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First-principles theory of antishielding effects in the nuclear quadrupole interaction in ionic crystals: Application to ^{57m}Fe in Fe_2O_3

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A first-principles procedure is developed for the quantitative study of the widely differing Sternheimer antishielding effects that can be ascribed to the induced electric field gradients due to the various sources of electric field gradient in ionic crystals. The method involves the perturbation of the electronic states in the crystal by the nuclear quadrupole moment of the central ion, and the use of these perturbed functions in an evaluation of components of the energy of the crystal which are linear in the quadrupole moment. With each term in this energy, one can associate an induced field gradient due to a specific source in the crystal and a specific perturbation of the central-ion charge distribution. We have applied this *ab initio* method to a study of the nuclear quadrupole interaction for ^{57m}Fe in Fe_2O_3 using a model in which an Fe^{3+} ion is surrounded by six O^{2-} ligands whose charge distributions overlap the Fe^{3+} ion. The application of our procedure to the model of overlapping ions leads to the important conclusion that the field gradients due to the various sources in the central cluster and the surrounding lattice are all subject to very different antishielding effects. The sources involved can be grouped broadly into three classes: local, nonlocal, and distant, with the local sources involving charge densities purely central in character, nonlocal sources involving charge densities composed of one central-ion orbital and one ligand-ion orbital, and the distant sources involving two categories, a distant electronic one composed of charge densities from purely ligand-ion orbitals, and a distant nuclear one, comprising the nuclear charges on the ligand ions (O^{2-}). The effective antishielding factors γ_{eff} associated with these sources were found to be, respectively, -0.2, -0.7, -3.8, and -6.5, all very different from $\gamma_\infty=-9.19$ for the Fe^{3+} ion appropriate for a totally external point-charge source and $R=+0.07$, the shielding factor with the field gradient due to the $3d$ valence shell in the Fe^{2+} ion, which have both been used in the past as approximate choices for the various γ_{eff}. The substantial differences between the various effective antishielding factors γ_{eff} found in the present work are explained physically by the consideration of the different degrees of penetration of the charge densities corresponding to the various sources producing the field gradients into the region of the Fe^{3+} ion. We have compared the calculated total electric field gradient at the ^{57m}Fe nucleus in Fe_2O_3, including the antishielding effects, with experimental Mössbauer data to obtain an estimate of the extent of charge-transfer covalency in this compound.

I. INTRODUCTION

The study of nuclear quadrupole interactions[1] (NQI) through various experimental techniques such as Mössbauer effect,[2] magnetic resonance,[3] nuclear quadrupole resonance,[4] and perturbed angular correlation[5] has provided valuable information[6] about the electronic structure and related properties of atoms, molecules, and solids. A major aim of such studies is the understanding of the nature and importance of the basic mechanisms contributing to the electric field gradients (EFG's) in these systems. In particular for ionic crystal systems, with which the present work is concerned, one is interested in understanding not only the absolute values of the components of the EFG but also their variation with chemical environment, the relationship between the EFG in ionic systems and that in related metallic systems, and the dependence of the EFG upon the degree of covalency.

The present work is aimed at a basic understanding of the origins of the EFG in ionic solids. In particular, we are concerned with one very important aspect of the study of these field gradients, namely an unambiguous first-principles formulation of Sternheimer antishielding effects[7] in the ionic solid, considered not as an assembly of point ions surrounding a central ion whose nucleus possesses a quadrupole moment, but as ions whose nuclei and electronic charge distributions overlap and interact with one another substantially. Our aim is to develop a procedure for the quantitative study of the influence of these interactions upon the EFG in the solid, which amounts to a study of the antishielding effects associated with each component of these interacting, overlapping charge distributions in the solid. As a practical application of this procedure we study the NQI at the ^{57m}Fe nucleus in α-Fe_2O_3, with the aim of illustrating the general methodology and at the same time understanding the role of overlap[8-10] and charge-transfer covalency[10-12] effects in α-Fe_2O_3, which has been a long-standing problem in the field of NQI.

The need for an *ab initio* procedure for the study of Sternheimer effects becomes evident upon careful examination of the sources contributing to the EFG in ionic solids and the methods used so far in the literature for their quantitative treatment. In the earliest investigations,[13-19] the field gradients at the central-ion nucleus were evaluated as being due to point monopoles and dipoles on the lattice sites. These point charges were further assumed to be totally external to the ion containing the nucleus in question, and a multiplying factor γ_∞ was used to incorporate the antishielding of this ionic contribution by the core electrons of the central ion. It is now generally recognized[8-12,20,21] that the extreme ionic model of separated nonoverlapping ions is not satisfactory because small departures from spherical symmetry of the ions produced by covalency effects such as, for example, the transfer of electrons from the negative ions into *p*- or *d*-like orbitals of the positive ions can produce very significant changes in the field gradient. It is possible to write the net field gradient in the form

$$q = q^{(0)}_{\text{lattice}}(1-\gamma_\infty) + q_{\text{electronic}} \, , \tag{1}$$

where $q_{\text{electronic}}$ embraces all contributions due to the electronic charge distributions of the central ion and the nearest-neighbor ligand ions as modifed from their free-ion configurations by overlap, charge transfer, and other effects in the solid, and $q^{(0)}_{\text{lattice}}$ is the unshielded EFG (Ref. 13) due to the bare nuclei of the nearest-neighbor ligand ions and effective charges on more distant ions. One might be concerned about the proper value of the Sternheimer antishielding factor γ_∞ to use in an equation of this type even though such considerations by themselves are not crucial to a quantitative understanding of the EFG in ionic solids. Among the various effects that can be included in γ_∞, those arising from the influence of electron-electron interactions[22-26] on the free-ion γ_∞ are amenable to a quantitative treatment, and have been included in a number of systems. These consistency and correlation effects have been shown[24-26] to influence the free-ion γ_∞ by no more than 15%. Another effect that can influence the value of γ_∞ has to do with the departure of the radial character of the ionic orbitals with respect to the free-ion state due to the field of the crystalline lattice.[26-28] This type of effect has been investigated approximately, and the general trends observed suggest that it causes an increase in the free-ion γ_∞ for positive ions and a decrease for negative ions.

In accordance with the expectation[29] that the contribution of the bare nuclei of the nearest neighbors to q may be antishielded by a factor differing substantially from the free-ion γ_∞, we separate this contribution from $q^{(0)}_{\text{lattice}}$ and include it with $q_{\text{electronic}}$. Thus we can write

$$q = (1-\gamma_\infty) q^{(0)}_{\text{DRL}} + q_{\text{cluster}} \, , \tag{2}$$

where q_{cluster} includes the total contribution due to all electrons and nuclei of the cluster composed of the central ion and its ligands, and $q^{(0)}_{\text{DRL}}$ is now the unshielded contribution due to charges on distant ions in the rest of the lattice outside the cluster. The major problem in a quantitative evaluation of the EFG q in Eq. (2) is the treatment of q_{cluster}. A Townes-Dailey-type model[11,30] involving the local anisotropy in the electron (or hole) distribution on the central ion has been found to be inadequate for the treatment of q_{cluster} in ionic solids containing the halogens[15,16,31] as well as in alkali-halide solid solutions.[32,33] Thus, in ionic systems, for both halogen nuclei as well as other nuclei, the local anisotropy on the ion in question is not enough to make the dominant contribution to the EFG. Therefore, contributions to the field gradient from sources in other regions of the solid and their separate antishielding effects have to be evaluated carefully. The importance of a proper treatment of antishielding effects can be illustrated best by a consideration of the model of overlapping ions[31-35] without charge-transfer effects that has been used in a number of instances[8,10,36-40] in previous treatments of NQI and other hyperfine interactions in ionic solids.

Consider a pair of overlapping ions A and B. The orbitals $\psi_{0\alpha}$ on A will, in general, be nonorthogonal to orbitals $\phi_{0\mu}$ on B, so that integrals of the type $\langle \psi_{0\alpha} | \phi_{0\mu} \rangle$ do not vanish. Representing the ground state of the ion pair AB by an antisymmetrized product Ψ_0^{nonortho} of the $\psi_{0\alpha}$ and the $\phi_{0\mu}$, one can obtain the zero-order (direct, unshielded) EFG at the nucleus of ion A by taking the expectation value of the operator corresponding to the sum of field gradients at A due to all the electrons of the ions A and B. Since our basis set is nonorthogonal, this expectation value does not reduce to a sum of diagonal one-electron matrix elements,[41] but contains in addition a large number of nondiagonal terms,[42] each of which is multiplied by an overlap integral $S_{\alpha\mu} = \langle \psi_{0\alpha} | \phi_{0\mu} \rangle$. The algebra is considerably simplifed by starting out with a basis set consisting of the orbitals of ion A orthogonalized to those of ion B by a Schmidt orthogonalization procedure.[34,43] We denote this set of orthogonalized atomic orbitals (OAO's) by $\{\psi'_{0\alpha}, \phi'_{0\mu}\}$. Taking the expectation value of the total field gradient operator using a Slater determinant of these OAO's leads to a zero-order contribution $q^{(0)}_{\text{electronic}}$ which can be written as[8,32,33]

$$q^{(0)}_{\text{electronic}} = q^{(0)}_L + q^{(0)}_N + q^{(0)}_{\text{DE}} + q^{(0)}_{\text{DO}} \tag{3}$$

and a similar zero-order EFG due to all charges of the cluster (i.e., the ion pair AB)

$$q^{(0)}_{\text{cluster}} = q^{(0)}_{\text{electronic}} + q^{(0)}_{\text{DN}} \, . \tag{4}$$

In Eqs. (3) and (4) $q^{(0)}_{\text{DN}}$ refers to the contribution to the field gradient from the charge on the nucleus of ion B, $q^{(0)}_L$ is the local electronic contribution involving only the orbitals on ion A, $q^{(0)}_N$ is the nonlocal contribution involving the two-centered charge densities represented by the products of orbitals on ions A and B, $q^{(0)}_{\text{DE}}$ is the distant electronic contribution to the field gradient at A due to charge densities arising from products of orbitals on ion B only, and $q^{(0)}_{\text{DO}}$ is a similar contribution but with the density from orbitals of ion B originating from the orthogonalization procedure applied to the orbitals of ion A. The situation embodied by the last two equations is in marked contrast with the representation of the EFG at the nucleus of ion A within the extreme ionic model.[44,45] Thus in the model of overlapping ions, Eqs. (2)—(4), there are six different sources of zero-order EFG, while in the extreme

TABLE I. Source-by-source arrangement of energy terms representing the induced electric field gradients at the central ion of a cluster in an ionic crystal. The integrals, operators, and orbitals are described in the text.

