Electric-field-gradient calculations using the projector augmented wave method

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The first application of the projector augmented wave method to calculate electric-field gradients is presented. The projector augmented wave method is an all-electron electronic structure method that provides an accurate description of the wave function near the nucleus, and thus is well suited to the prediction of hyperfine parameters. Electric-field gradients have been evaluated for a variety of molecules and crystals containing main-group and transition-metal elements. Our results compare well with experiment and previous calculations based on the linear augmented plane-wave method. [S0163-1829(98)00223-9]

I. INTRODUCTION

Hyperfine interactions are a powerful tool for characterizing different atomic sites in a given sample. Many experimental techniques[1] such as Mössbauer spectroscopy, nuclear magnetic and nuclear quadrupole resonance (NMR and NQR), or perturbed angular correlation measurements can access hyperfine parameters in fundamentally different ways. Hyperfine parameters describe the interaction of a nucleus with the electric and magnetic fields created by the chemical environment of the corresponding atom. The resulting level splitting of the nucleus is determined by the product of a nuclear and an extranuclear quantity. In the case of quadrupole interactions, the nuclear quantity is the nuclear quadrupole moment Q that interacts with the electric-field gradient (EFG) produced by the charges outside the nucleus. The analysis of experimental results faces two obstacles: (i) The nuclear quadrupole moments are often known only with limited accuracy and their determination is still an active field of research; (ii) EFG's depend sensitively on the anisotropy of the charge density close to the nucleus, and thus pose a severe challenge to electronic structure methods because an accuracy in the percent range is required for the electron density.

For a long time, a simple point-charge model in combination with so-called Sternheimer shielding factors was used to interpret experimental results. These predictions, however, depend on empirical parameters and often deviate significantly from experimental values.

In their pioneering work, Blaha, Schwarz, and Herzig[2] showed that the linear augmented plane-wave (LAPW) method was able to predict with high precision EFG's in solids without empirical parameters. The LAPW method has been applied to a large variety of systems from insulators to metals to superconductors.[3] Several other electronic structure methods such as the linear-muffin-tin orbital (LMTO) method for periodic[4] or nonperiodic[5] systems, the Korringa-Kohn-Rostoker (KKR) method,[6] the discrete variational method (DVM),[7] and the augmented spherical waves (ASW) method,[8] among others,[9] have been applied to calculate EFG's in solids to various degrees of accuracy. These methods are more or less suitable for different classes of systems.

As pointed out above, measured EFG's have an intrinsic uncertainty related to the accuracy with which the nuclear quadrupole moment is known. On the other hand, the quadrupole moment can be obtained by comparing experimental hyperfine splittings with very accurate electronic structure calculations. This has recently been done by Dufek, Blaha, and Schwarz[10] to determine the quadrupole moment of ^{57}Fe. Clearly, the calculation of accurate EFG's is an active and challenging field of research.

In this paper we apply the recently developed projector augmented wave method[11] (PAW) to EFG calculations in solids and molecules. Thereby we establish how accurately EFG's can be obtained with the PAW method. As an all-electron method, the PAW method lends itself naturally to EFG calculations. The PAW method has proven to be a powerful technique for studying complex systems including molecules, surfaces, and solids, and thus provides access to EFG's in systems that can otherwise not be studied or only with difficulty. As the PAW method is implemented in combination with the *ab initio* molecular-dynamics approach, it is hoped that our approach will provide the basis for studying finite-temperature effects of EFG's in the future.

The paper is organized as follows: In Sec. II we briefly summarize the theoretical background and mention conversion formulas used to compare measured quadrupole interactions with EFG calculations. In Sec. III we describe the theoretical approach to performing EFG calculations. In Sec. IV we compare our calculated results with experiment and LAPW calculations, and in Sec. V we summarize our conclusions.

II. ELECTRIC-FIELD GRADIENTS AND CONVERSION FORMULAS

The nuclear quadrupole interaction (NQI) represents the interaction of the nuclear quadrupole moment Q with the

EFG created by the charge density surrounding the nucleus. Various extensive reviews of this subject are available in the literature.[1,6,12] Here we summarize briefly the main ideas and provide conversions between experimental NQI splittings and EFG's.

Let us consider a nucleus in a state with a nuclear spin quantum number $I > 1/2$ and corresponding nuclear quadrupole moment $Q_{i,j} = e^{-1} \int d^3 r \rho(\mathbf{r}) r_i r_j$, where $\rho(\mathbf{r})$ is the nuclear charge density at point $\mathbf{r}$ and e is the proton's charge. The interaction of $Q_{i,j}$ with an EFG tensor $V_{i,j}$,

$$ H = e \sum_{i,j} Q_{i,j} V_{i,j}, \qquad (1) $$

splits the energy levels E_Q for different magnetic spin quantum numbers $m_I = I, I-1, \ldots, -I$ of the nucleus according to

$$ E_Q = \frac{eQV_{zz}[3m_I^2 - I(I+1)](1+\eta^2/3)^{1/2}}{4I(2I-1)} \qquad (2) $$

