Nuclear Quadrupole Coupling of ^{17}O and ^{33}S in Ionic Solids: Invalidation of the Sternheimer Model by Short-Range Corrections

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Electronic structure calculations of electric field gradients (EFG) at the nuclei of the anions F$^-$, O^{2-}, and S^{2-} for distorted octahedral environments representing the condensed phases of LiF, MgO, and MgS show dominant short-range corrections to the Sternheimer model. In this model, the EFG at the nucleus is proportional to that calculated from charges external to the ion with the constant of proportionality reflecting screening by the anion electron density. The short-range corrections suppress and even reverse the Sternheimer predictions and act in such a way as to damp the site specificity of the nuclear quadrupole coupling constants (NQCC) observed in magnetic resonance experiments. In contrast, the Sternheimer model is shown to describe accurately the calculated EFG at the nucleus of the Na$^+$ cation. The physical origin of the short-range corrections is connected to the well-characterized short-range contributions to the induced dipoles and quadrupoles on ions at low-symmetry sites in the condensed phase.

I. Introduction

Developments in two-dimensional multiple-quantum magic-angle spinning (MAS)[1−3] in NMR have made it possible to carry out accurate measurements of nuclear quadrupole coupling constants (NQCC) from spectra of complex materials containing multiple overlapping resonances. The quadrupole coupling reflects the magnitude of the electric field gradient (EFG) at a quadrupolar (spin $I > 1/2$) nucleus and hence is potentially useful in identifying those low-symmetry sites in an inorganic material that are occupied by ions containing quadrupolar nuclei in an inorganic material. If the NQCC could be predicted *quantitatively* from the configurations of neighboring ions around the site, then binding sites in disordered materials or at surfaces, which cannot be characterized by conventional crystallography, could be identified. Measurements of NQCC have been used, for example, to characterize the binding sites of extra-framework ^{23}Na nuclei ($I = 3/2$) in a zeolite,[4,5] by comparing the magnitudes of the measured NQCCs with EFGs calculated within the Sternheimer model[6] from the charges[7,8] on the ions in the zeolite framework at various proposed binding sites. In view of the importance of oxide materials in emerging nanotechnologies and surface science, the ^{17}O NQCC could become a useful diagnostic tool for identifying oxide ion sites. Chadwick and co-workers have already shown that distinct ^{17}O resonances from sites close to the surface of MgO nanoparticles can be resolved;[9] in principle, NQCC could be used to identify them. The main purpose of this paper is to examine how far it is possible to predict the magnitude of the NQCC directly from the geometry of the ionic site via the Sternheimer model, with particular reference to ^{17}O.

In the Sternheimer model for an initially spherical atom in an axial field,[6] the EFG at the nucleus of ion i is linear in the external field gradient and, with allowance for hyperpolarization,[10] quadratic in the external field:

$$F_{zz}^i = (1 + \gamma^i)E_{zz} + \epsilon^i E_z^2 \, ... \quad (1)$$

Here E_α and $E_{\alpha\beta}$ are components of the *external* electric field and field gradient (evaluated at the nucleus) arising from the charges of surrounding ions. γ and ϵ are the Sternheimer (*anti-*) shielding factors which reflect the additional contribution to the EFG at the quadrupolar nucleus in the ion of interest due to the polarization of its electron density by the external field. In the nuclear magnetic resonance literature, the EFG (F_{zz} in our notation) would be denoted eq_{zz} and the quadrupole coupling constant measured from a spectrum (usually quoted in MHz) would be

$$C_Q = e^2 q_{zz} Q/h \quad (2)$$

where Q is the nuclear quadrupole moment of the nucleus of interest and e and h are the electronic charge and Planck's constant.

The Sternheimer factors are response properties of the electron density of the ion, where γ is analogous to the usual electric quadrupole polarizability (C) and ϵ to the quadrupole hyperpolarizability (B),[11] and in normal circumstances, ϵ can be considered as giving a small correction to γ. The Sternheimer shielding factor, γ, is negative for atoms of s^2 outer configuration but positive (anti-shielding) for p^6; ϵ is negative for both s^2 and p^6 atoms.[12] An extended version of the Sternheimer formulation uses a Taylor series containing fully tensorial multipole response properties, $g_{\alpha\beta,\gamma}$, $g_{\alpha\beta,\gamma\delta}$, $\epsilon_{\alpha\beta,\gamma\delta}$, ... to describe the EFGs at nuclei in less symmetrical electronic environments.[13,14] The change induced in the EFG at nucleus i situated at the origin is then

$$F_{\alpha\beta}^i = E_{\alpha\beta} + g_{\alpha\beta,\gamma}^i E_\gamma + g_{\alpha\beta,\gamma\delta}^i E_{\gamma\delta} + ... + \frac{1}{2}\epsilon_{\alpha\beta,\gamma\delta}^i E_\gamma E_\delta \, ... \quad (3)$$

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where the response properties are all defined by derivatives of the EFG at the nucleus with respect to external field derivatives taken at the nucleus, and for a spherical system $g^i_{\alpha\beta,\gamma} = 0$, $\gamma^i = 1/5 g^i_{\alpha\beta,\alpha\beta} = 3/2 g^i_{zz,zz}$. The different conventions used in (1) and (2) for the hyperpolarization term imply that $\epsilon^i = 2\bar{\epsilon}^i$ where $\bar{\epsilon}^i = 2/15\epsilon^i_{\alpha\beta,\alpha\beta}$.

