



Calculation of electric field gradient tensor for simple point charge distributions and its application to real systems

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Abstract : Nuclei with the spin quantum number not smaller than unity have not only the nuclear magnetic moment but also the electric quadrupole moment. The quadrupole moment couples with the electric field gradient (EFG) to produce the nuclear quadrupole interaction. It is well known that two independent parameters, i.e. the quadrupole coupling constant (QCC) and the asymmetry parameter (η) together with the principal axis directions can fully describe the interaction and are very sensitive to the local symmetry and structure of the solid. In order to obtain quantitative estimates of the EFG tensor for various simple ionic configurations surrounding the nucleus under consideration, we employ the simple point charge approximation and apply the calculated results to some real crystals. General agreement is rather satisfactory.

INTRODUCTION

An arbitrary distribution of charges exhibits electrical properties such as electric potential (V) and field (E). Electric potential is the energy created by work done on a unit charge against electric forces while an electric field, i.e. electric force exerted on unit charge, being a space derivative of electric potential. The electric potential, as a scalar, has no directionality unlike an

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electric field. The directionality of the electric field created by space derivative ($-\nabla V$) causes its dependence on a spatial distribution of charges. It is also noted that the electric field does not always vanish where the electric potential does.

We can imagine the space derivatives of electric field, i.e. ($-\nabla^2 E$) which may probably involve more complexity in directionality. It is the second derivatives of electric potential called the electric field gradient (EFG) as a tensor of second rank. The increased complexity in directionality also produces more complex dependence on the spatial distribution of charges. There can be derived relations between an electric field and EFG just like between the electric potential and field. For example, EFG does not always vanish where an electric field may vanish.

Let us assume charge density $\rho(\mathbf{r})$ is, interacting with electric potential $V(\mathbf{r})$. To focus on the descending order of dominant factors contributing to the interaction energy, the potential energy W_E can be expanded up to the third order in a Taylor series at a given point:^{1,2}

$$W_E = V(0) \int \rho(\mathbf{r}) dv + \sum_i \left(\frac{\partial V}{\partial x_i} \right)_0 \int x_i \rho(\mathbf{r}) dv + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 \int x_i x_j \rho(\mathbf{r}) dv + \Lambda. \quad (1)$$

The first term of Eq. (1) is the electrostatic coulomb energy while the second term is the electric dipole energy. The third term describes the quadrupole interaction energy of the charge distribution. Among the terms on the right-hand side of Eq. (1), the important term in magnetic resonance that depends on the spatial distribution $\rho(\mathbf{r})$ is the last term. This is the case for charge density of some atomic nuclei. We note that the quadrupole moment of the nuclei couples to the EFG tensor to give the quadrupole interaction energy. Higher order terms may be ignored in our consideration.

Nuclei find electrostatic interaction energies at their positions due to their own atomic electrons and the surrounding charge distribution such as neighboring ions. The quadrupole interaction can give rise to the splitting of energy levels into sublevels. The nuclear quadrupole resonance (NQR) technique uses transitions between the sublevels for the investigation of the quantum-energy structure without applying the external magnetic field. However, for the splitting, the nuclear charge distribution should not be spherical. This condition leads to the nuclear spin quantum number not being less than 1. The spatial distribution of the charges surrounding the nucleus, e.g. in crystals, also should meet relevant geometrical symmetry conditions to produce non-vanishing EFG. For example, a cubic symmetry yields zero EFG.

The nuclear spin Hamiltonian for the nuclear magnetic resonance (NMR) investigation for

the quadrupolar nucleus is given by^{2,3}

$$H = H_z + H_Q. \quad (2)$$

Here H_z and H_Q describe the nuclear Zeeman and quadrupole interaction, respectively. The quadrupole Hamiltonian in a set of principal-axis coordinates (X, Y, Z) where the EFG tensor being diagonalized is given by

$$H_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I^2 + \frac{1}{2} \eta (I_x^2 - I_y^2)], \quad (3)$$

where eQ is the nuclear electric quadrupole moment and, eq is the largest component of the EFG tensor. Here I and η are the nuclear spin quantum number and the asymmetry parameter of EFG, respectively.

In this work, we adopt the point charge approximation method that assumes neighboring ions as simple point charges and disregards electronic orbital configurations. For simplicity, we limit only ions positioning at near sites from a nucleus under consideration. This approach enables us a simple classification of charge distributions around nuclei into seven types for the sake of an approximate estimate of EFG in the real complex systems. For EFG calculation, we denote laboratory axes by (x, y, z) whereas the principal EFG axes by (X, Y, Z).