in the first order of $V_{i,j}$.[12] Here, Q stands for the largest component of the nuclear quadrupole moment tensor in the state characterized by $m_I = I$. (Note that the quantum-mechanical expectation value of a charge distribution in an angular momentum eigenstate is cylindrical, which renders the expectation value of the remaining two components as having half the value and opposite sign.) The conventional choice is $|V_{zz}| > |V_{xx}| \geq |V_{yy}|$. Hence, V_{zz} is the largest eigenvalue of the EFG tensor, and the asymmetry parameter η is defined by the remaining two eigenvalues V_{xx}, V_{yy}:

$$ \eta = \frac{|V_{xx} - V_{yy}|}{|V_{zz}|}. \qquad (3) $$

Equation (2) shows that the electric quadrupole interaction splits the $(2I+1)$-fold degenerate energy levels of a nuclear state with spin quantum number I ($I > 1/2$) into I doubly degenerate substates (and one singly degenerate state for integer I). Experiments determine the energy difference Δ between the levels, which is called the quadrupole splitting. The remaining degeneracy can be lifted further by means of magnetic fields.

The most common probe nucleus in Mössbauer spectroscopy measurements is ^{57}Fe, which thus deserves special attention. For this probe, the nuclear transition occurs between the $I = 3/2$ excited state and $I = 1/2$ ground state, with a 14.4 keV γ-radiation emission. The quadrupole splitting between the $m_I = \pm 1/2$ and the $m_I = \pm 3/2$ states can be obtained by exploiting the Doppler shift of the γ radiation of the vibrating sample

$$ \Delta = \frac{V_{zz}eQ(1+\eta^2/3)^{1/2}}{2}. \qquad (4) $$

For systems in which the ^{57}Fe nucleus has a crystalline or molecular environment with axial symmetry or a threefold or fourfold rotation axis, the asymmetry parameter η is zero and Δ is given directly by

$$ \Delta = \frac{V_{zz}eQ}{2}. \qquad (5) $$

As η can never be greater than unity, the difference between the values of Δ given by Eqs. (4) and (5) cannot be more than about 15%. In the remainder of this section we simplify the expressions, as is often done, by assuming that $\eta = 0$. As Mössbauer experiments exploit the Doppler shift of the γ radiation, the splitting is usually expressed in terms of the velocity between sample and detector. The quadrupole splitting can be obtained from the velocity, which we denote here by Δ_v, by

$$ \Delta = \frac{E_\gamma}{c} \Delta_v, \qquad (6) $$

where $c = 2.9979245580 \times 10^8$ m/s is the speed of light and $E_\gamma = 14.41 \times 10^3$ eV is the energy of the emitted γ radiation of the ^{57}Fe nucleus.

Finally, we still need to know the nuclear quadrupole moment Q of the Fe nucleus itself. It is of the utmost importance, yet its value has been heavily debated. Recently, however, Dufek, Blaha, and Schwarz,[10] have determined the value $Q = 0.16$ b for ^{57}Fe (1 b $= 10^{-28}$ m^2) by comparing theoretical V_{zz} values obtained using the LAPW method with the measured quadrupole splitting at the Fe site for fourteen different compounds.

Now we relate the electric-field gradient V_{zz} to the Doppler velocity via

$$ \Delta_v = \frac{eQc}{2E_\gamma} V_{zz}. \qquad (7) $$

In the special case of the ^{57}Fe nucleus, we obtain

$$ V_{zz}[10^{21} \text{ V/m}^2] = 10^4 \frac{2E_\gamma[\text{eV}]}{c[\text{m/s}]Q[\text{b}]} \Delta_v[\text{mm/s}] \approx 6\Delta_v[\text{mm/s}]. \qquad (8) $$

EFG's can also be obtained with techniques such as NMR and NQR, where a convenient measure of the strength of the quadrupole interaction is expressed as a frequency ν_q, related to V_{zz} by

$$ \nu_q = \frac{3eQV_{zz}}{2hI(2I-1)}. \qquad (9) $$

The value of V_{zz} can then be calculated from the frequency in MHz by

$$ V_{zz}[10^{21} \text{ V/m}^2] = 0.027571 \frac{I(2I-1)}{Q[\text{b}]} \nu_q[\text{MHz}], \qquad (10) $$

where $(h/e) = 4.1356692 \times 10^{-15}$ [V/Hz]. The parameter V_{zz} is often also denoted as $eq = V_{zz}$.

In the literature, two conflicting definitions of ν_q are in use. One is given by Eq. (9), and the other, defined as

$$ \nu_q = \frac{e^2qQ}{h}, \qquad (11) $$

differs from the first by a factor of 2 and assumes the value $I = 3/2$. Finally, the definition of $q = V_{zz}/e$ has been introduced here. In order to avoid confusion we will refer here only to the definition given in Eq. (9).