For cations in ionic materials, the NQCC appears to vary systematically with the external EFG, as in the zeolite study mentioned above.[5] For anions, however, it does not seem to be so straightforward to predict the NQCC. In these circumstances, one must resort to comparing experimentally measured values with those predicted from ab initio calculations on specific models of the binding sites. In recent studies of ^{17}O coupling in silicates, for example, the Si−O−Si bond angles at particular binding sites were identified by comparing measured coupling constants with those calculated ab initio for clusters in which the Si−O−Si bond angles were known.[15,16] On a similar basis, Clark et al[17] have proposed an empirical relationship between the ^{17}O NQCC and the S−O−Si bond angle and the number of coordinating alkali cations in alkali silicates. However, this relationship does not appear to be simply connected to the external EFG, and Bull et al[8] noted that (previously proposed) relationships of this type lacked generality. In this paper, we examine the reasons for the poor correlation between the NQCC for ^{17}O and the external EFG in highly ionic materials (like MgO) where the issue is not masked by discussions of "covalency".

Even if the generalized Sternheimer model (2) itself were complete, one complication in applying it quantitatively is immediately evident from the analogy between shielding factors and polarizabilities. It is well-known that *anion* polarizabilities in condensed phases are strongly influenced by the confining effect of the neighboring ions, which compresses the anion electron density, relative to the isolated ion, and reduces its polarizability in a site-specific way.[18−20] For cations, on the other hand, in-crystal polarizabilities are very similar to those of isolated ions. The effect on polarizabilities can be characterized in electronic structure calculations on in-crystal anions and predicted from the positions of the neighboring ions via simple models.[21−24] A similar reduction of the Sternheimer factors for anions by the in-crystal environmental potential has been demonstrated by Fowler and Kelly.[25]

A modest site-specific variation of the Sternheimer factor of this kind would complicate the use of the NQCC in identifying anion binding sites but would not necessarily invalidate it. However, a more significant problem for our investigation is the question of the validity of the Sternheimer model itself when the source of the external EFG is the charge distribution of the neighboring ions, rather than some set of remote classical charges. Again, borrowing from what is known about the polarization of ions (i.e., the induction of dipoles and quadrupoles) in low symmetry sites in a crystal, an additional source of an electric field gradient at the nucleus can be expected.[26] In addition to its polarization by the external EFG, the charge density of the ion will be subject to modification by short-range interactions which arise from the overlap between the electron densities of the ion of interest and its neighbors. The distorted charge distribution will give rise to a further, nonmultipolar contribution to the EFG at the nucleus, an effect that is not contained within the Sternheimer model. The analogous short-range contributions to ion dipoles, quadrupoles, and in-crystal polarizabilities result in significant and often dominant corrections to the "asymptotic" induced moments.[26,27]

To characterize this short-range effect, we have performed electronic structure calculations to determine the EFG at the nucleus of an ion in a distorted crystal site. The electronic structure calculations themselves are of the same level as performed on specific clusters by several groups;[28,15,7,16,17] the novel aspect of our calculations is the attempt to isolate the contribution to the EFG from different physical effects. By making an independent determination of the Sternheimer factors from calculations on in-crystal ions in an ideal external EFG, and using them to predict the EFG at the nucleus within the Sternheimer model, we can isolate the short-range corrections to that model. Similar methods have previously been used to study short-range contributions to the induced dipoles and quadrupoles of ions in a condensed-phase environment. These calculations have led to accurate representations of the polarization contribution to interionic forces, to the infrared absorption of ionic materials, and to other electrooptic properties.[29−32]

We should remark that a short-range contribution to the NQCC of halide ions has previously been identified in electronic structure calculations on alkali halide molecules by Bacskay and Buckingham.[33] They showed that it was a large effect, comparable to the contributions included in the Sternheimer model but opposite in sign. In our study, we consider a realistic condensed-phase environment, where the anion electron density is substantially more compressed by its coordination environment than in the isolated molecule, and connect the findings to general ideas about ionic polarization arising from the study of induced multipoles in condensed phases.[27]