AN EFG TENSOR DUE TO AN ION

Let us consider the simplest case where there is an ion with a charge q_c at a position (a, b, c). In MKS unit, the electric potential $V(r)$ at (x, y, z) due to this charge is given by

$$V(r) = \frac{q_c}{4\pi\epsilon_0} \frac{1}{\sqrt{(x-a)^2 + (y-b)^2 + (z-c)^2}}, \quad (4)$$

where ϵ_0 is the electric permittivity. Then, the electric field $\vec{E}(r)$ is given by the space derivative of the potential as follows:

$$\mathbf{E}(r) = -\nabla V = -\left[\frac{\partial V}{\partial x}\hat{i} + \frac{\partial V}{\partial y}\hat{j} + \frac{\partial V}{\partial z}\hat{k}\right], \quad (5)$$

where \hat{i} , \hat{j} , and \hat{k} are the unit vectors along the x , y , and z directions, respectively. The space derivatives of the electric field, then, produce an EFG tensor as given by

$$V_{ij} = \nabla^2 V(r) = \begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 V}{\partial x^2} & \frac{\partial^2 V}{\partial x \partial y} & \frac{\partial^2 V}{\partial x \partial z} \\ \frac{\partial^2 V}{\partial y \partial x} & \frac{\partial^2 V}{\partial y^2} & \frac{\partial^2 V}{\partial y \partial z} \\ \frac{\partial^2 V}{\partial z \partial x} & \frac{\partial^2 V}{\partial z \partial y} & \frac{\partial^2 V}{\partial z^2} \end{pmatrix}. \quad (6)$$

In the case for $(x, y, z) = (0, 0, 0)$, then EFG tensor is

$$V_{ij}(0,0,0) = \frac{q_c}{4\pi\epsilon_0} \frac{1}{\sqrt{(a^2 + b^2 + c^2)^3}} \begin{pmatrix} 2a^2 - b^2 - c^2 & 3ab & 3ac \\ 3ba & 2b^2 - a^2 - c^2 & 3bc \\ 3ca & 3cb & 2c^2 - a^2 - b^2 \end{pmatrix}. \quad (7)$$

As shown above, an EFG tensor has nine elements in general. One can choose a proper set of axes (principal axes) to reduce the number of independent elements to three, i.e. diagonalization, in addition to three components associated with the principal axis directions. The diagonal elements of the principal EFG tensor are conventionally denoted as $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ while the trace being always zero due to the Laplace equation. The zero trace enables EFG tensor to be represented by two independent parameters. Accordingly, an EFG tensor is usually represented by two parameters, i.e. $|V_{zz}|$ ($\equiv eq$) and the asymmetry parameter η ($\equiv (V_{xx} - V_{yy})/V_{zz}$).^{2,4}

EFG TENSORS FOR SPECIAL CHARGE CONFIGURATIONS

For cases with more than one charge, we employ the superposition principle whereby contributions from all ions are summed together. Table 1 shows the calculated electric potential

and EFG tensor at the origin produced by various distributions of the equal point charge q_e , i.e. an isosceles triangle (A), a rhombus (B), a rectangle (C), a hexagon (D), an orthorhombic hexahedron (E), a tetrahedron (F), and an octahedron (G). Note that the axes shown in the table are for the EFG calculation. These results show that a condition $a = b = c$ gives null EFG tensors for the case of a cubic, a tetrahedron, and an octahedron. For example, crystals of the NaCl structure do not exhibit any nuclear quadrupole interaction due to their cubic symmetry. Likewise, Si and Ge crystals having the diamond structure would also have zero EFG tensors. In addition, the asymmetry parameter η vanishes for the cases of equilateral triangles and squares. More-than-three-fold rotation symmetries cause η to be zero. Accordingly, we may conclude that EFG tensors are very sensitive to the local symmetry of the surrounding charges.

APPLICATION OF EFG TENSORS

The valence state and the distances (r) of the neighboring ions not only determine the magnitude of EFG, but also the principal axis directions as well and these may be estimated by considering only ions at the first and second nearest neighboring coordinates, since EFG is proportional to r^{-3} . So the additional contributions of further neighbors would diminish very quickly.

