Sternheimer Factors and Electric-Field-Gradient Hyperpolarisabilities for Ions in Crystals *

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Analytic coupled Hartree-Fock calculations of the electric field gradient response properties γ (the Sternheimer shielding factor) and ε (the dipole-dipole-electric field gradient hyperpolarisability) have been carried out on anions in clusters that simulate that crystal environment. The systems studied are F^- in LiF and NaF, Cl^- in LiCl and NaCl, O^{2-} in MgO, S^{2-} in MgS, and H^- in LiH. Both properties show large reductions from free-ion values and significant variation with lattice parameter, and the results indicate that damped values of anion Sternheimer factors will be necessary in accurate simulation of NQR data or modelling of properties of ion-pairs.

1. Introduction

As a molecular property determined by the charge distribution, the electric field gradient (EFG) at a (quadrupolar) nucleus is potentially a useful probe of geometric and electronic structure [1–3] and, through its response to the environment of a molecule, can be a source of information on intermolecular forces.

Polarisation of the charge distribution in an applied field gradient causes a shift in EFG that can be much larger than the inducing gradient itself. Sternheimer introduced his now famous γ factor to account for quadrupolar polarisation of an anion by the internal field gradient in an ion pair [4], and the model was later refined by inclusion of hyperpolarisation by the internal field [5–7]. Higher EFG polarisabilities and hyperpolarisabilities have been evaluated for the hydrogen atom [8]. A theory of the effects of dispersion forces on EFG has been worked out in terms of dynamic response properties [9]. Engström et al. [10] extended the Sternheimer model to cover nuclei in molecules, for which shifts that are linear in the applied field are possible. In the most general formulation [11], the polarisation shift in the expectation value of the operator $V^I_{\alpha\beta}$, the true field gradient at nucleus I in a molecule subjected to an external non-uniform field, is given as a Taylor series:

$$\begin{aligned}\Delta V^I_{\alpha\beta} = {} & F_{\alpha\beta} + R^I_\gamma F_{\alpha\beta\gamma} + \tfrac{1}{2} R^I_\gamma R^I_\delta F_{\alpha\beta\gamma\delta} + \ldots \\ & + g^I_{\alpha\beta,\gamma} F_\gamma + g^I_{\alpha\beta,\gamma\delta} F_{\gamma\delta} + g^I_{\alpha\beta,\gamma\delta\varepsilon} F_{\gamma\delta\varepsilon} + \ldots \\ & + \tfrac{1}{2} \varepsilon^I_{\alpha\beta,\gamma\delta} F_\gamma F_\delta + \ldots ,\end{aligned} \tag{1}$$

where F_α, $F_{\alpha\beta}$ ... are the external field and its derivatives evaluated at an origin in the molecule, $\boldsymbol{R}^I$ is the position of nucleus I with respect to that origin and g, ε, ... are electronic properties describing the response of the density to the field. The three sets of terms in (1) correspond to the bare field gradient at I, the linear response and the non-linear response, respectively. If the origin is at the nucleus of interest then the bare gradient is just $F_{\alpha\beta}$, and for a spherical system the Sternheimer equation

$$\Delta V^I_{zz} = (1+\gamma) F_{zz} + \varepsilon F_z^2 \ldots \tag{2}$$

is recovered, with γ and ε representing appropriate isotropic averages of the g and ε tensors.

Versions of these expansions have been used to interpret the systematic shifts in quadrupole coupling constants $\chi(^{35}Cl)$ and $\chi(^{37}Cl)$ that occur on formation of a hydrogen-bonded complex B ··· HCl [12, 13], to interpret the results of supermolecule calculations of EFGs in systems with ^{14}N and ^{17}O nuclei (e.g. [14]) and to calculate solid-state shifts in water, ammonia and hydrogen cyanide ices [15, 16].

The use of (1) for modelling properties of complexes depends on the expectation that short-range effects on the density at sites remote from the intermolecular contact are likely to be small. The subject of the present paper is the evaluation of EFG response in a case where short-range forces are known to be important, that of ions in crystals. The crystalline environment

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provides a perturbation that has a strong short-range component, is not pairwise additive and is not amenable to Taylor expansion using the properties of the non-interacting species. In this paper we calculate the Sternheimer and EFG hyperpolarisability factors directly for in-crystal ions, and show that they differ significantly from corresponding results for the free species. Implications for NQR of crystals and for models of ion pairs are discussed.