The present paper describes electronic structure calculation on three chemical systems: F$^-$ in LiF, O^{2-} in MgO, and S^{2-} in MgS. Calculations of the nuclear EFG at the anion site are carried out for clusters modeling both the undistorted bulk environment and for distorted clusters representing environments of lower symmetry. In view of their experimental interest, the oxide and sulfide ions are the main subjects of the paper. O^{2-} and S^{2-} can be expected to show very large in-crystal effects as the free ions themselves would be unbound, with effectively infinite polarizability and Sternheimer shielding, so that the finite size, polarizability, and binding energy of these ions are all direct consequences of the crystalline environment.[22,34] The ion F$^-$ is chosen as a well understood calibration system, where in-crystal effects represent a strong perturbation of an existing bound system (the free ion). NQCC for systems containing F$^-$ are, in principle, accessible but require specialized nuclear-excitation techniques.[35]

The structure of the paper is as follows: the methods and calculations are briefly summarized in section 2; in section 3, the results for the listed systems are reported, and in section 4, we briefly discuss the implications for the interpretation of experiment.

II. Methods

The two main effects of the surrounding environment on the electronic properties of an anion are the long-range "Madelung" electrostatic compression of the anion as a consequence of its position in a confining potential well and the short-range "overlap" compression of the anion by exchange overlap interactions with the charge clouds of its cationic neighbors.[18,19] Both are included in the embedded-cluster method.

Three levels of calculation, with an increasingly realistic representation of these environmental effects, can be envisaged: FREE, XTAL, and CLUS.[18] The same anion basis sets are used at each level: for F$^-$, (15s10p5d3f) → [12s8p5d3f];[18] for O^{2-}, (13s9p5d3f) → [13s9p5d3f],[22] with f exponents equal

TABLE 1: Sternheimer Shieldings and Hypershieldings for the Three In-Crystal Anions, F⁻ in LiF, O²⁻ in MgO, and S²⁻ in MgS, Computed Using Coupled Hartree−Fock Calculations as Described in the Text

system	component	FREE	g XTAL	CLUS	component	FREE	ϵ XTAL	CLUS
LiF	zz,zz	19.94	18.53	8.99	zz,zz	−345.	−183.	−49.8
	xy,xy	14.95	8.00	6.94	xy,xy	−258.	−72.	−49.9
	γ	29.91	20.72	13.72	$\bar{\epsilon}$	−345.	−131.	−59.9
	$\Delta\gamma/\gamma$	0	0.57	−0.03	$\Delta\epsilon/\bar{\epsilon}$	0	1.5	−0.6
MgO	zz,zz		82.31	9.763	zz,zz		−864.	−76.9
	xy,xy		0.743	8.527	xy,xy		−37.25	−75.62
	γ		50.28	16.09	$\bar{\epsilon}$		316.	−91.26
	$\Delta\gamma/\gamma$		2.4	−0.15	$\Delta\epsilon/\bar{\epsilon}$		6.5	−0.6
MgS	zz,zz		136.3	28.96	zz,zz		−1800	−284.
	xy,xy		−0.172	18.2	xy,xy		189	−164
	γ		81.57	39.25	$\bar{\epsilon}$		−568.	−245
	$\Delta\gamma/\gamma$		2.5	0.18	$\Delta\epsilon/\bar{\epsilon}$		8.1	0.6

to the middle three d exponents; and for S²⁻, (15s12p4d3f) → [12s10p4d3f],[34] with f exponents equal to the final three d exponents.

The "FREE" calculation involves evaluation of electronic structure and properties of an isolated anion, treated here at the self-consistent field (SCF) level in a flexible basis set: because it is the only stable free ion among those considered, only F⁻ values are reported here. At the "XTAL" stage, the purely electrostatic effect of the environment is included by placing the anion in a lattice of point charges, usually a 5 × 5 × 5 unit cell cubic fragment of the crystal, with charges taking their nominal values on the interior sites and scaled by $(1/2)^n$ on sites that belong to n exterior faces. In the final "CLUS" stage, a cluster consisting of the central anion and its nearest cation neighbors is treated quantum mechanically, with all sites bearing their complement of electrons and basis functions, with the whole being embedded in the lattice of point charges. Special contracted basis sets for the small cations Li⁺ and Mg²⁺ ([1s1p] and [2s1p],[18,22] respectively) allow for an economical description of their role as fixed charge densities compressing a central, flexible anionic charge cloud.

Calculations are carried out at the CLUS and XTAL levels for clusters representing the equilibrium bulk crystalline environment and also for a series of distorted clusters representative of low-symmetry environments of interest in measurement of NQCC.

In calculations at the CLUS level, it is necessary to extract that part of the electronic contribution to the total calculated EFG that arises from the electrons of the anion of interest. To do this, properties of the central ion are obtained by subtraction, $P(\text{anion}) = P(\text{cluster}) - P(\text{cage})$, where $P(\text{cluster})$ is the property of interest calculated for the embedded cluster "supermolecule" consisting of the anion and its cation neighbors, and $P(\text{cage})$ is the property calculated for an empty cage of cations with *all* other centers replaced by point charges. $P(\text{cage})$ was checked for basis set superposition error (BSSE), by reintroducing the basis functions of the anion onto the central charge. The differences between $P(\text{cage})$ and its BSSE-corrected value were in all cases <0.1%.