We have also adopted the same sign convention for V_{zz} as Dufek, Blaha, and Schwarz[10] because it has been found to be consistent with the majority of experimental results.

III. THEORETICAL APPROACH

We obtain the EFG directly from the full potential $v(\mathbf{r})$ obtained with the PAW method as

$$V_{i,j} = \lim_{\mathbf{r} \to \mathbf{R}} (\partial_i \partial_j - \tfrac{1}{3} \delta_{i,j} \nabla^2) v(\mathbf{r}) \qquad (12)$$

evaluated at a nuclear site R.

With the PAW method[11] the potential is the sum of three terms,

$$v(\mathbf{r}) = \tilde{v}(\mathbf{r}) - \sum_R \tilde{v}_R^1(\mathbf{r}) + \sum_R v_R^1(\mathbf{r}). \qquad (13)$$

The first term, denoted by a tilde, is the so-called pseudopotential. Note, however, that the pseudopotential of the PAW method and that of the pseudopotential method are two different quantities: In the PAW method, it is simply the plane-wave part of the all-electron potential. The remaining two terms are the one-center expansions (denoted by a superscript 1) of the pseudopotential and all-electron potential, respectively, at an atomic site denoted R. Their difference $v_R^1(\mathbf{r}) - \tilde{v}_R^1(\mathbf{r})$ vanishes by construction differentiably outside a so-called augmentation region surrounding an atom at $\mathbf{R}$. Each term contributes individually to the EFG:

$$V_{i,j} = \tilde{V}_{i,j} - \tilde{V}_{i,j}^1 + V_{i,j}^1. \qquad (14)$$

The pseudopotential is obtained from its Fourier coefficients as

$$\tilde{v}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{v}(\mathbf{G}) e^{i\mathbf{Gr}}, \qquad (15)$$

where $\mathbf{G}$ is a reciprocal lattice vector. We obtain its contribution to the EFG as a summation in reciprocal space,

$$\tilde{V}_{i,j} = -\sum_{\mathbf{G}} (G_i G_j - \delta_{i,j} \tfrac{1}{3} |\mathbf{G}|^2) \tilde{v}(\mathbf{G}) e^{i\mathbf{GR}} f(|\mathbf{G}|). \qquad (16)$$

The damping function $f(|\mathbf{G}|)$ smoothly attenuates the contribution of the high Fourier components. This is necessary because taking the second derivative enhances the weight of the large $\mathbf{G}$ components, which makes its plane-wave convergence slow. By removing the oscillatory behavior of the high Fourier components we can substantially improve the plane-wave convergence.

The one-center potentials $v_R^1(\mathbf{r})$ and $\tilde{v}_R^1(\mathbf{r})$ are represented on a logarithmic radial grid multiplied by real spherical harmonics Y_L as

$$v_R^1(r) = \sum_L v_{R,L}^1(|\mathbf{r} - \mathbf{R}|) Y_L(\mathbf{r} - \mathbf{R}), \qquad (17)$$

where $v_{R,L}(|\mathbf{r}|)$ is the radial part of the potential for a given angular momentum $L = (l, m)$ centered at an atomc site R. In order to simplify the following equations, we introduce here a coordinate transformation to $\mathbf{s} = \mathbf{r} - \mathbf{R}$, which measures the position relative to the position of the nucleus under investigation. The italic symbol s denotes the absolute value of the new coordinate.

The contribution to the EFG resulting from the one-center expansions is obtained directly on the radial grid as shown in the following for the potential v^1. The contribution from $\tilde{v}^1$ is calculated in an equivalent way. Let us first consider the matrix of second derivatives near the nuclear site,

$$\partial_i \partial_j \sum_L v_{R,L}^1(s) Y_L(\mathbf{s}) = \lim_{s \to 0} \sum_L [(\partial_i \partial_j v_{R,L}^1(s) s^{-l})(Y_{R,L}(\mathbf{s}) s^l)$$
$$+ (\partial_i v_{R,L}^1(s) s^{-l})(\partial_j Y_L(\mathbf{s}) s^l)$$
$$+ (\partial_j v_{R,L}^1(s) s^{-l})(\partial_i Y_L(\mathbf{s}) s^l)$$
$$+ v_L^1(s) s^{-l}(\partial_i \partial_j Y_L(\mathbf{s}) s^l)]. \qquad (18)$$

