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First-Principles Calculation of the Electric Field Gradient of Li_3N

P. Blaha and K. Schwarz
Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 Vienna, Austria
and
P. Herzig
Institut für Physikalische Chemie, Universität Wien, A-1090 Vienna, Austria

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The electric field gradient can be obtained from self-consistent energy-band calculations by the linearized–augmented-plane-wave method provided that a general potential is used. This first-principles method, which does not rely on any Sternheimer antishielding factor, is tested for Li_3N and yields electric field gradients for Li(1), Li(2), and N in excellent agreement with NMR experiments. The electric field gradient is mainly determined by local distortions of the electronic charge density, especially in the case of the polarizable N^{3-} ion.

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All nuclei which have a nuclear-spin quantum number $I \gtrsim 1$ have a nonspherical nuclear charge distribution and an electric quadrupole moment Q. The nuclear (electric) quadrupole interaction (NQI) can be an aid to determine the distribution of electronic charge surrounding such a nuclear site. The experimental techniques to study the NQI are, for example, nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), or Mössbauer measurements. From such experiments the NQ coupling constant $eQ\phi/h$ can be obtained, where e is the charge of the electron, h is Planck's constant, and ϕ represents the electric field gradient (EFG) in form of the traceless tensor $\phi_{ij} = V_{ij} - \frac{1}{3}\delta_{ij}\nabla^2 V$. Generally speaking ϕ_{ij} can be obtained from measurements of the NQI but not V_{ij}. For review articles see Cohen and Reif[1] and Kaufman and Vianden.[2]

In early investigations, particularly in the case of ionic solids with which the present paper is concerned, an attempt was made to interpret the EFG due to point charges on lattice sites around the ion containing the nucleus in question. In such a model it was necessary to incorporate the so-called Sternheimer factor γ_∞ which accounts for the (anti)shielding of the ionic contribution by the core electrons of the central ion. Since this simple model was not very satisfactory, it has been improved in various ways, for example, by replacing the point charges by overlapping ions or by treating the antishielding factor on a first-principles basis rather than as a parameter. The recent work[3] on Fe_2O_3 may serve as a representative example for such an investigation which also contains many references to this topic. In that work an assumed ionic model leads to an NQ coupling constant of one-sixth of the experimentally observed value. From this discrepancy the authors deduce for Fe_2O_3 the presence of a covalency component which was not included in their study, and they emphasize the need for a first-principles (covalency) calculation in order to obtain a complete understanding of the origin of the NQI.

The present paper describes a completely new approach to calculating EFG's from first principles. This method is based on self-consistent energy-band-structure calculations which use the local-density approximation for treating exchange and correlation and allow the use of a general potential, from which the EFG's can be directly derived without the need of any Sternheimer factor. A second way to obtain EFG's will also be discussed starting from the self-consistent charge density of the crystal. The two procedures, which are just two different ways of solving Poisson's equation, lead to practically identical results. An interpretation is made easier with the second method as it allows the association of several contributions to the EFG's with different spatial regions.

We have applied the new method of calculating EFG's to the superionic conductor Li_3N, mainly because this highly ionic solid crystallizes in a relatively simple hexagonal structure, so that such a calculation is feasible. The other reason is that in Li_3N there are three independent EFG's which have all been measured: one for N and two for the crystallographically inequivalent Li(1) and Li(2) positions; thus there are three values for which the new method can be tested. Moreover, the EFG ratio for the two Li ions directly given by NMR experiments provides a particularly sensitive test, since it does not depend on the Q values, which are not well known.

The EFG's can be obtained from self-consistent energy-band calculations provided they are sufficiently accurate and they contain enough flexibility in their wave functions to describe the anisotropy of the charge distribution. The linearized–augmented-plane-wave (LAPW) method[4,5] should have this capability, if a general potential (GP) is employed instead of the often used muffin-tin (MT) approximation in which the potential is spherically averaged around each atomic site. Such full potential LAPW calculations (FLAPW) have recently been described.[6] We have extended our LAPW program accordingly so that we can handle a GP. In the LAPW method the unit cell is divided into nonoverlapping spheres and an interstitial region, where the wave functions are expressed in atomiclike functions and, respectively, in plane waves. Consequently, the charge density around the atom can be written as a linear combination of radial functions $\rho^m_{l;i}(r_i)$ times modified spherical harmonics $C^m_l(\hat{\mathbf{r}}) = [4\pi/(2l+1)]^{1/2} Y^m_l(\hat{\mathbf{r}})$ (or symmetrized lattice harmonics) and as a Fourier series in the interstitial region[7]

$$\rho(\mathbf{r}) = \begin{cases} \sum_{lm} \rho^{m*}_{l;i}(r_i)\, C^m_l(\hat{\mathbf{r}}_i) + Z_i \delta(\mathbf{r}_i), & i\text{th sphere} \\ \sum_{\mathbf{K}} \rho(\mathbf{K})\, e^{i\mathbf{K}\cdot\mathbf{r}}, & \text{interstitial.} \end{cases} \tag{1}$$