III. Results

The calculations are performed in two stages. First, the environmental effects on the Sternheimer shielding constants are calculated, by applying an ideal external field and field gradient to ions in the FREE, XTAL and CLUS environments appropriate to the perfect crystal structures, where there is no interionic field gradient because of the high symmetry. The anion in the equilibrium rocksalt lattice, adopted by the materials of interest, occupies a site of octahedral symmetry (with anion−cation distances:[18,20] $R(\text{LiF}) = 3.7965a_0$, $R(\text{MgO}) = 3.9760a_0$,

$R(\text{MgS}) = 4.9038a_0$). In the second stage, the nuclear EFGs for anions in distorted crystals with low-symmetry sites are calculated and compared to the Sternheimer predictions. The physical origin of the short-range effects which are identified thereby are then examined. In the final subsection, we contrast the anion and cation situations.

A. Sternheimer Shielding Constants. The Sternheimer (anti-)shielding γ^i and the hypershielding ϵ^i were evaluated using coupled Hartree−Fock theory (CHF),[25] i.e., fully analytically from first-order perturbed densities in the external fields and field gradients.[25] This was done for FREE F⁻ and for all three ions in XTAL and CLUS environments. For a spherical ion, each property is specified by a single component, the isotropic averages γ^i and $\bar{\epsilon}^i$ (eq 3 et seq.). In the octahedral site of a rocksalt crystal, however, each Cartesian component is a function of two independent parameters (cf. the C and B tensors[11]):

$$g^i_{\alpha\beta,\gamma\delta} = \gamma^i\left\{\frac{1}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) - \frac{1}{3}\delta_{\alpha\beta}\delta_{\gamma\delta}\right\} +$$
$$\Delta\gamma^i\left\{i_\alpha i_\beta i_\gamma i_\delta + j_\alpha j_\beta j_\gamma j_\delta + k_\alpha k_\beta k_\gamma k_\delta - \frac{1}{5}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\right\} \quad (4)$$

$$\epsilon^i_{\alpha\beta\gamma\delta} = \bar{\epsilon}^i\left\{\frac{3}{4}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) - \frac{1}{2}\delta_{\alpha\beta}\delta_{\gamma\delta}\right\} +$$
$$\Delta\epsilon^i\left\{\frac{2}{3}i_\alpha i_\beta i_\gamma i_\delta + j_\alpha j_\beta j_\gamma j_\delta + k_\alpha k_\beta k_\gamma k_\delta - \frac{2}{15}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\right\} \quad (5)$$

and the departure of the ratios $\Delta\gamma^i{:}\gamma^i$ and $\Delta\epsilon^i{:}\bar{\epsilon}^i$ from zero can be used as measures of the distortion of the soft anion in the octahedrally symmetric confining potential/pseudo-potential imposed by its neighbors.

As Table 1 shows, if the isotropic part alone of the Sternheimer shielding is considered, the amplification of an external field gradient by the antishielding effect of the electrons of F⁻ is halved in the crystalline environment, when compared with the free anion. The reduction is largest at the CLUS level where the anion is compressed by overlap repulsion by the surrounding cations as well as the Madelung potential. As discussed in connection with the calculation of in-crystal polarizability,[18] this factor of a half, calculated at the CHF level, probably underestimates the magnitude of the change, because a free F⁻ is a highly correlated system for which all response properties are much larger than their CHF estimates, whereas in the XTAL and CLUS environments for F⁻, the quenching of radial correlation by the environmental potential leads to better accuracy for the CHF method. The correlated calculations

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of Bacskay and Buckingham[33] indicate a correlation-induced enhancement of γ^i for a free F$^-$ of $\sim$30%, diminishing to 5% for Cl$^-$ and 1% for Br$^-$. For O^{2-} and S^{2-}, of course, the reduction factor by the crystalline environment is formally infinite, as the hypothetical FREE value would refer to an unbound system. The greater importance of the environmental potential for these ions, relative to the halides, is nevertheless evident in the substantial difference between the values for γ^i at the XTAL and CLUS levels.