As the functions $Y_L(\mathbf{s}) s^l$ are polynomials of order l, we can reduce the above expression: the first term vanishes except for the $l = 0$ contribution, the second and third terms except for the $l = 1$ contribution, and the last term except for the $l = 2$ contribution. The $l = 0$ term is proportional to $\delta_{i,j}$ as a result of its spherical symmetry and therefore does not contribute to the EFG tensor, which is defined to be traceless. The $l = 1$ contribution vanishes as well because $v_L(s) s^l$ are spherical functions and therefore have a vanishing gradient at the origin. Hence, only the $l = 2$ terms contribute to the EFG,

$$V_{i,j}^1 = \sum_{m;l=2} \left(\lim_{s \to 0} \frac{v_{R,L}^1(s)}{s^2} \right) [(\partial_i \partial_j - \tfrac{1}{3} \delta_{i,j} \nabla^2) Y_L(\mathbf{s}) s^2], \qquad (19)$$

and the individual components are

$$V_{xx}^1 = 2 \sqrt{\frac{15}{16\pi}} \lim_{s \to 0} \frac{v_{x^2-y^2}^1(s)}{s^2} - 2 \sqrt{\frac{5}{16\pi}} \lim_{s \to 0} \frac{v_{3z^2-r^2}^1(s)}{s^2},$$

$$V_{yy}^1 = -2 \sqrt{\frac{15}{16\pi}} \lim_{s \to 0} \frac{v_{x^2-y^2}^1(r)}{r^2} - 2 \sqrt{\frac{5}{16\pi}} \lim_{s \to 0} \frac{v_{3z^2-r^2}^1(s)}{s^2},$$

$$V_{zz}^1 = 6 \sqrt{\frac{5}{16\pi}} \lim_{s \to 0} \frac{v_{3z^2-r^2}^1(s)}{s^2}, \qquad (20)$$

$$V_{xy}^1 = V_{yx}^1 = \sqrt{\frac{60}{16\pi}} \lim_{s \to 0} \frac{v_{xy}^1(s)}{s^2},$$

$$V_{xz}^1 = V_{zx}^1 = \sqrt{\frac{60}{16\pi}} \lim_{s \to 0} \frac{v_{xz}^1(s)}{s^2},$$

$$V_{yz}^1 = V_{zy}^1 = \sqrt{\frac{60}{16\pi}} \lim_{s \to 0} \frac{v_{yz}^1(s)}{s^2}.$$

In Eqs. (20) we have dropped the R index and replaced the L index with the more intuitive angular dependence notation in terms of real spherical harmonics. The limit, $\lim_{s \to 0} [v_L^1(s)] / s^2$, is obtained by extrapolating from the first

TABLE I. Electric-field gradients in units of 10^{21} V/m^2. The Q values (Ref. 15) are given in units of 10^{-30} m^2 (or 10^{-2} b); the number of digits indicate the experimental accuracy to which it is known. The sign of the experimental V_{zz} is given only when known. The percentage deviation of the calculated values from measured data is given in the last column.

	Site	Q	V_{zz} (expt.)	V_{zz} (PAW)	Dev. (%)
HCl [a]	^{35}Cl	-8.165	34.25 [b]	$+33.80$	1
Cl$_2$	^{35}Cl	-8.165	55.18 [c]	$+54.23$	2
Br$_2$	^{79}Br	$+33.1$	95.69 [c]	$+94.44$	1
I$_2$	^{127}I	-78.9	113.0 [c]	$+119.01$	5
Li$_3$N	^{7}Li(1)	-4.01	-0.60 [d]	-0.71	18
Li$_3$N	^{7}Li(2)	-4.01	$+0.30$ [d]	$+0.33$	10
Li$_3$N	^{14}N	$+2.01$	1.04 [d]	$+1.02$	2
Fe(C$_5$H$_5$)$_2$ [a]	^{57}Fe	$+16$	$+14.2$ [e]	$+10.67$	25
Fe(CO)$_5$ [a]	^{57}Fe	$+16$	15.42 [f]	$+10.20$	34
Fe(CO)$_4$H$^-$ [a]	^{57}Fe	$+16$	8.16 [f]	$+5.68$	30
FeS$_2$ pyrite	^{57}Fe	$+16$	3.66 [g]	-3.40	7
FeS$_2$ marcasite	^{57}Fe	$+16$	3.00 [g]	-3.21	7
FeSi	^{57}Fe	$+16$	4.45 [h]	$+4.92$	11
Fe$_2$O$_3$	^{57}Fe	$+16$	$+2.16$ [a]	$+1.84$	15
TiO$_2$ rutile	^{47}Ti	$+29$	2.28 [i]	-2.06	10
TiO$_2$ rutile	^{17}O	-2.558	-2.38 [i]	$+2.14$	10
Cu$_2$O	^{63}Cu	-22	10.2 [j]	-8.60	16

[a]Reference 22.
[b]Reference 16.
[c]Reference 17.
[d]Reference 25.
[e]Reference 18.

[f]Reference 19.
[g]Reference 20.
[h]Reference 21.
[i]Reference 23.
[j]Reference 24.

four grid points on the logarithmic grid to the origin using a third-order polynomial. Further details of the PAW calculations are provided in the Appendix.

IV. RESULTS

We have selected a number of systems, molecules, and solids, for which EFG's are known from experiment and from accurate LAPW calculations.[2,3,10,13,14] Thus we compare EFG's not only with experimental data, which often suffer uncertainties of up to 20%, but also with reliable theoretical calculations.