Term in the expansion of ΔE_{eQ}[a]	Q-perturbed charge density	Source charge or charge density	Source label $S(t)$
$2\sum_{\alpha\beta\beta'}(\langle\delta\psi_{Q\alpha}\psi_{0\beta}\|\|\psi_{0\alpha}\psi_{0\beta'}\rangle$ $+\langle\delta\psi_{Q\alpha}\psi_{0\beta'}\|\|\psi_{0\alpha}\psi_{0\beta}\rangle)\left[\frac{1}{2}\sum_{\nu}S_{\beta\nu}S_{\beta'\nu}\right]$	$\delta\psi^*_{Q\alpha}\psi_{0\alpha}$	$(\psi^*_{0\beta}\psi_{0\beta'}+\psi^*_{0\beta'}\psi_{0\beta})$ $\times\left[\frac{1}{2}\sum_{\nu}S_{\beta\nu}S_{\beta'\nu}\right]$	L(C0)
$2\sum_{\alpha\beta\nu}\langle\delta\psi_{Q\alpha}\psi_{0\beta}\|\|\phi_{0\nu}\psi_{0\beta}\rangle(-S_{\alpha\nu})$	$(\delta\psi^*_{Q\alpha}\phi_{0\nu})(-S_{\alpha\nu})$	$\psi^*_{0\beta}\psi_{0\beta}$	L(C1)
$2\sum_{\alpha\beta\nu\nu'}\langle\phi_{0\nu'}\psi_{0\beta}\|\|\phi_{0\nu}\psi_{0\beta}\rangle(\delta S_{\alpha\nu'}S_{\alpha\nu})$	$(\phi^*_{0\nu'}\phi_{0\nu})(\delta S_{\alpha\nu'}S_{\alpha\nu})$	$\psi^*_{0\beta}\psi_{0\beta}$	L(C2)
$2\sum_{\alpha\nu}\langle\delta\psi_{Q\alpha}\|A\|\phi_{0\nu}\rangle(-S_{\alpha\nu})$	$(\delta\psi^*_{Q\alpha}\phi_{0\nu})(-S_{\alpha\nu})$	Central-ion nuclear charge	L(NC1)
$2\sum_{\alpha\nu\nu'}\langle\phi_{0\nu'}\|A\|\phi_{0\nu}\rangle(\delta S_{\alpha\nu'}S_{\alpha\nu})$	$(\phi^*_{0\nu'}\phi_{0\nu})(\delta S_{\alpha\nu'}S_{\alpha\nu})$	Central-ion nuclear charge	L(NC2)
$2\sum_{\alpha\beta\nu}(\langle\delta\psi_{Q\alpha}\psi_{0\beta}\|\|\psi_{0\alpha}\phi_{0\nu}\rangle$ $+\langle\delta\psi_{Q\alpha}\phi_{0\nu}\|\|\psi_{0\alpha}\psi_{0\beta}\rangle)(-S_{\beta\nu})$	$\delta\psi^*_{Q\alpha}\psi_{0\alpha}$	$(\psi^*_{0\beta}\phi_{0\nu}+\phi^*_{0\nu}\psi_{0\beta})$ $\times(-S_{\beta\nu})$	N(C0)
$2\sum_{\alpha\beta\nu\nu'}\langle\delta\psi_{Q\alpha}\phi_{0\nu}\|\|\phi_{0\nu'}\psi_{0\beta}\rangle(S_{\alpha\nu'}S_{\beta\nu})$	$(\delta\psi^*_{Q\alpha}\phi_{0\nu'})(-S_{\alpha\nu'})$	$(\phi^*_{0\nu}\psi_{0\beta})(-S_{\beta\nu})$	N(C1)
$2\sum_{\alpha\beta\nu\nu'}\langle\phi_{0\nu'}\psi_{0\beta}\|\|\psi_{0\alpha}\phi_{0\nu}\rangle(\delta S_{\alpha\nu'}S_{\beta\nu})$	$(\phi^*_{0\nu'}\psi_{0\alpha})(-\delta S_{\alpha\nu'})$	$(\psi^*_{0\beta}\phi_{0\nu})(-S_{\beta\nu})$	N(C1′)
$2\sum_{\alpha\mu}\langle\delta\psi_{Q\alpha}\phi_{0\mu}\|\|\psi_{0\alpha}\phi_{0\mu}\rangle$	$\delta\psi^*_{Q\alpha}\psi_{0\alpha}$	$\phi^*_{0\mu}\phi_{0\mu}$	DE(C0)
$2\sum_{\alpha\mu\nu'}\langle\phi_{0\nu'}\phi_{0\mu}\|\|\psi_{0\alpha}\phi_{0\mu}\rangle(-\delta S_{\alpha\nu'})$	$(\phi^*_{0\nu'}\psi_{0\alpha})(-\delta S_{\alpha\nu'})$	$\phi^*_{0\mu}\phi_{0\mu}$	DE(C1′)
$2\sum_{\alpha\mu\beta'}\langle\psi_{0\beta'}\phi_{0\mu}\|\|\psi_{0\alpha}\phi_{0\mu}\rangle\left[\sum_{\mu}S_{\beta'\nu}\delta S_{\alpha\nu}\right]$	$(\psi^*_{0\beta'}\psi_{0\alpha})\left[\sum_{\nu}S_{\beta'\nu}\delta S_{\alpha\nu}\right]$	$\phi^*_{0\mu}\phi_{0\mu}$	DE(RC0′)
$2\sum_{\alpha\mu\beta'}\langle\delta\psi_{Q\alpha}\phi_{0\mu}\|\|\psi_{0\beta'}\phi_{0\mu}\rangle\left[\frac{1}{2}\sum_{\nu}S_{\beta'\nu}S_{\alpha\nu}\right]$	$(\delta\psi^*_{Q\alpha}\psi_{0\beta'})\left[\frac{1}{2}\sum_{\nu}S_{\beta'\nu}S_{\alpha\nu}\right]$	$\phi^*_{0\mu}\phi_{0\mu}$	DE(RC0)
$2\sum_{\alpha}\langle\delta\psi_{Q\alpha}\|B\|\psi_{0\alpha}\rangle$	$\delta\psi^*_{Q\alpha}\psi_{0\alpha}$	Ligand-ion nuclear charge	DN(C0)
$2\sum_{\alpha\nu'}\langle\phi_{0\nu'}\|B\|\psi_{0\alpha}\rangle(-\delta S_{\alpha\nu'})$	$(\phi^*_{0\nu'}\psi_{0\alpha})(-\delta S_{\alpha\nu'})$	Ligand-ion nuclear charge	DN(C1′)
$2\sum_{\alpha\beta'}\langle\psi_{0\beta'}\|B\|\psi_{0\alpha}\rangle\left[\sum_{\nu}S_{\beta'\nu}\delta S_{\alpha\nu}\right]$	$(\psi^*_{0\beta'}\psi_{0\alpha})\left[\sum_{\nu}S_{\beta'\nu}\delta S_{\alpha\nu}\right]$	Ligand-ion nuclear charge	DN(RC0′)
$2\sum_{\alpha\beta'}\langle\delta\psi_{Q\alpha}\|B\|\psi_{0\beta'}\rangle\left[\frac{1}{2}\sum_{\nu}S_{\beta'\nu}S_{\alpha\nu}\right]$	$(\delta\psi^*_{Q\alpha}\psi_{0\beta'})\left[\frac{1}{2}\sum_{\nu}S_{\beta'\nu}S_{\alpha\nu}\right]$	Ligand-ion nuclear charge	DN(RC0)
$2\sum_{\alpha\beta\nu\nu'}\langle\delta\psi_{Q\alpha}\phi_{0\nu'}\|\|\psi_{0\alpha}\phi_{0\nu}\rangle(S_{\beta\nu'}S_{\beta\nu})$	$\delta\psi^*_{Q\alpha}\psi_{0\alpha}$	$(\phi^*_{0\nu'}\phi_{0\nu})(S_{\beta\nu'}S_{\beta\nu})$	DO(C0)

[a] See Eq. (53) in the text.

ionic model[44] there are only two, namely $q^{(0)}_{\text{lattice}}$ due to the charges at all ions in the lattice including the nearest neighbors, and $q^{(0)}_{\text{valence}}$ due to the open valence shell of the central ion.

The zero-order EFG due to each of the six sources within the model of overlapping ions is antishielded by the central-ion charge distribution. The total EFG at the nucleus of ion A including antishielding factors can be formally written as

$$\begin{aligned} q &= \sum_S (1-\gamma_S) q_S^{(0)} \\ &= (1-\gamma_L) q_L^{(0)} + (1-\gamma_N) q_N^{(0)} + (1-\gamma_{\text{DE}}) q_{\text{DE}}^{(0)} \\ &\quad + (1-\gamma_{\text{DO}}) q_{\text{DO}}^{(0)} + (1-\gamma_{\text{DN}}) q_{\text{DN}}^{(0)} + (1-\gamma_\infty) q_{\text{DRL}}^{(0)} \ . \end{aligned} \tag{5}$$

The quantities γ_S associated with each of the $q_S^{(0)}$ due to sources S refer to the appropriate antishielding factors. The primary aim of our present work is the understanding of these antishielding factors from a first-principles point of view. Prior to the present work, various parametric choices have been made for these antishielding factors in studying NQI in ionic solids. Thus, for example, it has been assumed in many previous calculations[8,32,33,37–39,46] that γ_∞ is a good approximation for all the distant antishielding factors γ_{DE}, γ_{DO}, and γ_{DN}. In other words, a parameter which is strictly applicable only to distant point charges external to the central ion has been used in past work as the antishielding factor for the EFG due to the ligand-ion electronic charge distribution (q_{DE}), the "overlapping" component of the ligand-ion electronic charge distribution (q_{DO}), and the bare nuclei of the ligand ions (q_{DN}) (see Table I). For γ_L, the atomic shielding factor R corresponding to a nonspherical atom or ion with an open valence shell has been used by many investigators.[8,10,31–33,37–39,44–47] For γ_N, two very different choices have been made in the past, one[8,37–39,44–47] being $\gamma_N = R$ and the other[32,33] being $\gamma_N = \gamma_\infty/2$. These two choices have been based on alternate considerations as to the region where the overlap charge density, arising from the electronic charge distributions on ions A and B, is concentrated, and the observation[7,29] that, for a point charge adjacent to an ion, the antishielding of the EFG is sensitively dependent upon the position of the point charge relative to the nucleus and core charge distribution of the ion. These different choices have been shown[16,31–33] to give widely different results for the NQI in alkali-halide molecules and alkali-halide solid solutions. For the case of the ^{57m}Fe NQI in Fe_2O_3, which is the system we shall be concerned with in the present work, the results for different parametric choices for the $\gamma_{\text{eff},S}$ are discussed in Section III (Table IV). We shall quote some of the parametric results briefly here to emphasize the need for an *ab initio* treatment of Sternheimer effects. Thus if one uses for γ_L and γ_N the most recent[48(a)] value of $R = 0.07$ for the Fe^{2+} ion including the influence of many-body effects [henceforth referred to as R (Fe^{2+})], and for γ_{DE}, γ_{DO}, and γ_{DN} the value[25] of $\gamma_\infty = -9.19$ for a Fe^{3+} ion [henceforth referred to as γ_∞ (Fe^{3+})], the calculated value of e^2qQ/h comes out as 5.36 MHz using the recent value[48(b)] of $Q(^{57m}\text{Fe}) = 0.082$ b. A somewhat different value of 4.47 MHz is obtained by using a value of q recently published in the literature[8] using a similar scheme for choosing γ_L, γ_N, γ_{DE}, γ_{DN}, and γ_{DO} except that an earlier overestimated value of $R = 0.32$ was used as well as a slightly different value of $\gamma_\infty(Fe^{3+}) = -9.14$. A drastically different value of $e^2qQ/h = 3.01$ MHz is obtained by using $\gamma_L = R = 0.07$ and $\gamma_N = \frac{1}{2}\gamma_\infty(Fe^{3+}) = -4.60$. This extreme sensitiveness of the theoretical value of the field gradient at the ^{57m}Fe nucleus to the choices of the various γ_S demonstrates clearly the importance of obviating the need for any parametric choices for the γ_S and the development of a procedure for incorporating Sternheimer effects in a first-principles manner.

The present work has precisely this aim, namely that of developing and applying to ionic crystals a procedure for evaluating the induced field gradients Δq_S associated with the various direct contributions of the local, nonlocal, and distant sources of EFG directly and in an *ab initio* manner. The induced field gradients are of course to be added to the zero-order field gradients to obtain the theoretical value of the net field gradient in the system under study. One can also define individual effective antishielding factors $\gamma_{\text{eff},S}$ as the ratio $-\Delta q_S / q_S^{(0)}$. The results for the various $\gamma_{\text{eff},S}$ will answer such questions as whether γ_N is actually closer to R or $\gamma_\infty/2$ or has a value somewhat in between the two, and if it is appropriate to use γ_∞ for γ_{DE} and γ_{DN} to obtain the field gradient due to the electronic and nuclear charges of the nearest-neighbor ions. We shall see from the results of the present investigations that one obtains somewhat surprising but physically understandable answers to the last two questions and a justifiably broad range of values for the various $\gamma_{\text{eff},S}$. For the system that we have chosen for an application of this procedure, namely Fe_2O_3, we assume overlapping Fe^{3+} and O^{2-} ions without any charge transfer. This system is chosen both for a comparison of the calculated $\gamma_{\text{eff},S}$ with the various parametric choices that have been made in the past, and for obtaining an estimate of the extent of charge-transfer covalency in this sytem by comparing the calculated field gradient, including the influence of Sternheimer effects, with the experimental result. From the facts that (a) there is a substantial indirect exchange interaction between the Fe^{3+} ions through the O^{2-} ions leading to antiferromagnetic coupling[49,50] between the Fe^{3+} ions at a finite Néel temperature; (b) there is substantial transferred[27] Al hyperfine interaction in ruby,[51] $Al_2O_3Cr^{3+}$, which has the same corundum-type structure as Fe_2O_3; (c) substantial charge-transfer covalency is found in *ab initio* wave-function calculations in other ionic ferric compounds,[52–54] one expects to find significant covalent bonding in Fe_2O_3. Consequently, one expects to find a substantial difference between the field gradient at ^{57m}Fe in Fe_2O_3 calculated with a model of overlapping ions and that obtained experimentally, and it will be interesting to examine the nature of this difference and the information it provides about charge-transfer covalency in this compound.

It should also be pointed out that while in the present work we study induced field gradients for a system described by a model of overlapping ions, the procedure developed here can be used conveniently to incorporate antishielding effects in the calculated field gradients due to valence electrons of a system such as Fe_2O_3 after the influence of charge-transfer covalency has been included.

Section II deals with the procedure for the study of the induced field gradients Δq_S and associated effective antishielding factors $\gamma_{\text{eff},S}$. Section III includes a presentation of the results for Δq_S and $\gamma_{\text{eff},S}$ and a discussion of their physical significance and the detailed nature of their origins. Comparison is made in this section between the parametric choices of γ_S and the results of our calculation. Section IV is concerned with a comparison of our results for e^2qQ in Fe_2O_3 with experiment and a discussion of its physical significance. In Sec. V the conclusions from our work are summarized and possibilities for future investigation aimed at furthering our understanding of Sternheimer effects in ionic crystals are suggested.