Inside the atomic sphere i the Coulomb potential is given by a similar expression

$$V_{Ci}(\mathbf{r}_i) = \sum_{lm} V^{m*}_{l;i}(r_i)\, C^m_l(\hat{\mathbf{r}}_i) \tag{2}$$

from which the spherical components of the EFG are directly given by

$$\Phi^m_{2;i} = \lim_{r_i \to 0} (1/r_i^2)\, V^m_{2;i}(r_i) \tag{3}$$

so that all information for the EFG comes immediately from the general potential upon which the band calculation is based.

In an alternative way of calculating EFG's one partitions the charge density given by (1) into electrically neutral densities for which—following Rudge[8]—Poisson's equation is solved separately. Since the details will be published elsewhere,[9] only the results should be given here:

$$\Phi^m_{2;i} = \frac{4\pi}{5} \int_0^{R_i} x^{-1} \rho^m_{2;i}(x)\, dx - 4\pi \sum_{\mathbf{K}\neq 0} \rho(\mathbf{K}) \frac{j_1(KR_i)}{KR_i} C^m_2(\hat{\mathbf{K}}) \exp(-i\mathbf{K}\cdot\mathbf{r}_i) + \sum_{l'm'i'} K(l'm', 2m)\, Q^{m'*}_{l';i'}\, \Psi^{m+m'}_{2+l'}(\mathbf{r}_i - \mathbf{r}_{i'}). \tag{4}$$

The first term is the contribution from the atomic sphere (with radius R_i), the second term stems from the Fourier series (where j_1 is a spherical Bessel function), which is extended throughout space, while the last term accounts for the multipole moments $Q^m_{l;i}$ at all other sites where K are coefficients and Ψ are lattice sums (for further details see Ref. 9). The multipole moment Q in the last term contains three contributions: one from the ith nuclear charge (only for $l=0$), another contribution from the electron density of the ith sphere, and finally a correction for extending the Fourier series into the atomic sphere region.

The present work is an extension of an earlier LAPW calculation in which the MT approximation was employed.[10] Since the same parameters (sphere radii, atomic positions) are used here, they need not be explained, but a few details should be mentioned: It is only the N 1s state which is treated as thawed core, but all others including the Li 1s state are obtained from the band calculation based on the GP. The lm expansion for the density and the potential according to Eqs. (1) and (2) is limited to $l \leq 6$; the LAPW basis consists of about 140 unsymmetrized plane waves; a uniform mesh of 28 **k** vectors is used in the irreducible wedge of the Brillouin zone.

Li_3N crystallizes in a hexagonal structure with space group *P6/mmm.* There are Li_2N layers in which the Li(2) atoms are arranged in a graphitelike structure with the nitrogen atoms at the center of the hexagon. Between these layers there are the Li(1) atoms atop the nitrogen atoms.

So far the energy bands of Li_3N have been calculated by the pseudopotential,[11] the LAPW method using the MT approximation,[10] and in a recent Hartree-Fock study.[12] The former two are similar and both differ from the HF results, but all three calculations conclude that lithium nitride is not too far away from the ideal ionic structure consisting of Li^+ and N^{3-} ions. This is in agreement with x-ray diffraction data which could be interpreted[13] by using scattering curves for Li^+ and for an N^{3-} ion immersed in a stabilizing Watson sphere.[14] It seems that none of these calculations are sufficiently accurate for obtaining such a sensitive quantity as the EFG.

Therefore new self-consistent LAPW calculations have been performed using the GP as outlined above. The results obtained are similar to the MT-LAPW calculation by Blaha, Redinger, and Schwarz,[10] but the N p bandwidth is increased from 2.21 to 2.72 eV and the indirect gap is reduced from 1.47 to 1.15 eV. The density of states reflects these changes, but the partial charges remain almost unaltered, where the largest deviation occurs for the N 2p charge, which is about 0.05 electron smaller in the GP than in the MT calculation. This is mainly due to a reduction of the $p_x p_y$-like charge, while the p_z-like contribution changes only slightly.