A. Comparison with experiment

As shown in Table I, the deviation between our calculations and experiment is small, that, is on average 12% and less than 18% in 14 out of 17 cases. Deviations of this magnitude are not unexpected given the uncertainties of the nuclear quadrupole moments and temperature conditions, which are not included in our present calculations.[9]

The three cases that exhibit larger deviations from experiment (around 30%) are the molecules containing iron. The underestimation of the EFG's on iron in molecules is possibly due to the local-density approximation (LDA) or the generalized gradient approximation (GGA). We will comment on these interesting cases in connection with the comparison between PAW and LAPW calculations in the next section.

The EFG's at the Cl site in the free molecule HCl, for which the quadrupole moment is more reliable, agree to within even less than 2%. The EFG's at the Cl, Br, and I

sites for the Cl$_2$, Br$_2$, and I$_2$ molecular crystals, respectively, agree with measurements within less than 5%, but quite a number of deviations for η exist.[14]

Li$_3$N is a particularly subtle case because the EFG's in Li$_3$N are extremely small, i.e., about 1% of the EFG in the halogens. This causes the larger percentage deviation of 18% in Li$_3$N, which is probably caused by numerical uncertainties.

The EFG's for the crystalline transition-metal compounds are consistently in excellent agreement with experimental data and fall well within the range of typical error bars of experimental predictions. We note that the nuclear quadrupole moment of the transition metals suffers a large uncertainty, as it can only be obtained by comparing experimental quadrupole splittings with theoretical calculations.

B. Comparison with LAPW calculations

In Table II we compare our results with LAPW calculations. The two methods agree to within more than 9% in all cases, with an average error of 3%, and they agree to within 4% in 11 out of 14 cases. Given the sensitivity of the EFG's for numerical approximations, such agreement can be considered excellent.

The main technical differences in performing the calculations, apart from using different electronic structure methods, are the following: (i) The PAW calculations use a limited k-point set, whereas with LAPW the k grid is chosen sufficiently fine to achieve k-mesh convergence. (ii) PAW uses

TABLE II. Calculated electric-field gradients in units of 10^{21} V/m^2 compared with the results of LAPW calculations. The last column gives the percentage deviation between the two methods.

	Site	V_{zz} (LAPW)	V_{zz} (PAW)	Dev. (%)
Cl$_2$	Cl	+53.7	+54.23	1
Br$_2$	Br	+96.6	+94.44	2
I$_2$	I	+118.8	+119.01	0
Li$_3$N	Li(1)	-0.69	-0.71	3
Li$_3$N	Li(2)	+0.34	+0.33	3
Li$_3$N	N	+1.12	+1.02	9
Fe(C$_5$H$_5$)$_2$	Fe	11.50	10.67	7
FeS$_2$ pyrite	Fe	-3.47	-3.40	2
FeS$_2$ marcasite	Fe	-3.36	-3.21	4
FeSi	Fe	+4.92	+4.92	0
Fe$_2$O$_3$	Fe	+1.99	+1.84	8
TiO$_2$ rutile	Ti	-2.09	-2.06	1
TiO$_2$ rutile	O	+2.13	+2.14	1
Cu$_2$O	Cu	-8.3	-8.60	4

the frozen core but LAPW uses a (spherically) soft core. (iii) Different versions of LDA/GGA parametrizations are employed in some cases.

Given these differences the present very good agreement establishes that both methods are state of the art for EFG's. Furthermore, the deviation of each method from experiment is much larger than that between the two completely independent methods and programs. Therefore, the discrepancy can be attributed to the density-functional error. This offers the unique opportunity to evaluate density-functional theory (DFT) improvements on a sensitive nonvariational quantity such as the charge distribution.

The results for the molecules containing Fe warrant further discussions. For all organometallic complexes we have studied here, the calculations underestimate the measured EFG's by 25–34 %. These results are consistent for both methods and, in the case of ferrocene Fe(C$_5$H$_5$)$_2$, *both methods* yield an EFG on Fe that is more than 20% too small. It should be mentioned that the theoretical EFG is extremely sensitive to small changes of the Fe-C bond distance.

Using the PAW method, we explored whether the discrepancy from experiment can be attributed to distortions of the molecule at finite temperatures. For this purpose we distorted ferrocene in the direction of the modes with the lowest frequencies. The torsion between the rings had a negligible effect on the EFG. The ring-metal-ring bending increased the value, but not sufficiently to explain an enhancement of 25%.

Iron-pentacarbonyl exhibits a discrepancy similar to that of ferrocene. In this context we also explored the possibility that the EFG is influenced by the fluxional transformations of the molecule. The square pyramid structure, an intermediate, would yield an EFG in agreement with experiment. An explanation based on the coexistence of different structures, however, is weakened by the fact that experiments show only a small temperature dependence, and that similar EFG's are measured in solution and in the crystal.

The charged Fe-containing molecule Fe(CO)$_4$H$^-$ falls in line with the other metalorganic complexes ferrocene and

iron-pentacarbonyl for which the calculated EFG's underestimate the measured values by 25–35 %.