2. Simulating the Crystalline Environment

To a first approximation, it should be possible to predict the electric field gradient at the nucleus of an ion in site of non-cubic symmetry in a fully ionic crystal by summation of two terms. The first arises from the infinite lattice of point charges and is the local 'Madelung' field gradient, which may need modification to take account of ionic polarisability if the solid has a high dielectric constant, but represents the 'bare' field gradient at the nucleus. The second is the Sternheimer term describing the shielding or antishielding of the local field gradient by the electron cloud of the ion of interest, and again this may require modification in the spirit of (1) if the field gradient is strong or if the ion is so polarisable that higher terms become important. The problem with this simple approach is that it is not all clear what Sternheimer factors to use.

The properties of negatively charged ions are known to be sensitive functions of the crystalline environment. Anions in crystals are smaller, less polarisable and more strongly bound than their free counterparts. The dipole polarisability α of a small anion is markedly affected by the crystal: the polarisability of F^- in LiF is smaller than the free-ion value by a factor of two or more [17]. Higher multipole properties [18] and non-linear polarisabilities [19] are also strongly affected. In some cases, such as those of O^{2-} and S^{2-}, the crystal field is responsible for the whole of the binding of the 'extra' outermost electrons, and it can be argued that the moderate in-crystal polarisabilities of these ions reflect an infinite reduction from the values appropriate to the free (and therefore dissociated) anions [20, 21]. Values of Sternheimer factors obtained in calculations on free ions, even where these are possible, are therefore unlikely to be appropriate for in-crystal anions. As the Sternheimer factor dominates the total field gradient for anions, it seems to be worth attempting to quantify the changes.

Calculations on a variety of ionic systems using ab initio methods have demonstrated that it is possible to obtain ionic dipole polarisabilities that account quantitatively for in-crystal refractive indices [17–22], but only if the crystalline environment is included in the calculation. These methods are extended in the present paper to γ and ε for some simple ionic systems. It will be seen that these properties are much reduced in magnitude for in-crystal anions and, like polarisability, vary appreciably with lattice parameter.

The method of including the crystalline environment has been described before [17–22], and is summarised only briefly here. An anion in a crystal is subject to two compressive influences. First, the electrostatic potential of an infinite lattice of point charges is stabilising for an electron on an anion site, and so the main effect of this Madelung potential in a symmetrical lattice is to provide a spherical well of radius equal to the nearest neighbour separation. The well acts to confine the diffuse anion wavefunction. Secondly, overlap between the filled orbitals of the anion and its nearest neighbours further compresses the anionic charge cloud. Both of these factors can be included in an ab initio calculation by treating not the free anion but a cluster consisting of the anion and its nearest shell of cation neighbours, the whole embedded in a finite fragment of the point-charge lattice. The size of the lattice fragment is not critical for small ions (e.g. F^-, Cl^-) because once the ion is compressed by electrostatic and overlap interactions with its cage of nearest neighbours, its properties are insensitive to the detailed long-range behaviour of the lattice potential. A $5 \times 5 \times 5$ cubic lattice fragment with scaled charges on its faces to preserve overall neutrality is sufficient in many cases to give converged properties [22]; in non-cubic lattices or for highly charged anions a larger number of charges may be needed [23].

The properties of a closed-shell cation with an inert-gas configuration are much less sensitive to crystal [17], and are well represented in a conventional calculation on the free ion. The effects of electrostatic and overlap interactions are opposed for these ions (because the Madelung potential is destabilising for an electron at a cation site), but both are in any case small; the tightly bound electron cloud is well localised within the nearest neighbour distance and therefore does not sample the edge of the Madelung potential plateau, and cations are 'harder' than anions so that they exert overlap compression on the anion and not vice versa.

Any program that calculates molecular wavefunctions, energies and properties can be modified to include the point-charge lattice potential as a finite perturbation to the Hamiltonian, and then the cluster can be treated as a single, charged supermolecule. The properties of the in-crystal anion can be extracted from those calculated for the cluster in several ways [22], the simplest being summation of orbital contributions, which is used here. All calculations used the Exeter version of the SYSMO package, which calculates electric and magnetic properties at the self-consistent field level. The computer program for the calculation of quadrupolar response properties of closed-shell atoms and molecules within Coupled Hartree-Fock theory has recently been described [18]. It is written as a module within SYSMO and follows closely the methods and conventions of that package [24]. Briefly, the first-order correction to the density matrix for a quadrupolar perturbation ($H' = -\frac{1}{3}\Theta_{\alpha\beta} F_{\alpha\beta}$) is calculated iteratively, exploiting any finite point group symmetry present in the unperturbed system, and used to compute a variety of second- and third-order response properties including the quadrupole polarisability and Sternheimer factor.

