On the Calculation of Electric Field Gradients in Layered Compounds

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An analytical formula is derived for the electric field gradient (EFG) of a thin slab with an arbitrary charge density in the x-y-plane without z-dispersion, based on its Fourier expansion. It turns out that the EFG is dominated by the leading Fourier-coefficients for thin slabs and reduces to a contact-term proportional to the charge density at the nucleus in the truly two-dimensional case. An extension to charge density distributions which are factorizable into a function $f(x, y)$ and $g(z)$ is given with an example for a Gaussian $g(z)$. The consequences for EFGs in layered compounds such as TaS_2 and $TaSe_2$ are discussed.

Key words: Electric Field Gradients; Layered Compounds.

1. Introduction

In 1957, Nijboer and de Wette [1] published a paper on the internal field in dipole lattices which formed the basis of a paper by de Wette in 1961 [2], where he described a model for the calculation of electric field gradients (EFG) in metals based on a point-ion and uniform background lattice, usually called the "point-charge-model". Hewitt and Taylor [3] modified this model to include an undulatory background in 1962. This de Wette-model was further refined by de Wette and Schacher [4] in 1965 for dipole lattices where the poorly converging sum over the point charges is broken up into a rapidly converging sum in real space using an auxiliary function and a rapidly converging sum in Fourier space. Common to all procedures was the plane-wise summation over slab-shaped regions. The quadrupolar polarizability of the core of the atom at the origin is accounted for by Sternheimer factors [5]. It should be pointed out that for fully ionic compounds only the point-charge-model should be adequate.

There are several problems with these models: first, the conduction electron background is certainly not uniform, and a Fourier-expansion of the real charge density, as required in the undulatory background model, is available only by ab-initio full-potential calculations; second, it is not clear whether Sternheimer factors calculated for isolated ions are applicable to solids, and it is thus better to include the core polarization effects in the ab-initio full-potential calculations; finally, with modern computers the slow convergence does not present a problem any more. Thus the point-charge models do not seem to be of particular use in understanding EFGs in solids, neither in metals nor in ionic compounds, at least if not fully ionic. Yet, there are cases where the point-charge model seems to yield quite realistic results, particularly when values for members of a family of compounds are compared with each other. It is not clear at present whether this happens by accident or not. The present paper addresses the question of EFGs in quasi-2-dimensions and gives an extension to the more realistic case of layered systems with finite extension into the third dimension under the assumption that the true charge density distribution can be factorized into a product of a function which depends on x, y and another function which depends on z only. Useful insight emerges from such simplified models concerning the question to what extent the charge density has to be known accurately in order to derive accurate EFGs for such systems. A short instructive discussion of the layered materials TaS_2 and $TaSe_2$ is given at the end.

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2. EFGs in quasi-two-dimensional Systems

Let the charge density – for the moment it may include the electronic charges from the core, the valence and conduction electrons (if conducting), as well as the nuclear charges, except that at the origin – be described by

$$n(x, y, z) = \sum_{\vec{k}\neq 0} n_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}\theta(\varepsilon - z)\theta(\varepsilon + z) \qquad (1)$$

$$\text{with } \vec{k} = (k_x, k_y) \text{ and } k_z = 0.$$

This means, we are dealing with a layer of thickness 2ε, and there is no z-dispersion because we are interested in the case ε close to zero only. We shall use cylinder coordinates throughout. Because of charge neutrality we exluded $\vec{k} = 0$. In order to guarantee that the charge density is real we require $n_k = n_{-k}$.

We start with the calculation of $V_{zz}(0)$. Sine-terms do not contribute to the EFG at the origin. In the following "GR∗.∗∗∗.∗" denotes an integral from the table of Gradshteyn and Ryzhyk [6].

$$V_{zz}(0) = \sum_{\vec{k}} n_{\vec{k}} \int_{-\varepsilon}^{+\varepsilon} \mathrm{d}\,z \int_{0}^{2\pi} \mathrm{d}\varphi \int_{0}^{\infty} \rho\,\mathrm{d}\,\rho \qquad (2)$$

$$\cdot \frac{2z^2 - \rho^2}{\left(z^2 + \rho^2\right)^{5/2}} \cos\rho(k_x\cos\varphi + k_y\sin\varphi)$$

$$= \sum_{\vec{k}} n_{\vec{k}} 2\pi \left\{ \int_{-\varepsilon}^{+\varepsilon} \mathrm{d}\,z \int_{0}^{\infty} \rho\,\mathrm{d}\,\rho \frac{2z^2 - \rho^2}{\left(z^2 + \rho^2\right)^{5/2}} \left(J_0(k\rho) - 1\right) \right.$$

$$\left. + \int_{-\varepsilon}^{+\varepsilon} \mathrm{d}\,z \int_{0}^{\infty} \rho\,\mathrm{d}\,\rho \frac{2z^2 - \rho^2}{\left(z^2 + \rho^2\right)^{5/2}} \right\}.$$

Here we have used GR3.937.2. In the second line we have written $J_0(kr) - 1$ in the first integral and corrected for this in the second integral. In this way the integrand of the first integral is finite even at $\rho = z = 0$ because J_0 decreases from unity at $k\rho = 0$ quadratically in the argument. The second integral is calculated in the traditional "cheese-hole" style: a spherical hole is cut around the origin with radius δ, and a circular disc with radius R is considered first. The constant charge density of such a sphere does not contribute to $V_{zz}(0)$ due to symmetry. In the limit of R going to infinity the integral then gives –4/3, independent of ε and δ. The z-integration of the first integral is carried out easily by noting that

$$\frac{\mathrm{d}}{\mathrm{d}\,z}\left[\frac{z}{\left(z^2 + \rho^2\right)^{3/2}} = -\frac{2z^2 - \rho^2}{\left(z^2 + \rho^2\right)^{5/2}}\right]. \qquad (3)$$