II. FORMALISM FOR THE STUDY OF ANTISHIELDING EFFECTS IN IONIC SOLIDS

The splitting of a nuclear level due to the electric quadrupole interaction is given by[1]

$$\Delta E'_Q = \frac{e^2qQ}{4I(2I+1)}(3I_z^2 - \vec{I}\cdot\vec{I}) , \tag{6}$$

where $\vec{I}$ and Q are the angular momentum and quadrupole moment of the nucleus, respectively, $q \equiv q_{zz}$ is the largest component of the EFG tensor at the position of the nucleus, and defines the principal coordinate system, and e is the positive elementary charge. If V is the electrostatic potential due to the external charge distribution, we can write

$$\begin{aligned} q \equiv q_{zz} &= \frac{1}{e}(V_{zz})_0 = \frac{1}{e}\left[\frac{\partial^2 V}{\partial z^2}\right]_0 = \frac{1}{e}[(\vec{\nabla}\vec{\nabla}V)_{zz}]_0 \\ &= \frac{1}{e}[(-\vec{\nabla}E)_{zz}]_0 . \end{aligned} \tag{7}$$

In Eq. (6) the EFG is assumed to have axial symmetry about the z axis. The EFG q ($\equiv q_{zz}$) at the site of the nucleus of a central ion in an ionic solid can be separated into a contribution from the cluster composed of the central ion plus the nearest-neighbor ligands and a contribution from the rest of the lattice ions. If a wave function Φ describes the electronic charge distribution of the isolated cluster, we can write

$$\begin{aligned} q = \langle \Phi \,|\, \hat{q}_{\text{el}} \,|\, \Phi \rangle + \sum_g Z_{Lg} \frac{3\cos^2\Theta_g - 1}{R_g^3} \\ + (1-\gamma_\infty)\sum_k \zeta_k \frac{3\cos^2\Theta_k - 1}{R_k^3} , \end{aligned} \tag{8}$$

where the radius vector $\vec{R}_g$ locates the nearest-neighbor ligands (nuclear charge $Z_{Lg}e$) surrounding the central ion and $\vec{R}_k$ locates ions with effective charges $\zeta_k e$ in the rest of the lattice outside the cluster. Also

$$\hat{q}_{\text{el}} = -\sum_i \frac{3\cos^2\theta_i - 1}{r_i^3} , \tag{9}$$

where $\vec{r}_i$ locates an electron in the cluster. The Sternheimer factor γ_∞ appropriately describes the induced EFG at the central-ion nucleus due to distortions of the electronic charge distribution of the cluster by the ions in the remainder of the lattice because these ions can safely be approximated as point charges with respect to the central ion.

As discussed in the Introduction, the major problem in the evaluation of the NQI in the solid has to do with the contribution $\langle \Phi \,|\, \hat{q}_{\text{el}} \,|\, \Phi \rangle$ from the cluster including the variety of antishielding effects enumerated before. The wave function Φ could be a Slater determinant composed of self-consistent-field (SCF) Hartree-Fock linear combination of atomic orbitals (—molecular orbitals) [LCAO(-MO)'s] of the cluster. In fact, the expression for q presupposes such a formulation of Φ in which the valence as well as the core electrons are involved in a variational calculation of one-electron molecular orbitals in the potential field of the nuclei and electrons of the cluster. The core electrons are subject to perturbative effects through the anisotropic potential produced by the charges on the nuclei and core electrons of the neighboring ligand ions and the valence electrons, and by the hybridization and overlap effects involving the core and valence electrons. These perturbation effects produce the anisotropies in the core-electron distributions responsible for the field gradients produced by the latter, reflecting their antishielding or shielding effects on the field gradients produced by the charges within the cluster. There is a practical difficulty in treating the influence of these perturbations of the core electrons by the SCF LCAO(-MO) procedure in that this method minimizes the energies of the one-electron orbitals. While the fractional changes of the energies of the valence orbitals compared to their energies in free ions are substantial, for the core electrons which are internal in location and have relatively large one-electron energies, the corresponding fractional changes are rather small. Consequently, unless a large enough basis set is used in minimizing the one-electron energies of the core orbitals, the accuracies of the one-electron wave functions may not be sufficient, especially for the study of localized properties such as field gradients at the nuclei, which put particular emphasis on the accuracy of the calculated electron distributions.

In the procedure we have adopted, the core wave functions are not directly involved in the initial calculation of the valence-electron wave functions except through their contribution to the potential experienced by the valence electrons. Instead, as descibed later in this section, the core electrons are perturbed by the nuclear quadrupole moment, a procedure similar to that used for studies of antishielding effects in free-atom and free-ion systems. Also, while this procedure can in principle be applied to a model where the valence orbitals are obtained by an SCF LCAO(-MO) procedure, we have studied here the NQI and antishielding effects in the case where only the covalency effects associated with the overlap (Pauli) distortion of the valence electrons of the transition-metal ion by the influence of the ligand ion are considered. In this model, which describes completely ionic bonding,[55] the cluster wave function is composed of OAO's. The present investigation is aimed not at calculating covalency effects or accurate values of the total EFG, but rather at a detailed understanding of shielding-antishielding effects in ionic solids. We confine ourselves to this model here because it avoids the complications of an SCF procedure and because a number of recent calculations of NQI in ionic crystals[8,31–40] have used this model for the charge distribution but have treated the Sternheimer effects parametrically. In the present work, these effects are calculated from first principles, so that the difference between our computed total EFG and the experimental value can be ascribed to the departure of the charge distribution in the overlap model from the actual (SCF) charge distribution. From this we can estimate the amount of charge-transfer covalency in ionic solids.

In the model of overlapping ions, the many-electron wave function of the cluster is a Slater determinant formed out of atomic orbitals of all the ions of the cluster orthogonalized to one another. The formalism and computations are considerably simplified if ligand-ligand interactions can be neglected, which is true for many ionic solids. In that case we have to consider only the central ion and any one of the ligands at a time. Only one such pair needs to be considered for all ligands related by symmetry. In all subsequent discussions, we shall therefore consider a central-ion—ligand-ion pair of the cluster.

If $\psi_{0\alpha}$ are atomic orbitals (AO's) of the central ion and $\phi_{0\mu}$ those of the ligand, we can write the OAO's as Schmidt-orthogonalized linear combinations[34] as follows:

$$\psi'_{0\alpha}=N_\alpha\left[\psi_{0\alpha}-\sum_{\mu}S_{\alpha\mu}\phi_{0\mu}+\tfrac{1}{2}\sum_{\beta}T_{\alpha\beta}\psi_{0\beta}\right], \tag{10}$$

$$\phi'_{0\mu}=\phi_{0\mu}, \tag{11}$$

with

$$N_\alpha=\left[1-\tfrac{3}{4}\sum_{\beta}T^2_{\alpha\beta}\right]^{-1/2}, \tag{12}$$

$$S_{\alpha\mu}=\langle\psi_{0\alpha}\,|\,\phi_{0\mu}\rangle, \tag{13}$$

and

$$T_{\alpha\beta}=\sum_{\mu}S_{\alpha\mu}S_{\beta\mu}. \tag{14}$$

The many-electron wave function for the pair of ions is

$$\Psi_0=\mathscr{A}[\psi'_{01}(1)\psi'_{02}(2)\cdots\phi'_{01}(i)\phi'_{02}(i+1)\cdots], \tag{15}$$

where $\mathscr{A}$ is the antisymmetrizing operator.

The zero-order EFG at the central-ion nucleus due to sources in the pair of ions is then given by

$$q^{(0)}=\langle\Psi_0\,|\,\hat{q}_{el}\,|\,\Psi_0\rangle+\frac{Z_{L1}(3\cos^2\Theta_1-1)}{R_1^3}, \tag{16}$$

where the sum over i in $\hat{q}_{\rm el}$ [Eq. (9)] is restricted to the number of electrons in the pair of ions, the ligand being the one with $g=1$. Denoting the operator $(3\cos^2\theta-1)/r^3$ by the symbol $|x|$, we have

$$\begin{aligned}q^{(0)}=&\left[2\sum_{\beta}\sum_{\beta'}\langle\psi_{0\beta}|x|\psi_{0\beta'}\rangle\left[\tfrac{1}{2}\sum_{\nu}S_{\beta\nu}S_{\beta'\nu}\right]\right]_L+\left[2\sum_{\beta}\sum_{\nu}\langle\phi_{0\nu}|x|\psi_{0\beta}\rangle(-S_{\beta\nu})\right]_N+\left[\sum_{\mu}\langle\phi_{0\mu}|x|\phi_{0\mu}\rangle\right]_{\rm DE}\\&+\left[\sum_{\beta}\sum_{\nu}\sum_{\nu'}\langle\phi_{0\nu'}|x|\phi_{0\nu}\rangle(S_{\beta\nu'}S_{\beta\nu})\right]_{\rm DO}+(Z_{L1}(3\cos^2\Theta_1-1)/R_1^3)_{\rm DN}\end{aligned} \tag{17}$$

$$=q_L^{(0)}+q_N^{(0)}+q_{\rm DE}^{(0)}+q_{\rm DO}^{(0)}+q_{\rm DN}^{(0)}. \tag{18}$$

Each of the terms on the right-hand side contained within bold parentheses is the zero-order EFG due to a source of the cluster pair to which we can ascribe a certain degree of externality with respect to the central-ion core as follows: $q_L^{(0)}$ arises from local charge densities composed entirely of central-ion orbitals; $q_N^{(0)}$ arises from nonlocal sources, the charge densities involved being composed of one central-ion orbital and one ligand orbital; $q_{\rm DE}^{(0)}$ arises from distant electronic sources, with the charge densities composed entirely of ligand orbitals; $q_{\rm DO}^{(0)}$ arises from distant overlap sources, the charge densities originating entirely from the small ligand-type components of the OAO's; $q_{\rm DN}^{(0)}$ arises from distant nuclear sources, the bare nuclear charges on the ligands.

Since the orthogonalization process is only a rearrangement of the nonorthogonal AO basis set,[56] it introduces no electron-electron interactions in the system, and hence no distortion effects of the antishielding type. All the terms in Eq. (18) must therefore be corrected for antishielding effects. This is the main point of discussion in the literature. In the absence of a standard procedure for making these corrections, one was forced to conjecture as to the antishielding factors for each of these terms. Since these corrections are not just small percentage changes in the uncorrected values, but are, in many instances, responsible for order-of-magnitude changes in the unshielded terms[21–29,57] (the antishielding of large negative ions being an extreme example), the total field gradient is very sensitive to the choice of Sternheimer factors for the various contributions to q. In view of the above, it is clear that for a reliable calculation of the total field gradient, the Sternheimer effects must be incorporated directly and rigorously into the theory so as to obviate the necessity for guessing the shielding or antishielding factors.

Our formalism is aimed at calculating the distortion effects directly from first principles using a first-order perturbation procedure. For this purpose we have adapted the moment-perturbation (MP) technique,[58] previously used for the calculation of exchange core-polarization effects for magnetic hyperfine fields in ionic crystals involving paramagnetic ions[59] or paramagnetic defect centers,[60] to the problem of the NQI. A brief description of the MP method and its adaptation to the nuclear quadrupole problem will now be given.

The quantitative evaluation of the contribution to the field gradient from Sternheimer effects requires the incorporation of the influence of the NQI to first order in the total energy of the ionic crystal. This can be accomplished in two essentially equivalent ways.[1,58] One can first allow the central-ion orbitals, including the core orbitals, to be distorted by the various sources of EFG in the system such as the nonspherical valence electrons of the central ion and the nuclear charges and electrons on ligand ions of the cluster, and then calculate the change (due to the induced distortions) in the energy of interaction of these distorted central-ion orbitals with the nuclear quadrupole moment. Alternatively, one can first perturb the orbitals of the central ion via the NQI thereby causing them to get distorted, and then calculate the changed energy of the cluster of central ion and ligand ions to first order in Q.

In both cases the various contributions to this energy change include Coulomb and exchange interactions between the electrons on the central ion and the electrons and nuclei on the neighboring ligand ions. The change in energy can be written as

$$\Delta E_{eQ} = e^2Q\,\Delta q = e^2Q\sum_S \Delta q_S = e^2Q\sum_S\sum_t \Delta q_{S(t)}\ . \quad (19)$$

The last expression in Eq. (19) is a statement of the fact that it should be possible, in principle, to identify groups of terms in the expansion of ΔE_{eQ} which correspond to contributions due to specific sources, S, of the system, in one-to-one correspondence with similarly identifiable sources in the expansion of $q^{(0)}$ in Eq. (18). In other words, we should be able to write

$$\Delta q = \Delta q_L + \Delta q_N + \Delta q_{\mathrm{DE}} + \Delta q_{\mathrm{DO}} + \Delta q_{\mathrm{DN}}\ . \quad (20)$$

Each source S may also be subdivisible into types t, where each subdivision corresponds to a different degree of ligand character mixed into the perturbed core charge distribution of the central ion. One can then arrive at individual effective Sternheimer factors for each source, in accordance with the conventional definition[57,61]

$$\gamma_{\mathrm{eff},S} = -\Delta q_S / q_S^{(0)} = -\left[\sum_t \Delta q_{S(t)}\right] \Big/ q_S^{(0)}\ , \quad (21)$$

where $q_S^{(0)}$ is the term due to the source S in the expansion of $q^{(0)}$ given in Eq. (18), which we shall henceforth call the zero-order or unshielded contribution.