This discrepancy with experiment, which is similar for two independent electronic structure methods, indicates that a certain contribution of the electron correlation is neglected, which modifies the electron density but has no noticeable effect on the atomic structure. This effect differs for crystals and molecules. One possible explanation is that LDA artificially destabilizes d electrons, which is seen from the underestimated s-d splittings in transition-metal atoms.[26] In ferrocene the EFG is dominated by the d-d contribution. A stabilization of the d orbitals would both increase their weight in the occupied states and localize the d electrons closer to the nucleus, hence increasing the EFG. However, more work is necessary to unravel these issues.

Rutile, TiO$_2$, is a particularly instructive system because the extraordinary sensitivity of its EFG's to structural distortions is especially evident: Experiments[23,27] have determined the quadrupole splittings on all atoms, including their sign and η values. We performed EFG calculations for two values of the internal structure parameter x of the 4(f) sites occupied by O atoms: the first value, $x = 0.305$, corresponds to the x-ray structure and the theoretical equilibrium value, whereas the second, $x = 0.3025$, is only slightly smaller. Table III lists for PAW and LAPW the EFG components and η values for both x parameters and compares them with experiment. With the experimental parameter $x = 0.305$, the PAW and LAPW results at the Ti site agree very well for all three components of the EFG tensor and therefore also for the η value. On oxygen, however, η is close to unity and thus two components of the EFG are comparable in size, but have opposite signs (and the third component is small). We find the same orientation of the tensor but the magnitude of the two large components is interchanged with respect to experiment. Note, however, that the deviation is less than 4% in the EFG's, which is very small. To see whether this error is caused by a structural error in the internal parameter x, the EFG's have been investigated for a slightly smaller value, $x = 0.3025$. As predicted earlier (see Fig. 3 of Ref. 13), reducing the x value interchanges the magnitude of the two large components, so that the agreement with experiment is substantially improved for the O site. However, the EFG on Ti decreases at the same time by 50%, in clear disagreement with experiment. This system illustrates in a most vivid way that EFG measurements combined with accurate *ab initio* calculations can be an extremely sensitive probe for the atomic and the electronic structure, and that the trends of the EFG with changing structure are well reproduced by both techniques.

Fe$_2$O$_3$ is another example of a system for which the EFG is extremely sensitive to the atomic positions. In both LAPW and PAW calculations, the experimental EFG is correctly reproduced only when the atomic internal parameters (see Table IV) are known up to 10^{-3}.

V. CONCLUSIONS

We demonstrated the capability of the recently developed PAW method to calculate EFG's in solids and molecules. We have studied the EFG's in fourteen different complexes, including both molecules and crystals. The results have been

TABLE III. EFG components (10^{21} V/m^2) in TiO$_2$ as a function of the internal position parameter x of O. The experimental EFG values were taken from Refs. 23 and 27.

	Site	V_{xx}	V_{yy}	V_{zz}	η
			$x = 0.305$		
Expt.	Ti	+0.79 (Ref. 23), +0.86 (Ref. 27)	+1.49 (Ref. 23), +1.34 (Ref. 27)	−2.28 (Ref. 23), −2.20 (Ref. 27)	0.30
PAW	Ti	+0.75	+1.31	−2.06	0.27
LAPW	Ti	+0.60	+1.49	−2.09	0.43
Expt.	O	+0.16	+2.22	−2.38	0.87
PAW	O	−0.08	+2.14 [a]	−2.06 [a]	0.93
LAPW	O	−0.17	+2.13 [a]	−1.96 [a]	0.84
			$x = 0.3025$		
PAW	Ti	+0.17	+1.08	−1.25	0.73
LAPW	Ti	0.22	+1.01	−1.24	0.64
PAW	O	+0.09	+2.23	−2.32	0.92
LAPW	O	+0.04	+2.20	−2.24	0.96

[a]The experimental orientation of the EFG tensor is used although in theory $|V_{yy}| > |V_{zz}|$.

compared with experiment and with accurate LAPW calculations. We obtained reliable results for main-group elements and transition-metal sites. Given the ease with which atomic structures are optimized with the PAW method owing to its implementation as an *ab initio* molecular-dynamics method, as well as the extreme sensitivity of EFG's to the atomic and electronic structure, it is likely that (with the help of measured EFG's) we will soon be able to unravel complex structures such as biochemical complexes for which x-ray structures are not available.

APPENDIX: COMPUTATIONAL DETAILS

We have applied the PAW approach described in Sec. III to calculate the EFG in fourteen different systems, namely the molecules HCl, Fe(C$_5$H$_5$)$_2$, Fe(CO)$_5$, Fe(CO)$_4$H$^-$, and the solids Cl$_2$, Br$_2$, I$_2$, FeS$_2$ in the pyrite and the marcasite structure, FeSi, Fe$_2$O$_3$, TiO$_2$ rutile, Cu$_2$O, and Li$_3$N. A brief summary of the structural information of these systems is given in Table IV, expressed in the convention of the International Tables for Crystallography.[28] The internal coordinates x,y,z for each occupied site [4(a), 6(e), etc.] given in the text below are completely and unambiguously defined into this reference under the structure number and

TABLE IV. Structural information about the systems studied here. The space group and numbers refer to the International Tables for Crystallography (Ref. 28). The lattice parameters a, b, and c are given in Å; x, y, and z are internal parameters (see text) in accordance with the occupied positions in the given structure (Ref. 28).