The Sternheimer factor is found by taking the trace of the product of the first-order density matrix and the matrix of the electric field gradient operator. By the interchange theorem for second-order properties, the same result could be obtained by using the nuclear quadrupole moment as the perturbation ($H' = -\frac{1}{3} V^I_{\alpha\beta} Q^I_{\alpha\beta}$) and evaluating the response of the quadrupole moment. The latter method is also implemented in our version of SYSMO and has the advantage that the ε hyperpolarisation factor can be evaluated by combining first-order wavefunctions from nuclear quadrupole moment and uniform electric field perturbations. The present calculations appear to be the first to evaluate ε for a many-electron system fully analytically; previous calculations used finite-field or mixed finite-field and analytic techniques [7].

3. Results

The systems treated here are F^- in LiF and NaF, Cl^- in LiCl and NaCl, O^{2-} in MgO, S^{2-} in MgS, and H^- in LiH, cases for which ionic dipole and quadrupole polarisabilities calculated by the cluster method are known from previous work [18, 20, 21, 25]. Details of basis sets and lattice parameters are listed in the earlier papers. Not all of these nuclei are accessible to the NQR technique, and all lie at cubic sites where the total field gradient vanishes by symmetry, but this series of calculations should give an indication of the size of the environmental effects. Calculations on systems of more direct relevance to the NQR experiment will be reported later.

Table 1. Dipole and quadrupole polarisabilities. Sternheimer factors and EFG hyperpolarisabilities (in a.u.) calculated for anions in different environments using coupled Hartree-Fock theory. In-crystal anion results were calculated using embedded clusters, as described in the text; polarisabilities are taken from our previous calculations of this type, and for most of the cases considered here correlation corrections to the dipole polarisability are available (see references in [18]). The polarisabilities α and C determine the dipole and quadrupole moments induced per unit external field and field gradient, respectively, in the limit of small perturbations. The signs of the EFG properties are defined by $V_{zz} = (1+\gamma) F_{zz} + \varepsilon F_z^2$, where V_{zz} is a true field gradient, so that a positive γ implies an antishielding effect.

Anion	α	C	γ	ε
F^- in LiF	5.48	9.84	+13.9	−30.0
NaF	5.99	12.0	+15.8	−40.2
in vacuo	10.65	37.3	+30.0	−173.0
Cl^- in LiCl	19.01	55.6	+38.4	−111.0
NaCl	19.51	60.9	+39.8	−125.0
in vacuo	31.50	70.6	+70.5	−463.0
O^{2-} in MgO	10.77	26.0	+16.0	−45.3
S^{2-} in MgS	29.29	106.0	+39.3	−123.0
H^- in LiH	10.45	18.9	−0.70	+2.20

Table 1 lists the calculated values of γ and ε for the various anions. The anionic Sternheimer factors were extracted from the total cluster response by summation of contributions from anion-centred orbitals, but in fact this procedure was hardly necessary as the contribution from the cage was negligible ($<0.5\%$) in all cases, reflecting the localised nature of the EFG operator. Taking the Sternheimer factors first, several trends can be seen in the results. First, γ is at least as sensitive as the polarisability to the crystalline environment. The in-crystal ion has a much smaller value of γ than does the free ion; in these uncorrelated calculations $\gamma(F^-)$ and $\gamma(Cl^-)$ are each reduced by about 50% in alkali halide crystals; in fact since electron correlation would be expected to increase γ significantly for the free anions, but much less for the in-crystal species, the reduction factor is probably underestimated. The present values for the free anions are close to the numerical Hartree-Fock shieldings reported by McEachran et al. [26] (see the comparison in [7]). Correlation effects on anion properties such as the polarisability are known to be quenched in the

crystal. For the ions O^{2-} and S^{2-} that are unbound in vacuo, γ has fallen from the infinite value appropriate to the free electron to physically reasonable values close to those of the iso-electronic in-crystal halide. Some sensitivity to lattice parameter is shown by X^- in NaX and LiX, and this is consistent with the decrease in volume available to the anion electrons with the change in counterion. The EFG hyperpolarisability ε is even more dramatically reduced by in-crystal compression, but the opposition in sign of ε and γ remains, with p^6 anions and atoms having positive (antishielding) γ but negative ε, and the s^2 hydride ion having negative γ and positive ε. A rationalisation of this sign pattern was given in [7].

Cations are not expected to show the same sensitivity to environment. A test calculation on Na^+ embedded in a point-charge lattice representing NaCl, for example, shows an increase for the free-ion value of less than 5% in γ and less than 3% in the magnitude of ε. In the full crystal, with charge clouds rather than point charges for neighbours, even these small increases would tend to be cancelled out by overlap compression. This asymmetry between the roles of anions and cations, which also appears in other in-crystal properties [25] is not brought out by using a model such as the Watson sphere [27], which though it predicts changes in polarisability [28] and shielding [29] in the correct direction for an anion, predicts large shifts in the opposite direction for a cation. The current method, embodying both electrostatic and overlap factors and using a reliable *ab initio* method has been extensively tested for other properties and found to be a useful way of deriving theoretical in-crystal anion properties. It is clear from the selection of results presented here that it would be unwise to neglect the compressive effect of the crystalline environment when calculating nuclear quadrupole interactions of anions.