Of the two procedures for evaluating ΔE_{eQ}, we choose the second, or MP procedure, for reasons of computational convenience and relatively easy extension to related systems. Thus the one-electron orbitals of the central ion are perturbed by the NQI represented by the perturbation Hamiltonian[1,61]

$$\sum_i \delta\mathcal{H}_Q(i) = -e^2Q\sum_i \frac{3\cos^2\theta_i - 1}{r_i^3} = -\left[\frac{4\pi}{5}\right]^{1/2} e^2Q\sum_i \frac{2Y_{20}(\theta_i,\varphi_i)}{r_i^3}\ . \quad (22)$$

In the uncoupled perturbation-theory[61,62] approach used by Sternheimer for the study of shielding-antishielding effects in atoms and ions, which we shall utilize here, one has to solve the perturbed Schrödinger equation

$$(\mathcal{H}_{0\alpha} + \delta\mathcal{H}_Q)(\psi_{0\alpha} + \delta\psi_{Q\alpha}) = (\epsilon_{0\alpha} + \delta\epsilon_{Q\alpha})(\psi_{0\alpha} + \delta\psi_{Q\alpha})\ , \quad (23)$$

where $\delta\epsilon_{Q\alpha}$ and $\delta\psi_{Q\alpha}$ are, respectively, the first-order perturbation energy and first-order perturbation of the wave function $\psi_{0\alpha}$ of the central ion with zero-order energy $\epsilon_{0\alpha}$ associated with the corresponding one-electron Hamiltonian $\mathcal{H}_{0\alpha}$. Neglecting terms which are second order in Q and using $\mathcal{H}_{0\alpha}\psi_{0\alpha} = \epsilon_{0\alpha}\psi_{0\alpha}$, we obtain from Eq. (23)

$$(\mathcal{H}_{0\alpha} - \epsilon_{0\alpha})\delta\psi_{Q\alpha} = -(\delta\mathcal{H}_Q - \delta\epsilon_{Q\alpha})\psi_{0\alpha}\ . \quad (24)$$

The unperturbed wave functions $\psi_{0\alpha}$ can be expanded in terms of radial and angular components in the form

$$\psi_{0\alpha} \equiv \psi_{0nlm}(\vec{r})\chi(s) = \frac{u'(nl;r)}{r} Y_{lm}(\theta,\varphi)\chi(s)\ , \quad (25)$$

$$\chi(s) = \begin{cases} \alpha(s), & m_s = \frac{1}{2} \\ \beta(s), & m_s = -\frac{1}{2} \end{cases}\ . \quad (26)$$

Depending upon the angular momentum quantum number l of the unperturbed orbital $\psi_{0\alpha}$, the effect of $\delta\mathcal{H}_Q$ can lead to one, two, or three perturbed functions $\psi_{Q\alpha} = \psi_{0\alpha} + \delta\psi_{Q\alpha}$, with the perturbation $\delta\psi_{Q\alpha}$ given by[7]

$$\delta\psi_{Q\alpha} \equiv \delta\psi_{Qnl\to l',m}(r)\chi(s) = Qc^2(lm,l'm)\frac{\delta u'(nl\to l';r)}{r} Y_{l'm}(\theta,\varphi)\chi(s)\ , \quad (27)$$

where the quantum number l' can have one or more of the possible values:

$$l' = \begin{cases} l+2 & \text{for all } l \\ l & \text{for } l > 0 \\ l-2 & \text{for } l \geq 2 \end{cases} \quad (28)$$

and

$$c^2(lm,l'm) = \int Y_{l'm}^{*}(\theta,\varphi)P_2(\cos\theta)Y_{lm}(\theta,\varphi) \times \sin\theta\, d\theta\, d\varphi\ . \quad (29)$$

With the use of Eq. (24), the radial part $\delta u'(nl\to l';r)$ of the perturbation function $\delta\psi_{Qnl\to l'm}(\vec{r})$ can be shown to satisfy the radial differential equation[7]

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2}\frac{l'(l'+1)}{r^2}+V_{0\alpha}(r)-\epsilon_{0\alpha}\right]\delta u'(nl\to l';r)$$
$$=\left[\frac{1}{r^3}-\left\langle\frac{1}{r^3}\right\rangle_{nl}\right]u'(nl;r)\ . \tag{30}$$

Here $V_{0\alpha}(r)$ is an appropriate Hartree-Fock potential[62,63] for the unperturbed central-ion orbital $\psi_{0\alpha}$. Using the Hartree-Fock equation satisfied by $u'(nl;r)$ and neglecting nonlocality effects in $V_{0\alpha}(r)$, one can formally make the replacement for $V_{0\alpha}(r)$ referred to as the Sternheimer approximation[61] and rewrite Eq. (30) as

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2u'(nl;r)}\frac{d^2u'(nl;r)}{dr^2}+\frac{l'(l'+1)-l(l+1)}{2r^2}\right]\delta u'(nl\to l';r)$$
$$=\left[\frac{1}{r^3}-\left\langle\frac{1}{r^3}\right\rangle_{nl}\right]u'(nl;r)\ . \tag{31}$$

These equations can be solved by using a variational procedure[57] or by numerical integration[61] to obtain $\delta u'(nl\to l';r)$.

Having obtained the Q-perturbed orbitals of the central ion, one must consider the effects of overlap distortion on the perturbed functions $\psi_{Q\alpha}=\psi_{0\alpha}+\delta\psi_{Q\alpha}$. This implies a Schmidt orthogonalization[34,43]

$$\psi_{Q\alpha}\to\psi'_{Q\alpha}=\psi'_{0\alpha}+\delta\psi'_{Q\alpha}\ . \tag{32}$$

Considering only the central ion and one ligand, we have

$$\delta\psi'_{Q\alpha}=N_\alpha\left[\delta\psi_{Q\alpha}-\sum_{\nu}\delta S_{\alpha\nu}\phi_{0\nu}+\sum_{\beta}\delta T_{\alpha\beta}\psi_{0\beta}\right]\ , \tag{33}$$

where

$$\delta S_{\alpha\nu}=\langle\delta\psi_{Q\alpha}\,|\,\phi_{0\nu}\rangle \tag{34}$$

and

$$\delta T_{\alpha\beta}=\sum_{\nu}\delta S_{\alpha\nu}S_{\beta\nu}\ . \tag{35}$$

The two-center integrals $S_{\alpha\nu}$ and $\delta S_{\alpha\nu}$ can be evaluated by using the α-function expansion method.[34,64] The N_α are normalization factors which are close to unity within terms of the order $\sum_\beta T^2_{\alpha\beta}$.

The next step in our procedure is to compute the change in the energy of the system due to the distortion produced by the nuclear quadrupole moment. This is accomplished as follows. One computes the total energy of the system using the perturbed OAO's on the central ion as well as those on the ligand ion as the occupied orbitals, retaining only terms which involve one order in the NQI.[58] In our formalism, this implies that only those terms in the expression for the total energy in which $\delta\psi_{Q\alpha}$ appears once are retained. In practice, one starts with the many-electron determinantal wave function constructed from the OAO's of Eqs. (10), (11), and (33):

$$\Psi=\mathscr{A}[\psi'_{Q1}(1)\psi'_{Q2}(2)\cdots\phi'_{01}(i)\phi'_{02}(i+1)\cdots]\ , \tag{36}$$

and the total Hamiltonian for the cluster composed of the central-ion M and N_g nearest-neighbor ligands (in our case we use $N_g=1$ for each central-ion—ligand-ion pair):

$$\mathscr{H}=-\sum_i\left[\tfrac{1}{2}\nabla_i^2+\frac{Z_M}{r_i}+\sum_{g=1}^{N_g}\frac{Z_{Lg}}{r_{ig}}\right]+\sum_{\substack{i,j\\ i>j}}\frac{1}{|\vec{r}_i-\vec{r}_j|}$$
$$+\sum_{g=1}^{N_g}\frac{Z_MZ_{Lg}}{R_g}+\sum_{\substack{g,g'\\ g>g'}}\frac{Z_{Lg}Z_{Lg'}}{|\vec{R}_g-\vec{R}_{g'}|}\ , \tag{37}$$

in atomic units. Z_M and Z_{Lg} are the charges on the central-ion nucleus and the ligand nucleus located at the point $\vec{R}_g$ with respect to the central-ion nucleus as origin. The distance of the ith electron as measured from the ligand nucleus at $\vec{R}_g$ is given by $\vec{r}_{ig}$. The total energy of the cluster is then given by

$$E_{\text{total}}=\langle\Psi\,|\,\mathscr{H}\,|\,\Psi\rangle\ . \tag{38}$$

This expectation value contains terms which are zero, first, second, and higher order in the quadrupole interaction $\delta\mathscr{H}_Q$, of which, as stated earlier, we are only interested in the first-order terms, i.e., those terms which have only one $\delta\psi'_{Q\alpha}$ in them. From an examination of Eqs. (36)—(38) these terms can be shown to be contained in the sum

$$\Delta E_{eQ}=2\sum_\alpha\langle\delta\Psi_{Q\alpha}\,|\,\mathscr{H}\,|\,\Psi_0\rangle\ , \tag{39}$$

where Ψ_0 is a determinantal wave function composed of all unperturbed central-ion OAO's and ligand-ion AO's, $\delta\Psi_{Q\alpha}$ is obtained from Ψ_0 with the replacement $\psi'_{0\alpha}\to\delta\psi'_{Q\alpha}$, and α runs over all the perturbed central-ion OAO's. Thus Ψ_0 and $\delta\Psi_{Q\alpha}$ differ by one orbital, and these differing orbitals are orthogonal, $\langle\psi'_{0\alpha}\,|\,\delta\psi'_{Q\alpha}\rangle=0$. Using the familiar rules for matrix elements of one- and two-electron operators[41,65] between such a pair of determinantal functions, we obtain, from Eq. (39),

$$\Delta E_{eQ}=2\left[\sum_\alpha\langle\delta\psi'_{Q\alpha}\,|\,f\,|\,\psi'_{0\alpha}\rangle\right.$$
$$+\sum_\alpha\sum_\eta(\langle\delta\psi'_{Q\alpha}\xi'_{0\eta}\,|\,g\,|\,\psi'_{0\alpha}\xi'_{0\eta}\rangle$$
$$\left.-\langle\delta\psi'_{Q\alpha}\xi'_{0\eta}\,|\,g\,|\,\xi'_{0\eta}\psi'_{0\alpha}\rangle)\right]\ , \tag{40}$$

where

$$\langle\delta\psi'_{Q\alpha}\,|\,f\,|\,\psi'_{0\alpha}\rangle=\int\delta\psi'^{*}_{Q\alpha}(1)f(\vec{r}_1)\psi'_{0\alpha}(1)d\tau_1 \tag{41}$$

and

$$\langle\delta\psi'_{Q\alpha}\xi'_{0\eta}\,|\,g\,|\,\psi'_{0\alpha}\xi'_{0\eta}\rangle=\int\int\delta\psi'^{*}_{Q\alpha}(1)\xi'^{*}_{0\eta}(2)g(\vec{r}_1,\vec{r}_2)\psi'_{0\alpha}(1)$$
$$\times\xi'_{0\eta}(2)d\tau_1d\tau_2\ , \tag{42}$$

with f and g the one- and two-electron parts of the Hamiltonian for a single central-ion—ligand-ion pair, namely Eq. (37) with $N_g = 1$, for example. Thus

$$\mathcal{H} = \sum_i f(\vec{r}_i) + \sum_{i>j} g(\vec{r}_i, \vec{r}_j) + \mathcal{H}_{NN} , \tag{43}$$

$$f(\vec{r}_i) = K(\vec{r}_i) + A(\vec{r}_i) + B(\vec{r}_i) , \tag{44}$$

$$K(\vec{r}_i) = -\tfrac{1}{2}\nabla_i^2 , \tag{45}$$

$$A(\vec{r}_i) = -\frac{Z_M}{r_i} , \tag{46}$$

$$B(\vec{r}_i) = -\frac{Z_{L1}}{|\vec{r}_i - \vec{R}_1|} , \tag{47}$$

$$g(\vec{r}_i, \vec{r}_j) = \frac{1}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{r_{ij}} , \tag{48}$$

and $\mathcal{H}_{NN}$ is the internuclear repulsion. In Eqs. (40) and (42) $\xi'_{0\eta}$ is the collective symbol for all of the unperturbed OAO's on the central ion and the ligand ion, so that the summation over η in Eq. (40) goes over all N occupied orbitals of the pair of ions.