A second feature of the results in Table 1 is that the two tensors are appreciably nonspherical, with larger deviations for the dianions and for the higher-order property ϵ. This effect is particularly striking for S^{2-} where, for example, the cross term $\gamma^i_{xy,xy}$ (where x, y, and z are defined such that the six nearest neighbors lie on the Cartesian axes) is almost entirely suppressed at the XTAL level. These results for LiF, MgO, and MgS argue for considerable dependence of both isotropic and anisotropic parts of the response tensors on the counterion. Use of the Sternheimer eq 2 for, say, sulfide ions in different compounds would therefore appear to require separate calculations for each material or modeling of the dependence of $g^i_{\alpha\beta,\gamma\delta}$ and $\epsilon^i_{\alpha\beta,\gamma\delta}$ on lattice parameter, in the spirit of previous treatments for in-crystal ionic polarizability.[36] However, as the results in section III.B will show, there are more serious problems with the applicability of the Sternheimer eq 2 for anions in condensed phase environments.

B. Field Gradients at Nuclei in Anions in Low-Symmetry Environments. In this section, we calculate the EFGs induced by the interionic interactions when ions are displaced off their lattice sites in order to lower the site symmetry. Three series of distorted clusters in the rocksalt environment have been considered (i) opposite cations displaced radially by $\Delta R = \pm 0(0.1)0.5a_0$ (D_{4h} symmetry), (ii) cation displaced radially by $\Delta R = \pm 0(0.1)0.5a_0$ (C_{4v} symmetry), and (iii) equatorial cations displaced in a scissors-bending motion where opposite M$-$X-M angles increase by $\Delta\theta = 0(2)14°$, all M$-$X distances remaining equal. In (i), the symmetry of the distorted site is D_{4h} which allows for an axial field gradient ($E_{zz} = -2E_{xx} = -2E_{yy}$, $E_{xy} = E_{xz} = E_{yz} = 0$) but no electric field. In (ii), an electric field is also allowed, leading to a contribution from the ϵ^i term in eq 1. In (iii), we see the effect of distorting the site without changing the nearest-neighbor separations; there is an off-diagonal ($E_{xy} = E_{yx}$) field gradient.

Central-ion EFGs are calculated for each distortion using the subtraction technique described above and are compared with those predicted by the generalized Sternheimer model, eq 2, using the response properties calculated either (a) for the anion in the undistorted cluster or (b) "self-consistently", with response properties $g^i_{\alpha\beta,\gamma}$, $g^i_{\alpha\beta,\gamma\delta}$, and $\epsilon^i_{\alpha\beta,\gamma\delta}$ calculated for the anion in the distorted cluster itself. In both cases, the response properties are obtained by coupled Hartree$-$Fock theory (CHF).

When sufficient terms in eq 2 are included, estimates (a) and (b) for the EFG at a nucleus are very similar, though, as we will see, both may differ substantially from the ab initio computed property. The interpretation of these differences leads to a model in which the EFG, as any other induced property of an anion in a condensed-phase environment, is a sum of an "asymptotic" electrostatic term (here the generalized Sternheimer contribution (2)) and a short-range term operationally defined such that the sum of asymptotic and short-range terms recovers the ab initio computed value.

1. Radial Distortions. The results of the calculations of EFG at the nucleus of F$^-$ in LiF are displayed in graphical form in Figure 1, which shows the effects of D_{4h} and C_{4v} radial
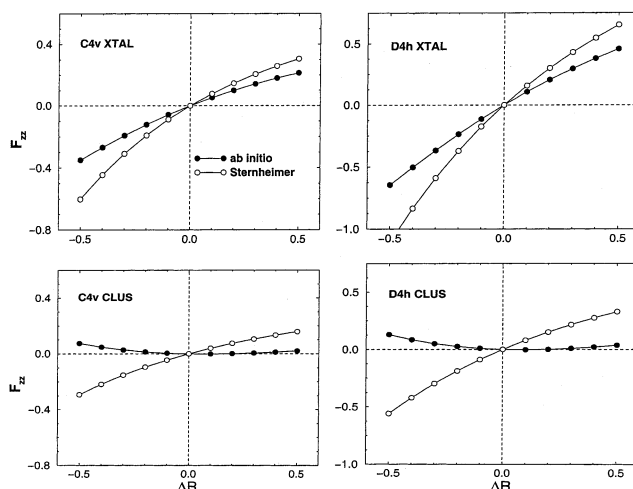

