different nuclei in the same compound, they play no role. In that case, the susceptibility contributions exactly cancel, obviously. Comparing shieldings in different systems, whereof at least one is a condensed matter system, they need careful consideration, particularly, when differences of \( \sim 1 \) ppm or less are important.

V. DISCUSSION AND CONCLUSIONS

The numerically exact multiwavelet shieldings of Ref. 10 were used as a benchmark to test the ultimate accuracy of the GIPAW method. These exact shieldings are available for small molecules containing light nuclei.

For nuclei other than H, the standard GIPAW implementation is sufficient, i.e., two-center corrections to the induced current are not needed for practical calculations. This is in keeping with standing practice: There is a vast literature employing the standard GIPAW method of Refs. 3 and 4, i.e., without two-center corrections, yielding reliable and accurate results (for an overview, see, e.g., Ref. 6). We have also observed high accuracy comparing GIPAW without two-center corrections to molecular and solid state AE methods.2 For these nuclei, two-center corrections can only be useful if one wants to attain ultimate accuracy for systems from the top rows of the Periodic Table.

For H, the situation is different. Two-center corrections are very substantial for some of the systems studied and still noticeable for many systems. They cannot be neglected, given the small shielding range of H. Moreover, they consistently improve results. To get reliable results, one needs both accurate PAW datasets and two-center corrections. The need for two-center corrections could be minimized by making very hard norm-conserving PAW potentials with very small core matching radii, but the price to pay will be excessively high cutoffs and long calculation times. Indeed, the potentials from our “accurate” set are already quite hard and still require two-center corrections. The augmentation procedure from Ref. 11 provides a computationally convenient way to calculate the two-center corrections.

The set of molecules from Ref. 10 contains difficult cases in many respects. Obviously, triple and double bonds already put severe demands on the PAW potentials (indeed, the “standard” potentials are not sufficiently accurate for those), but we also observe significant effects of the augmentation currents on the H shieldings for other molecules. Hence, whenever bonds between first and/or second row elements are present (e.g., in amino acids), hard (accurate) potentials with two-center corrections will improve H shieldings. Using them is the safe option. This is in keeping with the improvements, we observed for, e.g., \( \text{C}_2\text{H}_3 \) and venlafaxine free base molecule \( \text{C}_7\text{O}_2\text{NH}_2 \) in Ref. 11. However, as the a priori need for their usage is not obvious for all such systems, they may be discarded after a careful testing, e.g., if a marginal accuracy gain does not outweigh the added computational burden. Moreover, we like to stress that there are no compelling indications that two-center corrections should be used for all systems that contain H. Indeed, H goes interstitially into many materials, where it sits far from any other nucleus. In such cases, the standard GIPAW is sufficient. A safe discriminating criterion for using two-center corrections is probably whether H is covalently bonded (that also includes, e.g., \( \text{H}_2\text{S} \), for which we find some effect), but, as said above, such a criterion is likely too stringent. Further studies benchmarking on a much wider range of materials may help here.

Comparing GIPAW susceptibilities to MW6 magnetizabilities, we observe that the \( vGv \) expression performs better than \( pGv \). Both \( pGv \) and \( vGv \) are approximations, motivated by having the correct all-electron limiting behavior.2,25 \( pGv \) was introduced in the original GIPAW papers (see Refs. 3 and 4) as it is more consistent with the neglect of two-center corrections to the shielding (because the surface currents that are calculated from the susceptibility occur at a large distance from the nucleus). For both expressions, the key ingredients are already available in a GIPAW shielding implementation. \( vGv \) performs very well with accurate potentials, but demands on PAW quality are more stringent than for the shieldings: For \( \text{O}_3 \), we need an especially hard potential to reproduce the MW6 magnetizability, whereas for its shieldings, \( \text{O}_h \) is sufficient.

In general, the susceptibility only gives a modest contribution to the shieldings (several ppm), and inaccuracies will not lead to significant errors. When comparing shieldings for nuclei with a small chemical shielding range, e.g., H, between different crystalline systems, one should be aware of potential small inaccuracies. Two remarks are in order: (a) The susceptibility contribution depends on the shape of the sample. Hence, in an actual experiment, it may not even be uniform throughout the material. Generally, the shape effect is unknown, which adds to the error comparing calculations to experiments on different crystals (the calculation assumes spherical particles in vacuum). (b) Although both susceptibility and molecular magnetizability are just second derivatives of the total energy, the susceptibility is a genuine bulk property, depending on the response of itinerant electrons, that cannot be described as a molecular property, except, approximately, in the limit of a molecular crystal. It is probably better benchmarked against full potential results.7

SUPPLEMENTARY MATERIAL

See the supplementary material for all the reported GIPAW isotropic shieldings (Tables S1 and S2), convergence tests of the plane wave basis (Figs. S1 and S2), the difference between GIPAW shieldings calculated at 900 and 4000 eV plane wave kinetic energy cutoff (Fig. S3), and a comparison of molecular magnetizabilities (Figs. S4 and S5).

ACKNOWLEDGMENTS

We thank Professor A. P. M. Kortgens and Professor F. Mauri for useful discussions.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.
REFERENCES

5. We use the method for “infinitely periodic systems” from Ref. 4 and apply the Biot–Savart law in reciprocal space. Hence, the induced field is caused by currents in all periodic images.
12. The contribution to the shielding due to the PAW frozen core electrons is calculated separately and as a purely one-centre contribution.
21. Observed also for N, O, and F.
22. For Li, the standard and accurate potentials are identical.
23. The PAW calculations for the susceptibilities were carried out in supercells of 15 × 15 × 15 Å³. For shielding calculations, large supercells are used to suppress the magnetic fields caused by induced currents in the periodic images of the molecules in neighboring cells. This problem does not occur for the susceptibilities.
24. The contribution due to the core electrons is considered rigid and calculated separately (scalar relativistic).
28. This dataset has 3 s channels, 3 p channels, and 2 d channels and has f as local potential. Both the s and p channels are (almost) norm-conserving with PAW matching radii of 1.15 and 1.5 a.u., respectively. The calculation was carried out with an “overkill” cutoff of 4000 eV.