The integrals in Eq. (40) can be expressed in terms of the unorthogonalized functions $\psi_{0\alpha}$ and $\phi_{0\mu}$ and the overlap integrals $S_{\alpha\nu}$ and $\delta S_{\alpha\nu}$ by expanding out the OAO's according to Eqs. (10), (11), and (33). The integrals $\langle \delta\psi'_{Q\alpha} | f | \psi'_{0\alpha} \rangle$, where f is given in Eqs. (44)–(47), can be transformed into sums of one-electron integrals over the operators A and B, given in Eqs. (46) and (47), and two-electron integrals over the operator g, given in Eq. (48). This is accomplished through the use of the Hartree-Fock equations satisfied by the functions $\phi_{0\mu}$ and $\psi_{0\alpha}$, namely,

$$(K + B + V_{0\mu})\phi_{0\mu} = \epsilon_{0\mu}\phi_{0\mu} \tag{49}$$

and

$$(K + A + V_{0\alpha})\psi_{0\alpha} = \epsilon_{0\alpha}\psi_{0\alpha} , \tag{50}$$

where $V_{0\mu}$ and $V_{0\alpha}$ are the relevant Hartree-Fock potentials[63,65] given by

$$V_{0\mu}(\vec{r}_1)\phi_{0\mu}(1) = \sum_\nu \left[\left\langle \phi_{0\nu}(2) \left| \frac{1}{r_{12}} \right| \phi_{0\nu}(2) \right\rangle \phi_{0\mu}(1) - \left\langle \phi_{0\nu}(2) \left| \frac{1}{r_{12}} \right| \phi_{0\mu}(2) \right\rangle \phi_{0\nu}(1) \right] , \tag{51}$$

$$V_{0\alpha}(\vec{r}_1)\psi_{0\alpha}(1) = \sum_\beta \left[\left\langle \psi_{0\beta}(2) \left| \frac{1}{r_{12}} \right| \psi_{0\beta}(2) \right\rangle \psi_{0\alpha} - \left\langle \psi_{0\beta}(2) \left| \frac{1}{r_{12}} \right| \psi_{0\alpha}(2) \right\rangle \psi_{0\beta}(1) \right] . \tag{52}$$

In Eqs. (51) and (52), the summations over ν and β apply to all the occupied orbitals of the ligand and central ion, respectively.

The final expression for the quadrupolar interaction energy obtained by this procedure and which we have utilized for computation in Fe_2O_3 is

$$\begin{aligned}
\Delta E_{eQ} = \Biggl[2\sum_\beta \Biggl\{ \sum_\alpha \Biggl[\sum_{\beta'} \langle \delta\psi_{Q\alpha}\psi_{0\beta} || \psi_{0\alpha}\psi_{0\beta'} \rangle \Biggl[\tfrac{1}{2}\sum_\nu S_{\beta\nu}S_{\beta'\nu} \Biggr] + \sum_{\beta'} \langle \delta\psi_{Q\alpha}\psi_{0\beta'} || \psi_{0\alpha}\psi_{0\beta} \rangle \Biggl[\tfrac{1}{2}\sum_\nu S_{\beta\nu}S_{\beta'\nu} \Biggr] \\
+ \sum_\nu \langle \delta\psi_{Q\alpha}\psi_{0\beta} || \phi_{0\nu}\psi_{0\beta} \rangle (-S_{\alpha\nu}) + \sum_{\nu'}\sum_\nu \langle \phi_{0\nu'}\psi_{0\beta} || \phi_{0\nu}\psi_{0\beta} \rangle (\delta S_{\alpha\nu'}S_{\alpha\nu}) \Biggr] \Biggr\} \\
+2 \Biggl[\sum_\alpha \sum_\nu \langle \delta\psi_{Q\alpha} | A | \phi_{0\nu} \rangle (-S_{\alpha\nu}) + \sum_{\nu'}\sum_\alpha\sum_\nu \langle \phi_{0\nu'} | A | \phi_{0\nu} \rangle (\delta S_{\alpha\nu'}S_{\alpha\nu}) \Biggr] \Biggr]_L \\
+ \Biggl[2\sum_\beta \Biggl[\sum_\alpha \Biggl[\sum_\nu \langle \delta\psi_{Q\alpha}\psi_{0\beta} || \psi_{0\alpha}\phi_{0\nu} \rangle (-S_{\beta\nu}) + \sum_\nu \langle \delta\psi_{Q\alpha}\phi_{0\nu} || \psi_{0\alpha}\psi_{0\beta} \rangle (-S_{\beta\nu}) \\
+ \sum_{\nu'}\sum_\nu \langle \delta\psi_{Q\alpha}\phi_{0\nu} || \phi_{0\nu'}\psi_{0\beta} \rangle (S_{\alpha\nu'}S_{\beta\nu}) + \sum_{\nu'}\sum_\nu \langle \phi_{0\nu'}\psi_{0\beta} || \psi_{0\alpha}\phi_{0\nu} \rangle (\delta S_{\alpha\nu'}S_{\beta\nu}) \Biggr] \Biggr] \Biggr]_N \\
+ \Biggl[2\sum_\mu \Biggl\{ \sum_\alpha \Biggl[\langle \delta\psi_{Q\alpha}\phi_{0\mu} || \psi_{0\alpha}\phi_{0\mu} \rangle + \sum_{\nu'} \langle \phi_{0\nu'}\phi_{0\mu} || \psi_{0\alpha}\phi_{0\mu} \rangle (-\delta S_{\alpha\nu'}) \\
+ \sum_{\beta'} \langle \psi_{0\beta'}\phi_{0\mu} || \psi_{0\alpha}\phi_{0\mu} \rangle \Biggl[\sum_\nu \delta S_{\alpha\nu}S_{\beta'\nu} \Biggr] + \sum_{\beta'} \langle \delta\psi_{Q\alpha}\phi_{0\mu} || \psi_{0\beta'}\phi_{0\mu} \rangle \Biggl[\tfrac{1}{2}\sum_\nu S_{\alpha\nu}S_{\beta'\nu} \Biggr] \Biggr] \Biggr\} \Biggr]_{\mathrm{DE}} \\
+ \Biggl[2\sum_\beta \sum_\alpha \sum_{\nu'} \sum_\nu \langle \delta\psi_{Q\alpha}\phi_{0\nu'} || \psi_{0\alpha}\phi_{0\nu} \rangle (S_{\beta\nu'}S_{\beta\nu}) \Biggr]_{\mathrm{DO}}
\end{aligned}$$

$$+\left|2\sum_{\alpha}\left[\langle\delta\psi_{Q\alpha}|B|\psi_{0\alpha}\rangle+\sum_{\nu'}\langle\phi_{0\nu'}|B|\psi_{0\alpha}\rangle(-\delta S_{\alpha\nu'})+\sum_{\beta'}\langle\psi_{0\beta'}|B|\psi_{0\alpha}\rangle\left[\sum_{\nu}\delta S_{\alpha\nu}S_{\beta'\nu}\right]\right.\right.$$
$$\left.\left.+\sum_{\beta'}\langle\delta\psi_{Q\alpha}|B|\psi_{0\beta'}\rangle\left[\tfrac{1}{2}\sum_{\nu}S_{\alpha\nu}S_{\beta'\nu}\right]\right]\right]_{\mathrm{DN}}\ . \tag{53}$$

Since the overlap integrals are all real in our chosen coordinate system, we do not differentiate between complex conjugates.

The operator represented by the double vertical bars in Eq. (53) is $g(r_1,r_2)(1-P_{12})$ where P_{12} permutes particle labels. Thus each of the integrals $\langle\xi_1\xi_2||\xi_3\xi_4\rangle$ represents a Coulomb integral minus its exchange counterpart:

$$\langle\xi_1\xi_2||\xi_3\xi_4\rangle=\int\int\xi_1^*(1)\xi_2^*(2)\frac{1}{r_{12}}\xi_3(1)\xi_4(2)d\tau_1d\tau_2-\int\int\xi_1^*(1)\xi_2^*(2)\frac{1}{r_{12}}\xi_4(1)\xi_3(2)d\tau_1d\tau_2\ . \tag{54}$$

It can be noted from Eq. (53) that in addition to retaining terms that are first order in the quadrupole moment Q, we have only retained terms that are either bilinear in overlap integrals, or involve one order of overlap integral and integrals involving the ligand orbitals once or terms involving the ligand orbitals twice. Thus the results we shall obtain involve two orders in two-center character which is felt to be adequate for most ionic crystals considering the magnitudes of the overlap integrals that occur in such systems.

III. RESULTS OF THE APPLICATION OF THE FIRST-PRINCIPLES ANTISHIELDING FORMALISM TO Fe_2O_3

In this section we shall present the results of the application of the formalism developed in the preceding section to the ^{57m}Fe NQI in α-Fe_2O_3. We shall be mainly concerned here with the understanding of the antishielding effects in α-Fe_2O_3 within a model of overlapping ions in particular, and its implications for ionic crystals in general. In Sec. IV the nature of the agreement of the calculated nuclear quadrupole coupling constant in α-Fe_2O_3 with experiment will be discussed, and the possible role played by charge-transfer covalency effects will be analyzed.

The material α-Fe_2O_3 investigated in this work has the corundum structure.[66,67] The basic unit of interest to us consists of a central Fe^{3+} ion surrounded by a heavily distorted octahedron containing six O^{2-} ions. From the structural parameters from the x-ray diffraction data of Blake, Zoltai, Hessevick, and Finger[67] for pure synthetic α-Fe_2O_3 at room temperature, the oxygen ions are seen to form two equilateral triangles, one on either side of the iron, with the ions of one triangle lying at $4.00a_0$ and those of the other at $3.67a_0$ from the Fe^{3+} ion. In applying the formalism of Sec. II to α-Fe_2O_3, we need to calculate overlap integrals $S_{\alpha\nu}$ and $\delta S_{\alpha\nu}$, the one-electron integrals in Eq. (17), and the one- and two-electron integrals in Eq. (53) for the electronic orbitals of Fe^{3+} and O^{2-} ions in the basic unit.

In our calculations, the unperturbed Fe^{3+} ion wave functions $\psi_{0\alpha}$ were those[68,69] of Watson; these are in good agreement with recently published[70] Hartree-Fock wave functions. The O^{2-} wave functions were those of Watson,[71] who used a stabilizing potential well of two positive charges. The radial parts of the wave functions for Fe^{3+} and O^{2-} ions used in the present work are shown in Fig. 1, which will be useful in the understanding of the relative magnitudes of the zero-order and antishielding contributions discussed later in this section and Sec. IV. The Q-perturbed wave functions $\delta\psi_{Q\alpha}$ for the Fe^{3+} ion were generated by Sternheimer[72] by the procedure described earlier in Sec. II.

Equation (17) represents the direct or zero-order electric field gradients due to the five types of sources in the cluster as described earlier, while Eq. (53) represents the induced field gradient due to each of these sources. The terms in Eq. (53) are actually the first-order quadrupolar perturbation energies, each term being linear in Q, so that dividing by eQ cancels this factor, thereby providing us with the induced field gradients $e\Delta q_S$ in Eq. (20). Together with the zero-order contributions provided by Eqs. (17) and (18), we then have the pair-wise terms $(q_L^{(0)},\Delta q_L)$, $(q_N^{(0)},\Delta q_N)$, $(q_{\mathrm{DE}}^{(0)},\Delta q_{\mathrm{DE}})$, $(q_{\mathrm{DO}}^{(0)},\Delta q_{\mathrm{DO}})$ and $(q_{\mathrm{DN}}^{(0)},\Delta q_{\mathrm{DN}})$ from which we can obtain the effective antishielding factors $\gamma_{\mathrm{eff},L}$, $\gamma_{\mathrm{eff},N}$, $\gamma_{\mathrm{eff,DE}}$, $\gamma_{\mathrm{eff,DO}}$, and $\gamma_{\mathrm{eff,DN}}$ for each type of source in the cluster according to Eq. (21).

We shall consider now the net results for the induced field gradients $\Delta q_S=\Delta q_L$, Δq_N, Δq_{DE}, Δq_{DO}, and Δq_{DN},

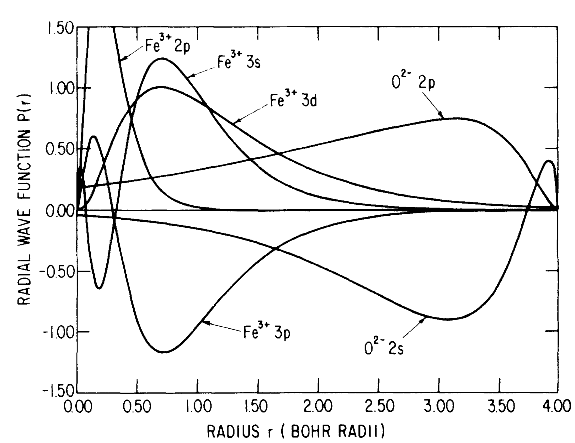

FIG. 1. Radial wave functions $P(r)=u'(nl;r)$ for some atomic orbitals of the Fe^{3+} and O^{2-} ions. The origin for the Fe^{3+} ion wave functions is at $r=0$. The origin for the O^{2-} ion wave functions is at a distance of $4.00a_0$ from the Fe nucleus, and r increases from right to left for these functions.