Figure 1. Electric field gradients F_{zz} (a.u.) at the F$^-$ nucleus in distorted LiF environments. ΔR is the radial displacement of one (C_{4v}) or two (D_{4h}) of the nearest neighboring Li$^+$ ions around the F$^-$ ion (in a.u., outward displacements positive). The labels reflect the symmetry of the F$^-$ site. Filled circles represent ab initio calculations, and open circles represent the predictions of the extended Sternheimer eq 2. Curves are drawn only as a guide to the eye. Results are shown for the XTAL environment, where the neighboring Li$^+$ ions are represented by point charges ($+1$), and for the CLUS environment, where the full electron density of the Li$^+$ is included.
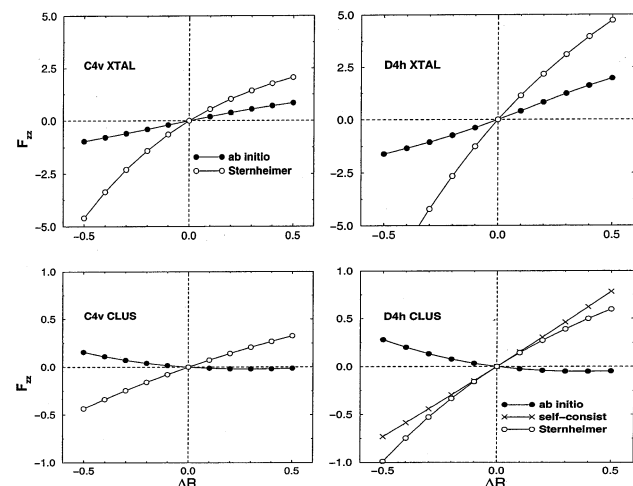

Figure 2. EFGs F_{zz} (a.u.) at the O^{2-} nucleus in distorted MgO environments. In other respects, the caption of Figure 1 applies. In D_{4h} CLUS figure (bottom right), the crosses (labeled "self-consist") represent "self-consistent" Sternheimer predictions (see text), using shielding tensors appropriate to the distorted calculation.

distortions (i) and (ii) at both XTAL and CLUS levels. Each panel in the figure compares the ab initio computed EFG with the prediction from the extended Sternheimer model (2) obtained using the response properties of the appropriate (XTAL or CLUS) anion, and in each case calculating the external field E_α and its gradient $E_{\alpha\beta}$ from the nominal charges on the distorting shell of neighbors. Figures 2 and 3 show the corresponding results for first-shell radial distortion for O^{2-} in MgO and S^{2-} in MgS. All of the results for the EFGs are given in atomic units. For the ^{17}O nucleus in MgO, the results (Figure 2) can be converted to predictions for the observable quadrupole coupling constant C_Q by multiplying by a conversion factor of -5.72 MHz (obtained, following Xue and Kanzaki,[15] from the experimental value of C_Q for ^{17}O in water and the EFG at the oxygen nucleus in H$_2$O calculated using similar methods to those employed here). Alternative recommended values are given by
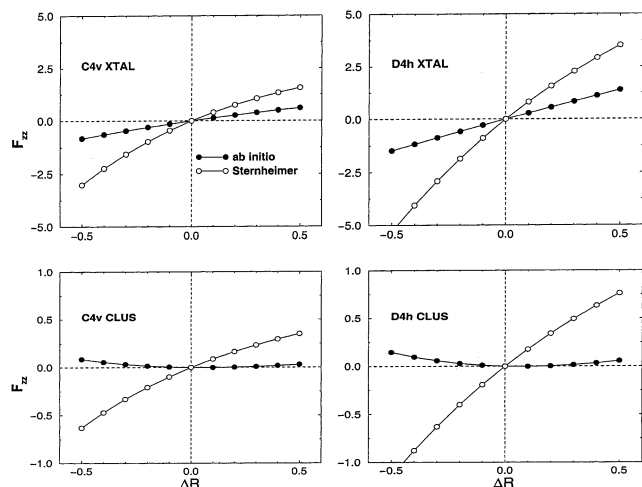
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Figure 3. EFGs F_{zz} (a.u.) at the S^{2-} nucleus in distorted MgS environments. In other respects, the caption of Figure 1 applies.

Pykko and Li[37] and lead to C_Q in MHz of -5.940 (^{17}O), -16.92 ($^{19}F*$), 25.59 (^{11}Na), and -15.93 (^{33}S) per atomic unit of field gradient, respectively.

The four calculations for each anion show a systematic picture. In every case, there is a large reduction in the computed EFG at the nucleus when compared to the prediction of the Sternheimer model. At the XTAL level (the top two panels in all three figures), the ab initio curves are shallower than the Sternheimer predictions but still show a rough proportionality between the distortion-induced property and that calculated by screening the external EFG with the appropriate XTAL Sternheimer factors. The effect of the electric field allowed in the C_{4v} environment is not very pronounced, as seen from the fact that the slopes of the curves in the right-hand (D_{4h}) panels are close to twice those in the left-hand panels, reflecting the ratio of the field gradients created by the movement of two ions in one case (D_{4h}) as opposed to the single ion displacement in the other (C_{4v}). At the CLUS level, the Sternheimer model itself predicts much reduced EFGs relative to the XTAL level (evident from comparison of the upper and lower panels in Figures 1–3; note the scale changes in Figures 2 and 3) as a result of greater damping of the (anti-)shielding factors by the stronger environmental potential. Furthermore, the suppression of the calculated EFG in the ab initio results with respect to the model becomes even more pronounced, so much so that the computed EFG is actually of the opposite sign to the model prediction for inward distortion. In all three CLUS calculations, i.e., in the calculations in which the modeling of the environmental effect is closest to the physical situation of an anion in a crystal, the response of the EFG is very strongly damped. This does not augur well for any attempt to correlate measurements of this property with site geometry.