Already the MT calculation has shown[10] that the charge density is not spherically symmetric around N [Fig. 1(b)]. This effect, however, is drastically increased in the present GP-LAPW calculation as can be seen in Fig. 1(a), which shows the difference between the calculated crystalline and the superposed ionic densities assuming Li^+ and N^{3-} ionic densities.[14] The new x-ray structure factors (available from the authors) also deviate much more (up to 4%) from the ideal ionic model than the previous MT calculation.

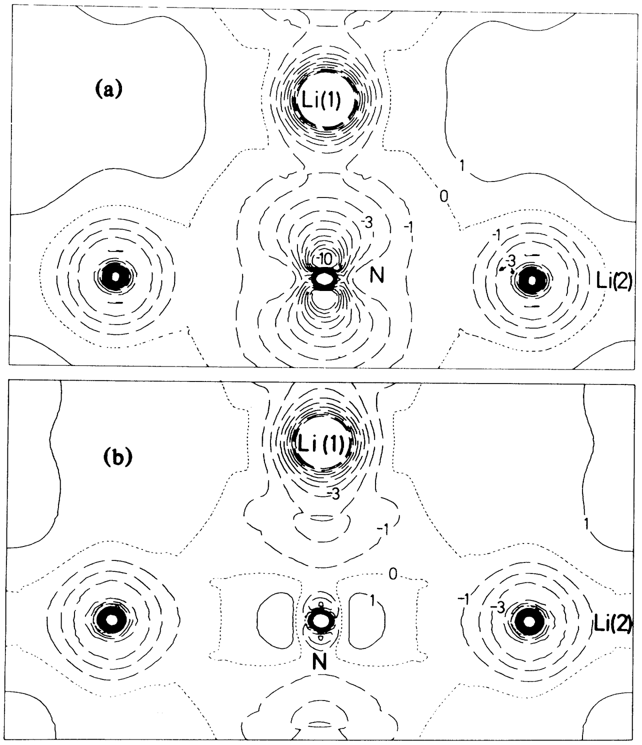

FIG. 1. Difference electron density of Li$_3$N in the $(1\bar{1}0)$ plane with respect to a superposition of Li$^+$ and N^{3-} ionic densities; contour intervals and numbers are in units of 0.01 e Å^{-3}: (a) GP-LAPW (present work), (b) MT-LAPW [taken from Fig. 5(b) of Ref. 10].

Evidence for such deviations was clearly demonstrated by analyzing the anisotropy in Compton profiles.[15]

Because of the hexagonal site symmetries the EFG's in Li$_3$N are completely defined by the Cartesian components Φ_{zz}, which are related to the spherical component for $m=0$ [Eq. (3)] by the relation $\Phi_{zz;i}=2\Phi^0_{2;i}$. It should be noted that the sign of the EFG as defined here is in agreement with Cohen and Reif[1] and Kaufmann and Vianden,[2] but differs from the convention used by other authors.[16]

The magnitude of the NQ coupling constants $|eQ\Phi/h|$ at all three positions of Li$_3$N are known from NMR experiments.[17,18] Lewis and Schwarzenbach tried to refine x-ray-diffraction data with the EFG's as constraints.[16] As these authors have pointed out there are uncertainties in the Q values which could be as large as 15%. These uncertainties carry over to the EFG's, but the EFG ratio for the two Li positions should be much more reliable, because this ratio does not suffer from such uncertainties. The sign of the coupling constant (and consequently also for the EFG's) is not determined experimentally, but high-temperature NMR data indicate opposite signs for the EFG at Li(1) and Li(2).

TABLE I. Electric field gradient Φ_{zz} in 10^{20} V m^{-2}.

Model for Φ_{zz}	Li(1)	Li(2)	Li(1)/Li(2)	N
Point charge	−20.37	9.01	2.26	0.33
Muffin-tin LAPW	−7.47	3.72	2.00	3.41
Present work	−6.94	3.41	2.04	11.16
Experiment	−5.87	2.88	2.04	13.04

Table I summarizes the EFG data, where we compare the results of the following: (i) the simple point charge model (assuming Li$^+$ and N^{3-}); (ii) the results of a muffin-tin (MT) LAPW calculation, where the EFG's can be obtained via the charge density according to the second formalism[9] [Eq. (4)]; (iii) the present results obtained from a GP-LAPW calculation using the second method again. The last results agree to within 1% with the direct calculation according to Eq. (2).