In the planar charge distributions (from A to D in Table 1), the largest component of EFG tensors turns out to be along the axis perpendicular to the plane of regular polygons. For instance, the experimental observation of V_{zz} at a Li^+ cation surrounded by three oxygen ions in LiNbO_3 shows that the Z-direction lies along the direction normal to the oxygen triangle.⁵ Also, borons, in a $\beta\text{-BaB}_2\text{O}_4$ crystal, bonded to three neighboring oxygens have been reported to show the principal Z-direction is vertical to the plane of the oxygen distribution.⁶ V_{zz} for Ga at the three-fold symmetry in a wurtzite structured GaN,⁷ which is an elongated tetrahedron along the crystallographic c axis, has also been reported to lie along the vertical direction of the nearest neighbor nitrogen plane.⁸

This simple approximation may also be applied to the EFG calculation of many real solids with three-dimensional ionic bonds. For example, an EFG change can be reflected at phase transitions of well-known ferroelectric crystals such as BaTiO_3 ^{9,10} and LaAlO_3 .¹¹

BaTiO_3 is cubic in the paraelectric phase ($> 403 \text{ K}$) so that a Ti ion locates at the center of the nearest neighboring octahedron of oxygens and the second neighboring right hexahedron of Ba ions.¹² We suppose the EFG at Ti is made up with superposition of the nearest neighboring oxygens and the second nearest neighboring Ba ions. The nearest oxygens give rise to the null EFG tensor, corresponding to Table 1(G) with $a = b = c$. Similarly, the second nearest Ba ions

also yield zero EFG due to Table 1(E) with $a = b = c$. Therefore, the EFG tensor at a Ti ion vanishes in the case of paraelectric phase.

However, the distortion of atomic positions takes place along the c -axis at room temperature giving rise to the ferroelectric phase.¹² The lattice constants are 0.3997 nm for a -axis and 0.40314 nm for c -axis [9]. The V_{zz} is calculated to be 4.294×10^{19} V/m² by superposing the contributions of the shifted six oxygen and eight Ba ions. In order to evaluate the QCC, we introduce one more factor as below

$$QCC = (1 - \gamma_{\infty}) |V_{zz}| eQ/h, \quad (8)$$

where γ_{∞} is the Sternheimer's shielding factor.¹³

With the $1 - \gamma_{\infty}$ factor of Ti⁴⁺ to be -12.9 ,¹⁴ the QCC is calculated to be 4.18 MHz and 3.46 MHz for ⁴⁷Ti and ⁴⁹Ti, respectively. These numbers are comparable with the experimental determination of 4.60 MHz and 3.78 MHz for ⁴⁷Ti and ⁴⁹Ti, respectively.⁹

SUMMARY

The nuclear quadrupole interaction characterizes the electrostatic interaction of a nucleus with surrounding charges. The interaction can be described by the nuclear quadrupole moment of the nucleus coupled with the EFG tensor, which is sensitive to the local symmetry and structure of charge distributions. The EFG tensor is calculated by employing the point charge approximation for various simple charge configurations. This approximation enables us simple estimates of V_{zz} for many cases and leads to a good agreement with the experimental QCC for BaTiO₃.

Acknowledgment

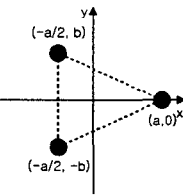
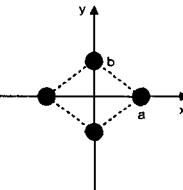
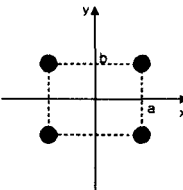
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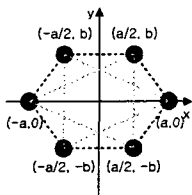
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Table 1. The electric potential and EFG tensor at the origin due to various distributions of same charges. Calculations of some interesting cases of EFG tensor in this table may be found in chap. 7 of ref. 4.