Compound	Structure	Space group (number)	a	b	c	α	x	y	z
Cl$_2$ [a]	orthor	$Cmca$ (64)	6.145	4.395	8.154		0.0	0.1237	0.1025
Br$_2$ [a]	orthor	$Cmca$ (64)	6.567	4.468	8.694		0.0	0.1390	0.1114
I$_2$ [a]	orthor	$Cmca$ (64)	7.136	4.686	9.784		0.0	0.1543	0.1174
FeS$_2$ pyrite [b]	cubic	$Pa\bar{3}$ (205)	5.407				0.384		
FeS$_2$ marcasite [c]	orthor	$Pnnm$ (58)	4.436	5.416	3.381		0.200	0.378	
FeSi [d]	cubic	$P2_13$ (198)	4.493				0.136 (Fe), 0.844 (Si)		
Fe$_2$O$_3$ [e]	trigo	$R\bar{3}c$ (167)	5.427			55°16.8′	0.3553 (Fe), 0.5556 (O)		
TiO$_2$ rutile [f]	tetrag	$P4_2/mnm$ (136)	4.594		2.959		0.305		
Cu$_2$O [g]	cubic	$Pn\bar{3}m$ (224)	4.252						
Li$_3$N [h]	hexag	$P6/mmm$ (191)	3.641		3.872				

[a]Reference 29.
[b]Reference 30.
[c]Reference 31.
[d]Reference 32.
[e]Reference 33.
[f]Reference 34.
[g]Reference 35.
[h]Reference 36.

corresponding space group. The crystal system (orthorhombic, trigonal, tetragonal, etc.) can be found on page 13 of the International Tables[28] and allows the construction of the direct lattice vectors of those structures. As specified in Table IV we have chosen the trigonal(rhombohedral) axes to build up the Fe_2O_3 hematite structure instead of the hexagonal axes; the reader interested in straightforward transformations between hexagonal and trigonal axes descriptions is referred also to Ref. 28. In Table IV, the references quoted for each structure refer to the experimental values of the a,b,c lattice constants, angle α (for the rhombohedral structure) and x,y,z internal parameters (whenever required for specified symmetry positions) available in the literature that are used in the present study.

(i) The solid halogens Cl_2, Br_2, and I_2 crystallize in a base-centered orthorhombic structure in which the molecules lie in planes perpendicular to the **a** axis and tilted with respect to the **b** axis by an angle α of about 57°. The intramolecular bond distance is very similar to that in the isolated molecule and there are eight atoms at positions $8(f)$.

(ii) The FeS_2 pyrite structure is cubic and consists of four Fe atoms in $4(a)$ and eight S atoms in $8(c)$ with one internal parameter x that determines the S position.

(iii) The FeS_2 marcasite structure is orthorhombic where two Fe atoms are in $2(a)$ and two internal parameters x and y specify the $4(g)$ position of the four S atoms. The calculations were performed in a supercell with 12 atoms corresponding to a cell that is twice the size of the original unit cell along the c direction.

(iv) FeSi is cubic with four formula units in the unit cell and both Fe and Si occupy positions $4(a)$ with different internal parameters x.

(v) Hematite α-Fe_2O_3 crystallizes in a trigonal(rhombohedral) structure characterized by the angle α between the three lattice vectors. It has two formula units per unit cell and different internal parameters x for Fe in $4(c)$ and O in positions $6(e)$ in a rhombohedral axis description. As we noted above one should be aware that the EFG is extremely sensitive to the internal O and Fe positions.

(vi) TiO_2 rutile is a tetragonal structure in which $4(f)$ sites with an internal parameter x are occupied by O atoms and $2(a)$ sites are occupied by Ti atoms. The Ti atoms are surrounded by a slightly distorted octahedron of O atoms, whereas the latter are coordinated threefold by Ti atoms in the (110) plane. We have used a supercell with 12 atoms corresponding to two tetragonal unit cells along the c direction.

(vii) Cu_2O (cuprite) crystallizes in a simple cubic structure with six atoms in the unit cell. Each copper atom has only two close oxygen neighbors, whereas each oxygen atom is surrounded by a tetrahedron of copper atoms.

(viii) The Li_3N structure consists of a layered hexagonal array in which each N in $1(a)$ position is surrounded by a hexagon of Li(2) atoms in $2(c)$ positions forming the Li_2N planes. The Li(1) atoms in position $1(b)$ are centered between two N atoms of adjacent Li_2N layers, so that LiN chains cross the Li_2N planes perpendicularly. The calculations were performed in a hexagonal $2\times2\times2$ supercell of 32 atoms.