TABLE II. Comparison of the induced electric field gradients and corresponding effective antishielding factors calculated in the present work with previous parametric treatments of antishielding effects.

Source	Zero-order electric field gradient $eq^{(0)}$ (10^{14} esu cm^{-3})	Induced electric field gradient from present work $e\Delta q$ (10^{14} esu cm^{-3})	Effective antishielding factor from present work $\gamma_{\text{eff}}=-\frac{\Delta q}{q^{(0)}}$	Parametric antishielding factors used in previous work[a] Choice I A	Choice I B	Choice II A	Choice II B
Local	6.843	1.355	−0.197	0.07	0.32	0.07	0.32
Nonlocal	−0.847	−0.602	−0.710	0.07	0.32	−4.60	−4.57
Distant electronic	2.311	8.724	−3.776	−9.19	−9.14	−9.19	−9.14
Distant nuclear	−1.957	−12.696	−6.489	−9.19	−9.14	−9.19	−9.14
Distant overlap	0.052	0.195	−3.785	−9.19	−9.14	−9.19	−9.14
Distant rest of the lattice	−0.066	−0.607[b]	−9.19[b]	−9.19	−9.14	−9.19	−9.14

[a] These choices are described in Sec. III.

[b] Not calculated in the present work. (See text.)

and the corresponding effective antishielding factors $\gamma_{\text{eff},S}=\gamma_{\text{eff},L}$, $\gamma_{\text{eff},N}$, $\gamma_{\text{eff,DE}}$, $\gamma_{\text{eff,DO}}$, and $\gamma_{\text{eff,DN}}$ [see Eqs. (17)–(21)]. The relationship of these antishielding factors to the Sternheimer atomic shielding factor R for the $3d$ valence shell[48(a)] of a free Fe^{2+} ion and the Sternheimer antishielding factor γ_∞ for a point charge outside a free Fe^{3+} ion[25] will be analyzed, and possible physical reasons for the differences of our results from these two factors $R(\text{Fe}^{2+})$ and $\gamma_\infty(\text{Fe}^{3+})$ will be discussed. A more detailed examination of the origins of the Δq_S and the $\gamma_{\text{eff},S}$ is attempted in Ref. 73 by analyzing the relative importance of individual contributions from different source charge distributions within each class of terms as defined in Sec. II.

In Table II we have listed the contributions to the field gradient at the ^{57m}Fe nucleus due to zero-order and induced effects, as well as the sum of the two, from the various sources, local, nonlocal, and distant, discussed in Secs. I and II. Also listed are the corresponding effective antishielding factors γ_{eff} for the various sources, obtained by taking the ratios of the induced and direct contributions. For purposes of comparison, we have also included in this table the various parametric choices made for these antishielding factors in the literature. For the parameters γ_S of Eq. (5), choice I utilizes $\gamma_L=\gamma_N=R(\text{Fe}^{2+})$ and $\gamma_{\text{DE}}=\gamma_{\text{DO}}=\gamma_{\text{DN}}=\gamma_{\text{DRL}}=\gamma_\infty(\text{Fe}^{3+})$.

The two sets of values listed under choice I differ by the use in the first case (choice I A) of the most recent[25,48(a)] values of $R(\text{Fe}^{2+})$ and γ_∞ for a Fe^{3+} ion, both including many-body effects, while the second case (choice I B) involves the earlier overestimated[8,74,75] value of $R(\text{Fe}^{2+})$ and also a slightly different earlier value[72] of $\gamma_\infty(\text{Fe}^{3+})$. The second case under choice I is included because it was the one used in earlier work[8] on the field gradient in α-Fe_2O_3. The two cases under choice II involve the parametric[32,33] choices $\gamma_L=R$, $\gamma_N=\gamma_\infty(\text{Fe}^{3+})/2$, and $\gamma_{\text{DE}}=\gamma_{DN}=\gamma_{\text{DRL}}=\gamma_\infty(\text{Fe}^{3+})$, the numerical values of $R(\text{Fe}^{2+})$ and $\gamma_\infty(\text{Fe}^{3+})$ employed in the two cases being the same as the ones used, respectively, for the two cases under choice I.

In examining the results in Table II, it is first interesting to compare the *ab initio* values of $\gamma_{\text{eff},L}$, $\gamma_{\text{eff},N}$, $\gamma_{\text{eff,DE}}$, and $\gamma_{\text{eff,DN}}$ that we have obtained with those used in the parametric treatments. Thus as far as $\gamma_{\text{eff},L}$ is concerned , there is a very significant difference from the value of $R(\text{Fe}^{2+})$, the two differing in both sign and magnitude. This drastic difference is not unexpected because the zero-order contribution $q_L^{(0)}$ in the model of overlapping ions for Fe_2O_3 receives a major contribution from the $3p$ orbitals of the Fe^{3+} ion while the zero-order field gradient in a free Fe^{2+} ion arises entirely from the $3d$ orbitals. The *ab initio* value of $\gamma_{\text{eff},N}$ is found to be intermediate between the extreme parametric values $\gamma_N=R$ and $\gamma_\infty/2$ used in choices I and II, respectively. This behavior suggests that the overlap region between the Fe^{3+} and O^{2-} ions from which the nonlocal field gradient $q_N^{(0)}$ derives its major contribution is neither as internal to the Fe^{3+} ion as choice I would imply, nor as external as would be indicated by choice II. Perhaps the most remarkable difference between the *ab initio* results and the results obtained using parametric choices of γ_S is manifested in the case of

TABLE III. Contributions from Q perturbations of various electronic shells of the ferric ion to induced electric field gradients at ^{57m}Fe in Fe_2O_3 and corresponding effective antishielding factors for the individual perturbations.

Ferric ion Q perturbations	Individual induced electric field gradients and effective antishielding factors[a] Local[b] $e\,\Delta q$	Local[b] γ_{eff}	Nonlocal[b] $e\,\Delta q$	Nonlocal[b] γ_{eff}	Distant electronic[c] $e\,\Delta q$	Distant electronic[c] γ_{eff}	Distant nuclear[c] $e\,\Delta q$	Distant nuclear[c] γ_{eff}	Distant overlap[c] $e\,\Delta q$	Distant overlap[c] γ_{eff}	Total induced EFG $e\,\Delta q$
$2p \to p$	0.621	−0.091	0.0	0.0	1.681	−0.727	−1.547	−0.791	0.0	0.0	0.755
$3p \to p$	0.157	−0.023	−0.809	−0.954	6.972	−3.018	−10.910	−5.576	0.167	−3.227	−4.421
$3d \to d$	0.215	−0.032	0.207	0.246	1.810	−0.783	−1.568	−0.802	0.029	−0.560	0.692
Total radial	0.994	−0.145	−0.602	−0.710	10.462	−4.528	−14.025	−7.168	0.195	−3.785	−2.974
Total angular	0.361	−0.053	0.0	0.0	−1.739	0.753	1.329	0.679	0.0	0.0	−0.049
Total	1.354	−0.198	−0.602	−0.710	8.724	−3.776	−12.696	−6.489	0.195	−3.785	−3.023[d]

[a] Effective antishielding factors are obtained by dividing the negative of the source-wise induced EFG for each perturbation by the net zero-order EFG from the source in question. The latter values are $eq_L^{(0)}=6.843$; $eq_N^{(0)}=-0.847$; $eq_{\text{DE}}^{(0)}=2.311$; $eq_{\text{DN}}^{(0)}=-1.957$; $eq_{\text{DO}}^{(0)}=0.052$. Units for the EFG are 10^{14} esu cm^{-3}.

[b] For the local and nonlocal terms, the contribution to γ_{eff} for each perturbation can be compared with individual contributions to R for each perturbation calculated for a Fe^{2+} ion including many-body effects: $R(2p \to p)=-0.128$, $R(3p \to p)=0.049$, and $R(3d \to d)=0.033$. See Ref. 48(a).

[c] For the distant electronic, distant nuclear, and distant overlap terms, the contributions to γ_{eff} for each perturbation can be compared with individual contributions to γ_∞ for a Fe^{3+} ion: $\gamma_\infty(2p \to p)=-0.70$; $\gamma_\infty(3p \to p)=-7.89$; $\gamma_\infty(3d \to d)=-1.59$. See Ref. 72. Note that $\gamma_{\infty,\text{ang}}=+1.04$, leading to a total $\gamma_\infty(Fe^{3+})=-0.70-7.89-1.59+1.04=-9.14$.

[d] This total is exclusive of the distant rest-of-the-lattice contribution $e\,\Delta q_{\text{DRL}}=-0.603$.

$\gamma_{\text{eff,DE}}$ and $\gamma_{\text{eff,DN}}$. Thus the *ab initio* value of $\gamma_{\text{eff,DE}}$ is close to $\gamma_\infty/3$ while that of $\gamma_{\text{eff,DN}}$ is close to $2\gamma_\infty/3$, both substantially smaller than γ_∞. The physical reason for this difference is that neither the nuclear charges on the O^{2-} ions nor the electrons on them are totally external with respect to the electrons of the Fe^{3+} ion core as seen from Fig. 1, the penetration being stronger for the electrons on the O^{2-} ions as compared to that for the O^{2-} nuclear charges.

The *ab initio* values of the effective antishielding factors $\gamma_{\text{eff},L}$ through $\gamma_{\text{eff,DN}}$ have of course been obtained from the corresponding calculated induced field gradients and, therefore, reflect the natures of the latter. Among the various contributions to the induced field gradient, the calculated local component is seen to augment the corresponding direct contribution $q_L^{(0)}$, since our $\gamma_{\text{eff},L}$ is antishielding in nature. There is a difference of 27% between the *ab initio* value of Δq_L and the value obtained with a parametric choice using $\gamma_L=0.07$ corresponding to a free Fe^{2+} ion, a substantial change in view of the very sizeable magnitude of $q_L^{(0)}$. The change is even more pronounced, namely ~52% of $q_L^{(0)}$, if one uses for γ_L the value of $R=0.32$ as was done in earlier calculations.[8] The nonlocal induced field gradient Δq_N obtained here is comparable in magnitude to the zero-order $q_N^{(0)}$ and of the same sign, in contrast with both the very small contribution of opposite sign to be expected for the parametric choice $\gamma_N=R=0.07$ (choice I A) and the very large contribution of the same sign which results from the choice $\gamma_N=\gamma_\infty/2=-4.6$ (choice II B). The influence of antishielding effects on Δq_{DE} and Δq_{DN} is the most pronounced, both of them having substantially smaller magnitudes than one would have with the assumption $\gamma_{\text{DE}}=\gamma_{\text{DN}}=\gamma_\infty$ made in earlier calculations.[8] What is even more important is that since $q_{\text{DE}}^{(0)}$ is antishielded substantially less than $q_{\text{DN}}^{(0)}$, the magnitude of Δq_{DE} is smaller than Δq_{DN}, an opposite trend when compared to that of $q_{\text{DE}}^{(0)}$ and $q_{\text{DN}}^{(0)}$. Consequently, whereas $q_{\text{DE}}^{(0)}$ is larger in magnitude than $q_{\text{DN}}^{(0)}$, the two of them having opposite signs, as far as the net field gradients are concerned, $q_{\text{DN}}=q_{\text{DN}}^{(0)}+\Delta q_{\text{DN}}$ is now larger in magnitude than $q_{\text{DE}}=q_{\text{DE}}^{(0)}+\Delta q_{\text{DE}}$ and the net sign for the sum of q_{DN} and q_{DE} is opposite to that of the sum of $q_{\text{DN}}^{(0)}$ and $q_{\text{DE}}^{(0)}$. For the contribution to the induced EFG from the charges on the lattice outside the cluster of the Fe^{3+} ion and the six nearest O^{2-} ions, we have assumed the antishielding factor to be γ_∞ as mentioned earlier.

The net field gradient at the ^{57m}Fe nucleus from our *ab initio* calculation is seen from Table II to be 2.709×10^{14} esu cm^{-3}, leading to a theoretical value for the nuclear quadrupole coupling constant of 1.61 MHz, substantially smaller than the experimental value of 10.21 MHz. Possible sources that could bridge the gap between the *ab initio* theoretical value and experiment will be discussed in Sec. IV, where the theoretical results for the net field gradient using the four sets of parametric choices listed in Table II. will also be discussed.