Charge Configuration	Potential	EFG Tensor
<p>A</p> 	$\frac{q_c}{4\pi\epsilon_0} \left(\frac{1}{a} + \frac{2}{\sqrt{\frac{a^2}{4} + b^2}} \right)$	$\frac{q_c}{4\pi\epsilon_0} \begin{pmatrix} \frac{2}{a^3} + \frac{a^2 - 2b^2}{\sqrt{\left(\frac{a^2}{4} + b^2\right)^3}} & 0 & 0 \\ 0 & -\frac{1}{a^3} + \frac{-\frac{a^2}{2} + 4b^2}{\sqrt{\left(\frac{a^2}{4} + b^2\right)^3}} & 0 \\ 0 & 0 & -\frac{1}{a^3} + \frac{-\frac{a^2}{2} - 2b^2}{\sqrt{\left(\frac{a^2}{4} + b^2\right)^3}} \end{pmatrix}$
<p>B</p> 	$\frac{2q_c}{4\pi\epsilon_0} \left(\frac{1}{a} + \frac{1}{b} \right)$	$\frac{2q_c}{4\pi\epsilon_0} \begin{pmatrix} \frac{2}{a^3} - \frac{1}{b^3} & 0 & 0 \\ 0 & -\frac{1}{a^3} + \frac{2}{b^3} & 0 \\ 0 & 0 & -\frac{1}{a^3} - \frac{1}{b^3} \end{pmatrix}$
<p>C</p> 	$\frac{q_c}{4\pi\epsilon_0} \frac{4}{\sqrt{a^2 + b^2}}$	$\frac{q_c}{4\pi\epsilon_0} \frac{4}{\sqrt{(a^2 + b^2)^3}} \begin{pmatrix} 2a^2 - b^2 & 0 & 0 \\ 0 & -a^2 + 2b^2 & 0 \\ 0 & 0 & -a^2 - b^2 \end{pmatrix}$

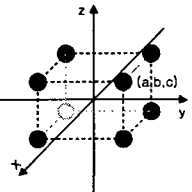
D



$$\frac{2q_c}{4\pi\epsilon_0} \left(\frac{1}{a} + \frac{2}{\sqrt{\frac{a^2}{4} + b^2}} \right)$$

$$\frac{2q_c}{4\pi\epsilon_0} \begin{pmatrix} \frac{2}{a^3} + \frac{a^2 - 2b^2}{\left(\frac{a^2}{4} + b^2\right)^{3/2}} & 0 & 0 \\ 0 & -\frac{1}{a^3} + \frac{-\frac{a^2}{2} + 4b^2}{\left(\frac{a^2}{4} + b^2\right)^{3/2}} & 0 \\ 0 & 0 & -\frac{1}{a^3} + \frac{-\frac{a^2}{2} - 2b^2}{\left(\frac{a^2}{4} + b^2\right)^{3/2}} \end{pmatrix}$$

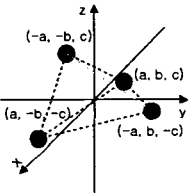
E



$$\frac{q_c}{4\pi\epsilon_0} \frac{8}{\sqrt{a^2 + b^2 + c^2}}$$

$$\frac{q_c}{4\pi\epsilon_0} \frac{8}{\sqrt{(a^2 + b^2 + c^2)^3}} \begin{pmatrix} 2a^2 - b^2 - c^2 & 0 & 0 \\ 0 & -a^2 + 2b^2 - c^2 & 0 \\ 0 & 0 & -a^2 - b^2 + 2c^2 \end{pmatrix}$$

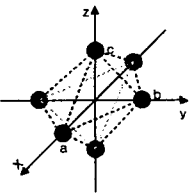
F



$$\frac{q_c}{4\pi\epsilon_0} \frac{4}{\sqrt{a^2 + b^2 + c^2}}$$

$$\frac{q_c}{4\pi\epsilon_0} \frac{4}{\sqrt{(a^2 + b^2 + c^2)^3}} \begin{pmatrix} 2a^2 - b^2 - c^2 & 0 & 0 \\ 0 & -a^2 + 2b^2 - c^2 & 0 \\ 0 & 0 & -a^2 - b^2 + 2c^2 \end{pmatrix}$$

G



$$\frac{q_c}{4\pi\epsilon_0} \left(\frac{2}{a} + \frac{2}{b} + \frac{2}{c} \right)$$

$$\frac{2q_c}{4\pi\epsilon_0} \begin{pmatrix} \frac{2}{a^3} - \frac{1}{b^3} - \frac{1}{c^3} & 0 & 0 \\ 0 & -\frac{1}{a^3} + \frac{2}{b^3} - \frac{1}{c^3} & 0 \\ 0 & 0 & -\frac{1}{a^3} - \frac{1}{b^3} + \frac{2}{c^3} \end{pmatrix}$$