Given the strong variation in response tensors with environment, it might be argued that the discrepancy between ab initio and Sternheimer curves reflects the use of constant response properties, appropriate to the perfect crystal, even for the distorted crystals. However, the lower right-hand panel of Figure 2 shows that when the tensors are calculated self-consistently for each distortion there is little change: a small improvement for inward distortions, where $g_{\alpha\beta,\gamma\delta}$ and $\epsilon_{\alpha\beta,\gamma\delta}$ are being reduced, is countered by a worsening for outward displacements, where these properties are increasing. The ab initio versus model discrepancy is therefore intrinsic to the nature of the perturbation.

Thus, even with the reduced response properties appropriate to the compressed in-crystal anion, the "asymptotic" Sternheimer model cannot represent the physical response of the anion to distortions in the first-neighbor shell. As discussed previously in the context of the distortion-induced moments and polarizabilities,[26] this failure is a consequence of the many-body nature of the interactions defining the confining pseudopotential that compresses the anion. In a distorted CLUS calculation, outward movement of a cation creates more space into which the anion electrons may flow toward that cation site, as when the lid on the overlap box is loosened, but it also creates a nonuniform electric field that would tend to push the anion electrons away from this region of space.

In the XTAL calculation, these effects are less pronounced, though still operating. Outward movement of a point-charge cation has two effects: it produces a nonuniform electric field (whose effects *are* included in the Sternheimer model), which tends to push the electrons away from the displaced cation; it also distorts the Madelung potential well giving an opposing outward displacement of the anion electrons. The latter has been called the "dent-in-the-wall" effect[26] and is not included by the Sternheimer model, which is based on a Taylor expansion of the electric potential at the anion site. Given that the ions, or point charges, moving in these distortions are precisely those that define the confining pseudopotential which itself has such a drastic effect on the size, shape, and energetics of the central ion and given the discontinuous slope of that potential (See Figure 1 of ref 26), it is hardly surprising that a simple Taylor-series approach breaks down.

2. Bending Distortions. The calculations based on radial distortions (i) and (ii) in the first-neighbor shell can be taken as indicative of the effects of the variation in coordination number on anion properties. Effects of varying angular distribution of neighbors can also be significant, as the calculations (iii) on D_{2h}-symmetric CLUS ions, F^- in LiF, O^{2-} in MgO, and S^{2-} in MgS reported in Figure 4 show. The ab initio computed results are again compared with the predictions of the extended Sternheimer model, this time in the self-consistent version where γ^i is itself taken to be a function of the bending angle θ, avoiding the need for calculation of higher tensors such as $g_{\alpha\beta,\gamma\delta,\epsilon\phi}$ for the undistorted cluster.

Comparison between ab initio and model EFGs is complicated here by the strongly nonspherical nature of the anion charge clouds of O^{2-} and S^{2-} noted earlier. Whereas the ab initio results for F_{xy} for F^- in LiF and O^{2-} in MgO show a roughly linear change with θ, with a slope about twice that predicted from the Sternheimer model, in S^{2-} the ab initio EFG is actually enhanced by ~15% over the model predictions. Again, this nonsystematic relationship between the calculated EFG and that deduced from the model bodes ill for predictive structure–property correlations in these materials.