(ix) $Fe(CO)_5$ is a trigonal bipyramid with axial bond lengths of $d(Fe-C)_{ax}=1.803$ Å and $d(C-O)_{ax}=1.165$ Å and equatorial bond lengths of $d(Fe-C)_{eq}=1.801$ Å and $d(C-O)_{eq}=1.168$ Å. This compares well with recent experiments by Braga, Grepioni, and Orpen[37] $[d(Fe-C)_{ax}=1.811$ Å, $d(C-O)_{ax}=1.117$ Å, $d(Fe-C)_{eq}=1.801$, 1.804 Å, $d(C-O)_{eq}=1.128$, 1.136 Å] and of Boese and Baser[38] $[d(Fe-C)_{ax}=1.805$ Å, $d(Fe-C)_{eq}=1.805$, 1.755 Å].

(x) $Fe(C_5H_5)_2$ is built up by two cyclopentadienyl rings that ''sandwich'' the Fe atom. A detailed description and comparison with measurements of the ground-state geometry of the ferrocene structure used here can be found elsewhere.[39]

(xi) The structure of the $Fe(CO_4)H^-$ anion has still not been established unequivocally. Our results confirm the experimental structure suggested in the literature,[19,40] where the three equatorial carbon ligands in the pentacarbonyl are displaced and yield C_{3v} symmetry in the hydride. In the present calculations the three equatorial C-Fe-C angles are 117.7° with bond lengths of $d(Fe-C)_{eq}=1.767$ Å and $d(C-O)_{eq}=1.189$ Å ; the H–Fe–C axial angle is 179.9° and the axial bond lengths are $d(C-O)_{ax}=1.87$ Å and $d(Fe-H)=1.532$ Å.

For solids, we used the experimental lattice parameters and the internal atomic positions taken from the literature. For molecules, all structural parameters were fully optimized. We should note that in order to compare our results with LAPW calculations we have chosen to present in Tables I and II our EFG results for ferrocene obtained using the structure in Ref. 39. The EFG of the fully optimized ferrocene structure currently obtained differs from the value in Tables I and II by less than 3%. For all solid systems including the halogens, Brillouin-zone integration was performed with eight k points in the full Brillouin zone using a Monckhorst and Pack special k-point set that includes the Γ point.[41] As our k-point sampling is currently an inherent limitation of our PAW implementation, we improved the sampling by taking larger supercells in some cases as described above.

Describing truly isolated molecules using a plane-wave-based electronic structure program requires certain precautions: We left a vacuum region of at least 6 Å between the periodic images and corrected for both the artificial electrostatic interaction of periodic images with themselves and the compensating charge background.[42]

Exchange and correlation are described within DFT (Ref. 43) using LDA. The EFG's have been calculated within LDA using the parameterization of the simulations of Ceperley and Alder by Perdew and Zunger,[44] and for the relaxation we added the GGA of Becke and Perdew.[45]

Another important quantity for the EFG calculation is the augmentation specified by the projector functions. Here we have used (i) two projector functions per angular momentum up to $l=2$ for Ti, Fe, and Cu; (ii) two s, two p, and one d for O; (iii) two s and two p for N; (iv) one s for Li; (v) two s, one p, and one d for I; (vi) two s and one p for Br and Cl.

We have treated the $3s$ and $3p$ semicore states in Fe and Ti explicitly as valence electrons. For all other elements we used the natural division into valence and core orbitals.

The EFG depends sensitively on the plane-wave conver-

gence, namely, the plane-wave cutoff $G_{max}^2/2$ for the augmented plane waves (E_{pw}) and for the pseudodensity (E_{cd}). Although atomic structures and total energies are accurate with a plane-wave cutoff of $E_{pw}=30$ Ry and $E_{cd}=60$ Ry, it was necessary for the calculation of EFG's to use $E_{pw}=50$ Ry for the wave functions and a consistent plane-wave cutoff of $E_{cd}=200$ Ry for the plane-wave part of the charge density. These are the values we have used for all solids except TiO_2 and Li_3N, for which full convergence was achieved only with plane-wave cutoffs of $E_{pw}=60$ Ry and $E_{cd}=240$

Ry for TiO_2 and $E_{pw}=80$ Ry and $E_{pw}=320$ Ry for Li_3N. In order to ensure the complete neglect of convergence errors in our results for the molecules containing Fe, their structure was relaxed and the EFG's were calculated with large cutoffs ($E_{pw}=80$ Ry, $E_{cd}=320$ Ry), the same procedure followed for the small HCl molecule, for which cutoffs of $E_{pw}=60$ Ry and $E_{cd}=240$ Ry were used. Note that in all molecules the EFG results obtained with smaller plane-wave cutoffs ($E_{pw}=50$ Ry and $E_{cd}=200$ Ry) agreed within less than 2% with the results shown in Tables I and II.

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