Finally, the discussion returns to the ion pair, the place where the Sternheimer shielding factor was first found to be necessary. Whether because of our inability or unwillingness to calculate electronic structure rigorously (as Lucken says on page 79 of [2]), or because of a proper wish to understand complicated facts in terms of simpler models (as we believe), much effort has been invested in models for the energetic and electrical properties of ionic diatomics (e.g. [30, 31]). In many of these models the properties ascribed to the anion are heavily damped [32] or at variance with accurate calculations on the free anion [6, 7]. Use of undamped free-ion properties can lead to diverging results, even though the evidence for ionicity may be clear [33]. In the light of the present calculations, we take this as an indication that the ion-pair environment is closer to the crystal than to the free-ion limit.

[1] W. Gordy and R. L. Cook, Microwave Molecular Spectra, Vol. IX of Techniques of Organic Chemistry, ed. A. Weissberger, Interscience, New York 1970.
[2] E. A. C. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, New York 1969.
[3] J. A. S. Smith, Chem. Soc. Rev. **15,** 225 (1986).
[4] R. M. Sternheimer, Phys. Rev. **80,** 102 (1950).
[5] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93,** 734 (1954).
[6] A. D. Buckingham, Trans. Faraday Soc. **53,** 1277 (1962).
[7] P. W. Fowler, Chem. Phys. Lett. **156,** 494 (1989).
[8] P. W. Fowler, and E. Steiner, Mol. Phys. **66,** 797 (1989).
[9] P. W. Fowler, Chem. Phys. **143,** 447 (1990).
[10] S. Engström, H. Wennerström, B. Jönnson, and G. Karlström, Mol. Phys. **34,** 813 (1977).
[11] P. W. Fowler, P. Lazzeretti, E. Steiner, and R. Zanasi, Chem. Phys. **133,** 221 (1989).
[12] A. C. Legon and D. J. Millen, Proc. Roy. Soc. London, Ser. A **417,** 21 (1988).
[13] J. Baker, A. D. Buckingham, P. W. Fowler, E. Steiner, P. Lazzeretti, and R. Zanasi, J. Chem. Soc. Faraday Trans. 2 **85,** 901 (1989).
[14] G. B. Bacskay, D. I. Kerdraon, and N. S. Hush, Chem. Phys. **144,** 53 (1990).
[15] P. L. Cummins, G. B. Bacskay, and N. S. Hush, Mol. Phys. **61,** 795 (1987).
[16] P. L. Cummins, G. B. Bacskay, and N. S. Hush, Mol. Phys. **62,** 193 (1987).
[17] P. W. Fowler and P. A. Madden, Mol. Phys. **49,** 913 (1983).
[18] H. M. Kelly and P. W. Fowler, Mol. Phys. **80,** 135 (1993).
[19] P. W. Fowler and P. A. Madden, Phys. Rev. B **30,** 6131 (1985).
[20] P. W. Fowler, and P. A. Madden, J. Phys. Chem. **89,** 2581 (1985).
[21] P. W. Fowler and P. Tole, Chem. Phys. Lett. **149,** 273 (1985).
[22] P. W. Fowler, Mol. Simulation **4,** 313 (1990).
[23] P. W Fowler, and P. Tole, J. Chem. Soc. Chem. Comm. 1652 (1989).
[24] P. Lazzeretti and R. Zanasi, SYSMO program, University of Modena, Italy.
[25] P. W. Fowler and P. A. Madden, Phys. Rev. B **29,** 1035 (1984).
[26] R. P. McEachran, A. D. Stauffer, and S. Greita, J. Phys. B **12,** 3119 (1979).
[27] R. E. Watson, Phys. Rev. **111,** 1108 (1958).
[28] P. C. Schmidt, K. D. Sen, T. P. Das, and A. Weiss, Phys. Rev. B **22,** 4167 (1980).
[29] K. D. Sen, J. Phys. C **18,** 3153 (1985).
[30] E. S. Rittner, J. Chem. Phys. **19,** 1030 (1951).
[31] S. L. Davis, J. Chem. Phys. **88,** 1080 (1988).
[32] T. Torring, W. E. Ernst, and S. Kindt, J. Chem. Phys. **81,** 4614 (1984).
[33] P. W. Fowler, A. C. Legon, C. A. Rego, and P. Tole, Chem. Phys. **134,** 297 (1989).