C. Cations. In contrast with the unpromising situation for anions, equivalent calculations for the EFGs at cation sites suggest that the Sternheimer model may be used quantitatively. Cations of s^2 and p^6 outer electron configurations are known to be relatively insensitive to the in-crystal environmental effects,[19,22,20] and calculations performed for the induced dipoles on cations in distorted CLUS calculations[38] have shown that the short-range effects are much less pronounced than for anions. It has already been shown[25] that the Sternheimer (anti-)shielding factor for Na^+ in the XTAL environment of NaCl (5.18) is only ~5% lower than the isolated-ion value. Here, the EFGs in a distorted crystalline environment, modeled at the XTAL level, are considered.
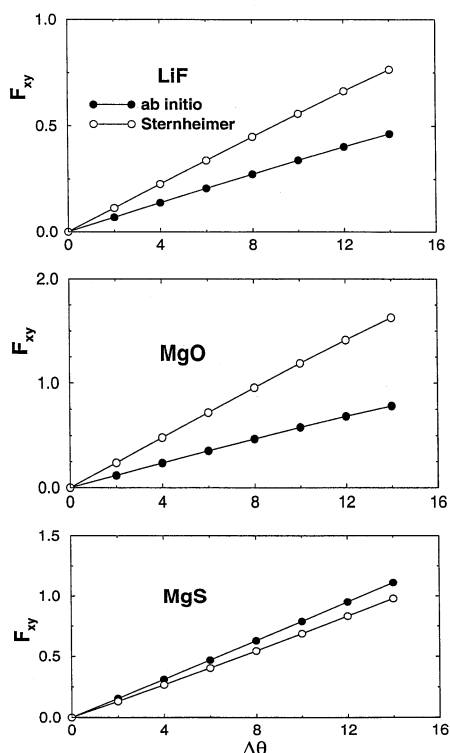
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Figure 4. EFGs F_{xy} (a.u.) at the anion nucleus in CLUS in-crystal environments subjected to D_{2h} bending distortions for (top to bottom) LiF, MgO, and MgS. Filled circles represent ab initio calculations, and open circles represent the predictions of the self-consistent extended Sternheimer eq 2. Curves are drawn as a guide to the eye. $\Delta\theta$ is the angular displacement of each equatorial neighbor in the xy plane (in degrees).
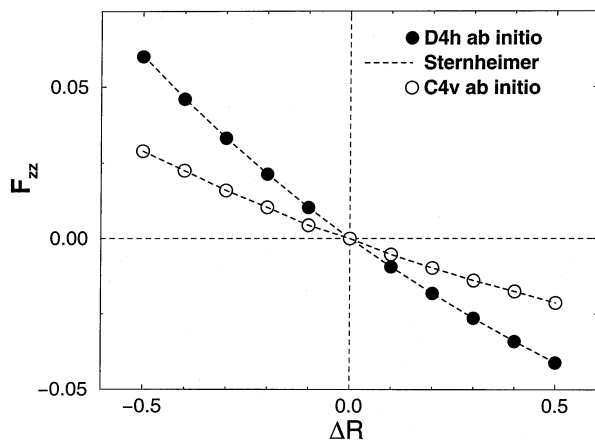

Figure 5. EFGs F_{zz} (a.u.) at the Na^+ nucleus in XTAL point-charge simulations of NaCl subject to D_{4h} (filled circles) and C_{4v} (open circles) distortions. The dashed curves represent the predictions of the extended Sternheimer eq 2 which, in contrast to the anion case, is in excellent agreement with the ab initio results.

Distorted lattice XTAL calculations analogous to those described in section III.B.1 above were performed for Na^+ in NaCl, using a previously tested 13s9p5d3f basis,[12] and the results are shown in Figure 5. Compared to the anion results (Figures 1−3), the slopes of the cation plots are smaller, reflecting the smaller value of the (anti-)shielding factor for cations and have the opposite sign for $\partial F_{zz}/\partial\Delta R$, reflecting the opposite charge of the displaced counterions in the two cases. These features are qualitatively consistent with the Sternheimer model and, in fact, the quantitative predictions of this model (shown by the dashed lines in the figure) are indistinguishable

from the ab initio calculated EFGs. It would therefore seem that for closed-shell cations the Sternheimer model, incorporating the isolated-ion shielding constants, and field gradients calculated with formal charges should be sufficiently accurate to correlate measured quadrupole coupling constants with site geometries, though it may be necessary to allow for the contribution to the field gradient from the polarization of the neighboring anions for accurate assignments.[7,8]

IV. Discussion

To realize the goal of routine assignment of nuclear quadrupole coupling constant values to ions in specific sites, without needing independent ab initio calculations of the EFGs for each site, it would be necessary for the Sternheimer model to hold in some modified form or for the corrections to it to be readily predicted from the positions of neighboring ions. Put at its simplest, the EFG at a site should be proportional to the field gradient calculated from the positions and formal charges of the surrounding ions, with a constant of proportionality that could be determined once-and-for-all for a given ion. The electronic structure calculations described in the present work have shown two impediments to the realization of this hope for anions, i.e., sensitivity of the Sternheimer shielding parameters to the in-crystal environmental compression and strong short-range effects that lie outside the domain of the multipolar (asymptotic) model. Throughout, the analogy between the environmental effects of the EFG and the induction of multipoles at low symmetry sites in ionic materials has been stressed. In the case of *dipolar* induction, it has proven possible to model the dependence of the ionic polarizability[32,24] (the analogue of the Sternheimer shielding parameter) and the short-range corrections to the asymptotic model[27] on the positions of neighboring ions and to use the models in the construction of interaction potentials,[29,30] the simulation of infrared spectra,[31] etc. However, the extent of the corrections to the simplest asymptotic model for the EFG, exposed by the present calculations, is considerably greater than for dipole induction. Typically, the short-range correction *changes the sign* of the asymptotic prediction, a situation similar to quadrupole induction.[27] In these circumstances, a model has to deal with a delicate balance of effects, difficult to represent with useful accuracy, and we suggest that this is not a useful direction to pursue.

For closed-shell cations, on the other hand, neither of the impediments to the applications of the asymptotic model appears to be serious, and the use of the Sternheimer model for site assignment is supported.

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