Finally in this section we would like to present the breakdown of the induced field gradients according to the individual Q-perturbed Fe^{3+} ion orbitals. This is shown in Table III for the radial perturbations, which make the dominant contribution to the antishielding effects. For the angular perturbations only the net induced EFG and shielding factors are shown. Space does not permit a discussion of all the interesting trends that are observed in this table, a detailed discussion of these being available elsewhere.[73] We shall merely note that the $3p \rightarrow p$ perturbation makes the largest contribution to the antishielding effects except for the local contribution to the EFG, where $2p \rightarrow p$ is the leading contributor and that for all the sources of EFG and all the perturbations the induced contribution is antishielding in nature except for the $3d \rightarrow d$ perturbation for the nonlocal source case. The first feature involving dominance of the $3p \rightarrow p$ perturbation for nonlocal and distant sources is identical with the situation for γ_∞ and is a result of the fact that the $3p$ orbital among all the orbitals of the Fe^{3+} ion has both sizable deformability and density at the nucleus. For the local source, however, the penetration of the source into the inner regions of the Fe^{3+} ion makes the density at the nucleus of the Fe^{3+} orbital concerned more important than the deformability, and so the $2p \rightarrow p$ perturbation becomes more effective than $3p \rightarrow p$. Regarding the second feature of the induced EFG from the $3d \rightarrow d$ perturbation, it can perhaps be understood by the fact that this perturbation leads to a diffuse distribution which overlaps the nonlocal source charge density substantially and therefore produces the observed shielding effect, much like R for the local contribution for the Fe^{2+} ion.[75]

IV. COMPARISON OF THE EFG AT ^{57m}Fe IN Fe_2O_3 CALCULATED *AB INITIO* WITH EXPERIMENT AND EARLIER CALCULATIONS USING PARAMETRIZED ANTISHIELDING FACTORS

In the preceding section we have analyzed the results of our *ab initio* calculation of induced field gradients in Fe_2O_3 to draw conclusions regarding the nature of antishielding effects in the solid associated with local, nonlocal, and distant contributions to the EFG at the iron site. In this section we shall use the results of our calculations to make comparison with the observed nuclear quadrupole coupling constant in Fe_2O_3 and with results of calculations using Eq. (5) with different choices of antishielding parameters γ_S for the local, nonlocal, and distant induced field gradients. Some of these choices have been used in recent published results[8] for Fe_2O_3. Table IV lists the results of our theoretical calculations and those of four other calculations where the induced field gradients were obtained by multiplying the local, nonlocal, and distant zero-order contributions to the field gradient with different choices of antishielding parameters representing two distinct types of parametric treatment of NQI in ionic solids used in the literature. Choice I, in keeping with Table II, amounts to using only two distinct parameters R and γ_∞, while choice II employs three distinct parameters, namely R, $\gamma_\infty/2$, and γ_∞. In choice I the induced field gradients due to both local and nonlocal sources were obtained by multiplying the respective values of $q_S^{(0)}$ by the same factor R [that is, γ_N and γ_L in Eq. (5) were both assumed to be equal to R], while the induced field gradients due to all four distant sources including the point sources in the rest of the lattice outside the cluster were obtained by multiplying the respective zero-order field gradients by the same factor γ_∞. Two different sets of numerical values are listed under choice I (columns marked A and B in Table IV). The set A represents a choice of numerical values based on the results of many-body calculations[22,25,48(a)] for R $(=+0.074)$ and γ_∞ $(=-9.19)$ for Fe^{2+} and Fe^{3+}, respectively. The set B, which represents the choice used in estimating the EFG in earlier published calculations[8], uses an earlier estimate[74] of R $(=0.32)$ and an earlier one-electron result[72] for γ_∞ $(=-9.14)$. The choices of γ_∞ are, in effect, quite close to each other in both sets A and B, while the choice of R in set B represents a serious overestimate,[74,75] as pointed out earlier in Sec. I. Choice II deviated from choice I only in the treatment of the nonlocal field gradient. In an attempt to account for the nature of the nonlocal sources of EFG, which is intermediate between the natures of the local and distant sources, a parametric value of $\gamma_\infty/2$ was used in choice II to obtain the induced EFG due to nonlocal sources. The numerical values of R and γ_∞ within this choice are the same as for choice I. Sets of antishielding parameters based on assumptions similar to those made in formulating choice II have been used in some of the earlier calculations[16,31–33] of field gradients in alkali-halide molecules and solid solutions.

The results of Table IV, and in particular the differences between the various terms eq (local, nonlocal, etc.) obtained from the *ab initio* versus the parametric calculations, and the resulting differences between the various calculated values of e^2qQ/h clearly emphasize the importance of carrying out a first-principles treatment of Sternheimer antishielding effects for the ionic crystal Fe_2O_3, such as has been done here. A detailed analysis of the reasons for the substantial differences between the *ab initio* results for the field gradients due to the various sources and the results for parametric choices for antishielding and shielding effects is presented in Ref. 73. The reasoning is based on a consideration of the charge-density terms in the source terms belonging to the classes of local, nonlocal, distant electronic, and distant nuclear and their penetration into the region ascribed to the charge distribution associated with the Fe^{3+} ion.

We refer now to a discussion of our results from the point of view of the next motivation for the present work, namely an assessment of the degree of charge-transfer covalency in Fe_2O_3, by a comparison of the nuclear quadrupole coupling constant obtained from the calculated EFG using a model of overlapping ions and no charge transfer between the Fe^{3+} and O^{2-} ions with the experimental result. Our net electric field gradient at ^{57m}Fe, comprising all zero-order and induced contributions given in Table IV, leads to a nuclear quadrupole coupling constant e^2qQ/h of 1.61 MHz using the recent value[48(b)] of $Q(^{57m}\mathrm{Fe})=0.082b$. This theoretical value of e^2qQ/h is seen to be less than one-sixth of the experimentally observed coupling constant,[19] namely 10.21 MHz, in $^{57m}Fe_2O_3$. The balance, it appears, has to be sought in the influence of charge-transfer covalency which is not includ-

TABLE IV. Source-by-source comparison of induced and total electric field gradients at ^{57m}Fe in Fe_2O_3 obtained from our *ab initio* calculation with those estimated using various parametric choices of antishielding factors.

	Zero-order electric field gradient[a]	Induced and total[b] electric field gradients[a] from *ab initio* treatment of antishielding effects		Induced and total[c] EFG[a] estimated using parametric choices of antishielding factors							
				Choice I (A) $\gamma_L = \gamma_N = R = 0.074$ $\gamma_D = \gamma_\infty = -9.19$		Choice I (B) $\gamma_L = \gamma_N = R = 0.32$ $\gamma_D = \gamma_\infty = -9.14$		Choice II (A) $\gamma_L = R = 0.074$ $\gamma_N = \gamma_\infty / 2 = -4.60$ $\gamma_D = \gamma_\infty - 9.19$		Choice II (B) $\gamma_L = R = 0.32$ $\gamma_N = \gamma_\infty / 2 = -4.57$ $\gamma_D = \gamma_\infty = -9.14$	
Source	$eq^{(0)}$	$e\,\Delta q$	eq	$e\,\Delta q$	eq	$e\,\Delta q$	eq	$e\,\Delta q$	eq	$e\,\Delta q$	eq
Local	6.843	1.355	8.198	−0.506	6.337	--2.190	4.653	−0.506	6.337	−2.190	4.653
Nonlocal	−0.847	−0.602	−1.449	0.063	−0.784	0.271	−0.576	−3.892	−4.739	−3.871	−4.718
Distant electronic	2.311	8.724	11.035	21.238	23.549	21.123	23.434	21.238	23.549	21.123	23.434
Distant nuclear	−1.957	−12.696	−14.653	−17.985	−19.942	−17.887	−19.844	−17.985	−19.942	−17.887	−19.844
Distant overlap	0.052	0.195	0.247	0.478	0.530	0.475	0.527	0.478	0.530	0.475	0.527
Distant rest-of-the-lattice	−0.066	−0.603	−0.669	−0.607	−0.673	−0.603	−0.669	−0.607	−0.673	−0.603	−0.669
Total	6.336	−3.627	2.709	2.681	9.017	1.189	7.525	−1.274	5.062	−2.953	3.383
e^2qQ/h (MHz)			1.610		5.360		4.473		3.009		2.011

[a] EFG in units of 10^{14} esu cm^3.

[b] Total EFG $eq_S = eq_S^{(0)} + e\,\Delta q_S$ for each source S, where Δq_S is calculated from first principles.

[c] Total EFG $eq_S = eq_S^{(0)} + e\,\Delta q_S$, where Δq_S is obtained from the corresponding zero-order EFG $q_S^{(0)}$ of column 2 by multiplying by the factor $-\gamma_L$ for the local term, $-\gamma_N$ for the nonlocal term, and $-\gamma_D$ for all the distant terms.

ed in the model of overlapping ions. In particular, we can examine the possibility of bridging the gap through transfer of electrons from the ligands to the $3d$ shell of the Fe^{3+} ion. We have calculated the contribution of a single $3d_{z^2}$ electron to the coupling constant to be

$$\nu_{Q,3d_{z^2}}=\frac{e^2Q}{h}\left\langle \psi_{3d_{z^2}}\left|\frac{3\cos^2\theta-1}{r^3}\right|\psi_{3d_{z^2}}\right\rangle$$
$$\cong 63.0\ , \tag{55}$$

measured in MHz. The difference of 8.60 MHz between our *ab initio* results and experiment requires about 13.6% additional population in the $3d_{z^2}$ state as compared to the other four $3d$ states, which could result perhaps from ligand charge transfer to the Fe^{3+} ion $3d_{z^2}$ state of spin antiparallel to that of the five $3d$ electrons already present. In terms of conventional notation[11,76] for the covalency effect, the difference of 8.60 MHz requires a value of $f_\sigma - f_\pi = 0.136$, the σ direction referring to the axis of symmetry, the c axis. The net transfer $f_\sigma + f_\pi$ to the $3d$ shell of the Fe^{3+} ion can, of course, be somewhat larger. A net transfer as large as 20% is not unreasonable compared to the estimates of charge-transfer covalency arrived at from interpretations of transition-metal ion and transferred ligand hyperfine constants in iron-group compounds,[11,52–54,76,77] and from first-principles covalency calculations[78] in ferric compounds.

The above analysis emphasizes the need for a first-principles covalency calculation if one is to obtain a complete understanding of the origin of the NQI in Fe_2O_3. Such a calculation would require large amounts of computer time, and in view of the need to predict the anisotropy of the charge distribution, makes acute demands on the accuracy and flexibility of the basis set as compared to those necessary to explain isotropic properties such as isomer shifts and the contact hyperfine interaction; but its results should be rewarding in terms of furthering our understanding of the origins of the NQI in this and related systems. To be complete, the covalency calculation would have to include transfer of ligand charge to both $4s$ and $4p$ states in addition to the $3d$ states, and a detailed analysis of the wave functions obtained from such a calculation can be made by testing not only the quadrupole coupling constant but also the isotropic and anisotropic hyperfine interactions of the metal-ion nucleus ^{57m}Fe and those of the ligand-ion nucleus ^{17}O.

In addition to the first-principles covalency calculations, *ab initio* antishielding calculations, such as the present one with the model of overlapping ions, in systems other than Fe_2O_3, would further aid in the understanding of antishielding effects in actual ionic crystals and of their departure from the case of free ions and atoms. Thus it would be very useful to investigate related transition-metal compounds as well as other ionic crystals with more tightly bound positive ions such as Al_2O_3,[79] or more tightly bound negative ions such as the cadmium halides where both the ^{111}Cd (excited nuclear state with $I=\frac{5}{2}$) and the halogen nuclear quadrupole coupling constants are available.[80]

V. CONCLUSIONS

An *ab initio* procedure has been developed for the study of antishielding effects in the NQI in ionic crystals. While the procedure has been applied quantitatively here to a model of overlapping ions, it can be easily extended to a treatment of antishielding effects due to inner shells of the central ion in an evaluation of EFG which employs wave functions incorporating charge-transfer covalency. The application of our procedure to the model of overlapping ions for Fe_2O_3 has shown that the antishielding effects associated with the various sources in this model are rather sensitive to the charge distributions in the crystal and are very different from the effects represented by the valence-electron shielding factor R for the $3d$ electron in a ferrous ion and by the external-charge antishielding factor γ_∞ for a ferric ion. These differences can be explained on the basis of the extent of interpenetration between the various sources producing the EFG and the electronic charge distribution on the Fe^{3+} ion. Within this model our procedure gives a nuclear quadrupole coupling constant for ^{57m}Fe in Fe_2O_3 which is about one-sixth of the experimental value. A simple analysis indicates that a reasonable amount of charge-transfer covalency can bridge this gap between theory and experiment.

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[1] T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy* (Academic, New York, 1957); E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants* (Academic, New York, 1969).

[2] T. C. Gibb, *Principles of Mössbauer Spectroscopy* (Chapman and Hall, London, 1976).

[3] M. H. Cohen and F. Reif, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5; C. P. Slichter, *Principles of Magnetic Resonance,* 2nd ed. (Springer, New York, 1978).

[4] See, for example, the series of articles in *Advances in Nuclear Quadrupole Resonance,* edited by J. A. S. Smith (Heyden, London, 1974). See also Refs. 1 and 3.

[5] See, for example, articles in *Perturbed Angular Correlations,* edited by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland, Amsterdam, 1964); R. S. Raghavan, P. Raghavan,

and J. M. Friedt, Phys. Rev. Lett. 30, 10 (1973), and references therein.

[6] B. Starck, J. Demaison, W. Hüttner, and R. Tischer, in *Molecular Constants,* Vol. 6 of *Landolt-Bornstein, New Series,* edited by K. H. Hellwege and A. M. Hellwege (Springer, New York, 1974); S. L. Segal and R. G. Barnes, Ames Laboratory, AEC Report (unpublished); P. Rageazan, E. N. Kaufmann, R. S. Raghavan, E. J. Ansaldo, and R. A. Naumann, Phys. Rev. B 13, 2835 (1976).