A very simple point charge model is not satisfactory. Since even the ratio Li(1) to Li(2) differs from experiment, a common Sternheimer factor for the two Li positions cannot bring these values in agreement with experiment. The MT results behave differently; they are already reasonably close to experiment for the Li sites, but the EFG at N is off by a factor of almost 4. The present GP-LAPW results are in good agreement as regards value and sign, i.e., they are perfect for the reliable ratio, while each EFG agrees to about 15% with experiment, which is the underlying accuracy of the Q values.

In Table II the present results are divided into the following three contributions to the EFG's: (i) from the atomic sphere around the nucleus for which the EFG is calculated [first term in (4)]; (ii) from the Fourier series [second term in (4)] corrected for the contribution to the multipole moments which is caused by extending the series into the atomic sphere; and (iii) from the multipole moments of all other sites excluding the correction above.

In Table II we notice a large compensation between the second and third term, so that the EFG is essen-

TABLE II. Contributions to the EFG, Φ_{zz}, in 10^{20} V m^{-2} obtained by the present GP-LAPW calculation.

Term	Li(1)	Li(2)	N
(1) inside sphere	−3.53	3.23	10.86
(2) Fourier-series	−10.32	7.63	2.43
(3) lattice sum	6.92	−7.45	−2.13
Total	−6.94	3.41	11.16
Li 1s band	0.08	0.17	0.001

tially determined by the first term. This observation holds true for Li(2) and N, but not for Li(1). This exception might be caused by the small sphere size of Li(1) which—as a consequence of the crystal structure—has only about half the volume of the Li(2) sphere. A similar analysis of the MT results have shown that the largest effect of the GP calculation occurs for the first term corresponding to the N sphere. This agrees with the observed stronger deviation from spherical symmetry in the GP difference density [Fig. 1(a)] in comparison with the MT result [Fig. 1(b)]. The last line of Table II shows that the contribution of the Li 1*s* band is almost negligibly small. Therefore the EFGs are determined by the N 2*s* and N 2*p* bands. This justifies the treatment of the N 1*s* states as atomic states which do not contribute to the EFG's.

We conclude that the present calculations have shown a new method for obtaining EFG's from first principles. It has provided excellent results for Li_3N where mainly the very local distortions of the electron density determine the EFG's. The contributions from the remaining sites largely compensate for the effect of the interstitial region. Therefore, in our approach the neighboring atoms act not so much directly (via multipole contributions), but rather affect the self-consistent charge density of, and consequently the EFG at, the central atom. The MT calculation can explain the EFG's at the Li positions, but it fails for the nitrogen site with its polarizable electron density. The new method, however, based on GP-LAPW calculations leads to excellent agreement with the experimental EFG's, which are very sensitive quantities. There might even be a possibility to obtain more accurate Q values from such calculations. There is a fair chance that this new scheme will prove as successful for other compounds (including metallic systems) as it has been for Li_3N.

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[1] M. H. Cohen and F. Reif, in *Solid State Physics: Advances in Research and Applications,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich, Vol. 5 (Academic, New York, 1957), p. 321.

[2] E. N. Kaufmann and R. J. Vianden, Rev. Mod. Phys. **51**, 161 (1979).

[3] A. C. Beri, T. Lee, T. P. Das, and R. M. Sternheimer, Phys. Rev. B **28**, 2335 (1983).

[4] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[5] D. D. Koelling and G. O. Arbman, J. Phys. F **5**, 2041 (1975).

[6] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).

[7] P. Blaha and K. Schwarz, Int. J. Quantum Chem. **23**, 1535 (1983).

[8] W. E. Rudge, Phys. Rev. **181**, 1020, 1024 (1969).

[9] P. Herzig, Theor. Chim. Acta (to be published).

[10] P. Blaha, J. Redinger, and K. Schwarz, Z. Phys. B **57**, 273 (1984).

[11] G. Kerker, Phys. Rev. B **23**, 6312 (1981).

[12] R. Dovesi, C. Pisani, F. Ricca, C. Roetti, and V. R. Saunders, Phys. Rev. B **30**, 972 (1984).

[13] H. Schulz and K. Schwarz, Acta Crystallogr. Sect. A **34**, 999 (1978).

[14] K. Schwarz and H. Schulz, Acta Crystallogr. Sect. A **34**, 994 (1978).

[15] P. Pattison, N. K. Hansen, and J. Schneider, Acta Crystallogr. Sect. B **40**, 38 (1984).

[16] J. Lewis and D. Schwarzenbach, Acta Crystallogr. Sect. A **37**, 507 (1981).

[17] K. Differt and R. Messer, J. Phys. C **13**, 717 (1980).

[18] D. Brinkman, W. Freudenreich, and J. Roos, Solid State Commun. **28**, 233 (1978).