[7] R. M. Sternheimer, Phys. Rev. 80, 102 (1950); 84, 244 (1951); 95, 736 (1954); 105, 158 (1957); 146, 140 (1966); 164, 10 (1967); Phys. Rev. A 6, 1702 (1972); 9, 1783 (1974).

[8] R. R. Sharma, Phys. Rev. Lett. 26, 563 (1971).

[9] A. J. Freeman and D. E. Ellis, J. Phys. (Paris) Colloq. 35, C6-3 (1974).

[10] G. A. Sawatzky and F. van der Woude, J. Phys. (Paris) Colloq. 35, C6-47 (1974).

[11] F. A. Cotton and C. B. Harris, Proc. Natl. Acad. Sci. 56, 12 (1966); R. Bersohn and R. Shulman, J. Chem. Phys. 45, 2298 (1966); B. B. Garrett, J. Magn. Reson. 14, 335 (1974).

[12] P. F. Walch and D. E. Ellis, Phys. Rev. B 7, 903 (1973); J. A. Tossell, D. J. Vaughan, and K. H. Johnson, Am. Mineral. 59, 319 (1974); D. E. Ellis and F. W. Averill, J. Chem. Phys. 60, 2856 (1974); A. Trautwein, R. Reschke, R. Zimmerman, I. Dezsi, and F. E. Harris, J. Phys. (Paris) Colloq. 35, C6-235 (1974); R. Reschke, A. Trautwein, and J. P. Desclaux, J. Phys. Chem. Solids 38, 837 (1977).

[13] R. Bersohn, J. Chem. Phys. 29, 326 (1958); Phys. Rev. Lett. 4, 609 (1960).

[14] G. Burns, Phys. Rev. 124, 524 (1961); R. Ingalls, *ibid.* 133, A787 (1964); P. A. Casabella and N. C. Miller, J. Chem. Phys. 40, 1363 (1964); see also Ref. 45 and M. H. Cohen and F. Reif, Ref. 3.

[15] B. G. Dick and T. P. Das, J. Appl. Phys. 33, 2815 (1962); Phys. Rev. 127, 1035 (1962).

[16] T. P. Das and M. Karplus, J. Chem. Phys. 30, 848 (1959).

[17] R. R. Sharma and T. P. Das, J. Chem. Phys. 41, 3581 (1964).

[18] J. O. Artman, Phys. Rev. 143, 541 (1966).

[19] J. O. Artman, A. H. Muir, and H. Wiedersich, Phys. Rev. 173, 337 (1968).

[20] See T. P. Das and M. Karplus, Refs. 16 and 32; D. Ikenberry and T. P. Das, in Ref. 33.

[21] R. Ingalls, Ref. 14; Phys. Rev. 188, 1045 (1969); C. E. Johnson, W. Marshall, and G. J. Perlow, *ibid.* 126, 1503 (1962).

[22] S. N. Ray, T. Lee, and T. P. Das, Phys. Rev. A 9, 93 (1974).

[23] S. N. Ray, T. Lee, T. P. Das, and R. M. Sternheimer, Phys. Rev. A 9, 1108 (1974).

[24] M. Vajed-Samii, S. N. Ray, and T. P. Das, Phys. Rev. B 11, 4591 (1975).

[25] S. N. Ray, T. Lee, T. P. Das, R. M. Sternheimer, R. P. Gupta, and S. K. Sen, Phys. Rev. A 11, 1804 (1975); A. C. Beri, S. N. Ray, T. P. Das, and R. M. Sternheimer, *ibid.* 12, 1168 (1975).

[26] P. C. Schmidt, K. D. Sen, and A. Weiss, Phys. Rev. B 22, 4167 (1980).

[27] G. Burns and E. G. Wikner, Phys. Rev. 121, 155 (1961); E. Paschalis and A. Weiss, Theor. Chim. Acta 13, 381 (1969).

[28] K. D. Sen and P. T. Narasimhan, Phys. Rev. B 15, 95 (1977).

[29] N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956); T. P. Das, Phys. Scr. 11, 121 (1975); P. C. Pattnaik, M. D. Thompson, and T. P. Das, Phys. Rev. B 16, 5390 (1977); 19, 4326 (1979); 19, 4328 (1979).

[30] C. H. Townes and B. P. Dailey, J. Chem. Phys. 17, 782 (1949); B. P. Dailey and C. H. Townes, *ibid.* 23, 118 (1955); see also Ref. 1.

[31] J. L. Marsh and P. A. Casabella, Phys. Rev. 150, 546 (1966).

[32] T. P. Das and M. Karplus, J. Chem. Phys. 42, 2885 (1965).

[33] D. Ikenberry and T. P. Das, Phys. Rev. 184, 989 (1969).

[34] P. O. Lowdin, J. Chem. Phys. 18, 365 (1950); Adv. Phys. 5, 1 (1956).

[35] A. Mukherji and T. P. Das, Phys. Rev. 111, 1479 (1958); B. S. Gourary and F. J. Adrian, *ibid.* 105, 1180 (1957); W. E. Blumberg and T. P. Das, *ibid.* 110, 647 (1958); T. P. Das, A. N. Jette, and R. S. Knox, *ibid.* 134, A1079 (1964).

[36] D. Ikenberry and T. P. Das, Phys. Rev. 138, A822 (1965); J. Chem. Phys. 43, 2199 (1965).

[37] D. R. Taylor, J. Chem. Phys. 48, 536 (1968).

[38] G. A. Sawatzky and J. Hupkes, Phys. Rev. Lett. 25, 100 (1970).

[39] R. R. Sharma, Phys. Rev. Lett. 25, 1622 (1970).

[40] R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. 155, 338 (1967); 171, 378 (1968); P. Novak and I. Veltrusky, Phys. Status Solidi B 73, 575 (1976); D. Ikenberry, A. N. Jette, and T. P. Das, Phys. Rev. B 1, 2785 (1970); A. N. Jette and F. J. Adrian, *ibid.* 14, 3672 (1976); S. Ray and T. P. Das, Phys. Rev. 174, 32 (1968); see Ref. 60; F. van der Woude and G. A. Sawatzky, Phys. Rev. B 4, 3159 (1971); O. F. Schirmer, J. Phys. C 6, 300 (1973); D. Sengupta, J. O. Artman, and G. A. Sawatzky, Phys. Rev. B 5, 1484 (1971); R. R. Sharma and Bung Ning Teng, Phys. Rev. Lett. 27, 679 (1971); R. R. Sharma and A. K. Sharma, *ibid.* 29, 122 (1972); M. Ya Flyagin, A. E. Nikiforov, and A. N. Men, Phys. Status Solidi B 72, 379 (1975).

[41] J. C. Slater, Phys. Rev. 38, 1109 (1931).

[42] K. J. Duff and T. P. Das, Phys. Rev. 168, 43 (1968).

[43] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), Vol. I.

[44] R. Ingalls, Phys. Rev. 128, 1155 (1962).

[45] A. J. Nozik and M. Kaplan, Phys. Rev. 159, 273 (1967).

[46] R. R. Sharma and Bung Ning Teng, Ref. 40; D. Sengupta, J. O. Artman, and G. A. Sawatzky, Ref. 40.

[47] R. Ingalls, Phys. Rev. 133, A787 (1964).

[48] (a) S. N. Ray and T. P. Das, Phys. Rev. B 16, 4794 (1977); see also R. M. Sternheimer, Ref. 75, where the value R $(\mathrm{Fe}^{2+})=0.12$ was obtained; (b) K. J. Duff, K. C. Mishra, and T. P. Das, Phys. Rev. Lett. 46, 1611 (1981).

[49] E. Simanek, Nai Li Huang, and R. Orbach, J. Appl. Phys. 38, 1072 (1967); G. A. Sawatzky and F. van der Woude, Ref. 10.

[50] For a review of recent calculations of indirect exchange effects see D. J. Newman, in *Proceedings of the International Conference on Magnetism, Amsterdam, 1976,* edited by P. F. Chatel and J. J. M. Franse (North-Holland, New York, 1976), Part II, p. 1018.

[51] N. Laurance, E. C. McIrvine, and J. Lambe, J. Phys. Chem. Solids 23, 515 (1962); P. F. Liao and S. R. Hartmann, Phys. Rev. B 8, 69 (1973); P. F. Liao, P. Hu, R. Leigh, and S. R. Hartmann, Phys. Rev. A 9, 332 (1974).

[52] K. J. Duff, Phys. Rev. B 9, 66 (1974).

[53] J. W. Richardson, D. M. Vaught, T. F. Soules, and R. R. Powell, J. Chem. Phys. 50, 3633 (1969); S. Larsson and J. W. D. Connolly, *ibid.* 60, 1514 (1974).

[54] A. Trautwein, E. Kreber, and U. Gonser, J. Phys. Chem. Solids 36, 325 (1975); see also Ref. 12.

[55] R. G. Shulman and S. Sugano, Phys. Rev. 130, 506 (1963).

[56] See K. J. Duff in Appendix I of Ref. 59; see also B. S. Gourary *et al,* Ref. 35, and J. Killingbeck, Mol. Phys. 18, 417 (1970).

[57] T. P. Das and R. Bersohn, Phys. Rev. 102, 733 (1956); R. E. Watson and A. J. Freeman, *ibid.* 135, A1209 (1964); P. W. Langhoff and R. P. Hurst, *ibid.* 139, A1415 (1965).

[58] G. D. Gaspari, Wei-Mei Shyu, and T. P. Das, Phys. Rev. 134, 852 (1964).

[59] D. Ikenberry, B. K. Rao, S. D. Mahanty, and T. P. Das, J. Magn. Reson. 1, 221 (1969).

[60] D. Ikenberry and T. P. Das, Phys. Rev. B 2, 1219 (1970).

[61] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. 93, 734 (1954); R. M. Sternheimer, Phys. Rev. 86, 316 (1952).

[62] For a discussion of Hartree-Fock perturbation theory, in particular the coupled and uncoupled perturbation procedures and orthogonality effects, see A. Dalgarno, Proc. R. Soc. London Ser. A 251, 282 (1959); C. Schwartz, Ann. Phys. (N.Y.) 2, 156 (1959); P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966); K. J. Duff and T. P. Das, Phys. Rev. 168, 43 (1968); R. M. Sternheimer, Refs. 7 and 61.

[63] D. R. Hartree, *The Calculation of Atomic Structures* (Wiley, New York, 1957); H. Bethe and R. W. Jackiw, *Intermediate Quantum Mechanics,* 2nd ed. (Benjamin, New York, 1968).

[64] See Ref. 34; R. R. Sharma, J. Math. Phys. 9, 505 (1968); K. J. Duff, Int. J. Quantum Chem. 5, 111 (1971); A. N. Jette, Int. J. Quantum Chem. 7, 131 (1973).

[65] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960).

[66] L. Pauling and S. B. Hendricks, J. Am. Chem. Soc. 47, 781 (1925).

[67] R. L. Blake, T. Zoltai, R. E. Hessevick, and L. W. Finger, Investigation of the U. S. Bureau of Mines Report No. 7384, 1970 (unpublished).

[68] R. E. Watson, Phys. Rev. 118, 1036 (1960).

[69] These wave functions deviate inappreciably from those tabulated by E. Clementi, IBM J. Res. Dev. Suppl. 9, 2 (1965); see also J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, J. Chem. Phys. 36, 1057 (1962).

[70] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).

[71] R. E. Watson, Phys. Rev. 111, 1108 (1958).

[72] R. M. Sternheimer, Phys. Rev. 130, 1423 (1963).

[73] A. C. Beri, Ph.D. thesis, State University of New York, Albany 1979 (unpublished).

[74] R. Ingalls, Phys. Rev. 128, 1155 (1962); A. J. Freeman and R. E. Watson, *ibid.* 131, 2566 (1963); R. Ingalls, Ref. 14.

[75] See Ref. 48(a) and R. M. Sternheimer, Phys. Rev. A 6, 1702 (1972) for discussions of the origins of the error in the earlier value of R for a free Fe^{2+} ion.

[76] See Ref. 11; H. Kubo, I. Yahara, and K. Hirakawa, J. Phys. Soc. Jpn. 41, 442 (1976); see also experimental results in Ref. 77.

[77] J. Owen and J. H. M. Thornley, Rep. Prog. Phys. 29, 675 (1966).

[78] K. J. Duff, Ref. 52; F. van der Woude and G. A. Sawatzky, Ref. 40; see also Refs. 12, 53, and 54.

[79] R. V. Pound, Phys. Rev. 79, 685 (1950); H. Lew and G. Wessel, *ibid.* 90, 1 (1953); A. H. Silver, T. Kushida, and J. Lambe, *ibid.* 125, 1147 (1962); see also Ref. 51.

[80] R. S. Raghavan, P. Raghavan, and J. M. Friedt, Ref. 5.