Hence, we obtain with GR6.565.4:

$$V_{zz}(0) = -4\pi \sum_{\vec{k}} n_{\vec{k}} \qquad (4)$$

$$\cdot \left(\int_{0}^{\infty} \rho\,\mathrm{d}\,\rho \left(J_0(k\rho) - 1\right) \frac{\varepsilon}{\left(\varepsilon^2 + \rho^2\right)^{3/2}} + \frac{2}{3} \right)$$

$$= -\frac{8\pi}{3} n(0) + 4\pi \sum_{\vec{k}} n_{\vec{k}}\left(1 - e^{\varepsilon}\right).$$

Here we have separated the "contact-term" $-8\pi n(0)/3$, with $n(0)$ being the sum over all $n_{\vec{k}}$. It arises from the fact that a uniform density of $n(0)$ has been subtracted from $n(x, y, z)$ in the integral of (4) in order to ensure a vanishing density at the origin. Note that $n(0)$ has to be added again. It does not mean that there is indeed a uniform density.

Instead of calculating $V_{xx}(0)$ and $V_{yy}(0)$ separately, we better calculate $V_{xx}(0) - V_{yy}(0)$ and use the fact that the EFG tensor is a traceless tensor. We have

$$V_{xx}(0) - V_{yy}(0) = \sum_{\vec{k}} n_{\vec{k}} \int_{-\varepsilon}^{+\varepsilon} \mathrm{d}\,z \int_{0}^{2\pi} \mathrm{d}\varphi \int_{0}^{\infty} \rho\,\mathrm{d}\,\rho \qquad (5)$$

$$\cdot \frac{\rho^2\cos^2\varphi}{\left(\rho^2 + z^2\right)^{5/2}} \cos\rho(k_x\cos\varphi + k_y\sin\varphi).$$

The "contact-terms" cancel and $[\rho^2(3x^2 - z^2] - [\rho^2(3y^2 - 1) - z^2]$ reduces to $3\rho^2\cos 2\phi$. Keeping in mind that the ϕ-integral vanishes for odd integrands, we arrive with the help of GR3.715.9 at

$$V_{xx}(0) - V_{yy}(0) = -6\pi \sum_{\vec{k}} n_{\vec{k}} \frac{k_x^2 - k_y^2}{k^2} \qquad (6)$$

$$\cdot \int_{-\varepsilon}^{+\varepsilon} \mathrm{d}\,z \int_{0}^{\infty} \rho\,\mathrm{d}\,\rho \frac{\rho^2}{\left(\rho^2 + z^2\right)^{5/2}} J_2(k\rho)$$

$$= -12\pi \sum_{\vec{k}} n_{\vec{k}} \frac{k_x^2 - k_y^2}{k^2} \int_0^{+\varepsilon} \mathrm{d}\, z \frac{k}{3} e^{-kz}$$

$$= -4\pi \sum_{\vec{k}} n_{\vec{k}} \frac{k_x^2 - k_y^2}{k^2} \left(e^{-\varepsilon k} - 1\right).$$

In the second step we used GR6.565.2, which is strictly valid only for $z > 0$. Since we have subtracted a constant contibution $n(0)$, and since the density starts at the origin quadratically with ρ, we can equally well replace the lower limit for the ρ-integral by an arbitrarily small $\delta > 0$. Note that the z-integrand is even in z, which is clearly visible before the ρ-integration is carried out. Hence we integrate from 0 to ε and multiply by 2. With the trace equal zero condition we finally get

$$V_{xx}(0) = \frac{4\pi}{3} n_0 - 4\pi \sum_{\vec{k}} n_{\vec{k}} \frac{k_x^2}{k^2} \left(1 - e^{-\varepsilon k}\right),$$

$$V_{yy}(0) = \frac{4\pi}{3} n_0 - 4\pi \sum_{\vec{k}} n_{\vec{k}} \frac{k_y^2}{k^2} \left(1 - e^{-\varepsilon k}\right). \quad (7)$$

It remains to calculate $V_{xy}(0)$. Instead of cos 2ϕ we now have sin 2ϕ in the integrand. With the help of GR3.715.9 and GR6.565.2 we arrive at

$$V_{xy}(0) = \sum_{\vec{k}} n_{\vec{k}} \int_{-\varepsilon}^{+\varepsilon} \mathrm{d}\, z \int_0^{2\pi} \mathrm{d}\, \varphi \int_0^{\infty} \rho \, \mathrm{d}\rho \rho^2 \frac{3 \cos\varphi \sin\varphi}{\left(\rho^2 + z^2\right)^{5/2}} \cdot \cos\rho\left(k_x \cos\phi + k_y \sin\phi\right)$$

$$= -4\pi \sum_{\vec{k}} n_{\vec{k}} \frac{k_x k_y}{k^2} \left(1 - e^{-\varepsilon k}\right). \quad (8)$$

These results are identical to those derived earlier by Fourier-techniques for a comb of identical slab-shaped layers in the limit of infinite interlayer spacing [7]. It is immediately clear that for infinitely small ε only the "contact-terms" survive as long as k remains finite, i. e. the details of the charge distribution are irrelevant. What matters is only the density at the nucleus, like in the case of the isomer shift in Mößbauer-spectroscopy. This might be a little surprising at first glance. For finite but small ε only the first terms in the Fourier-expansion (e. g. all symmetry-related leading terms) of the charge density are relevant. In other words, the anharmonicities in the charge density do not propagate into the EFG tensor provided the slab thickness is small enough.

So far for mathematics. Returning to physics, we have to discuss the charge density in more detail. First, by omitting the nuclear charge at the origin in the total charge density we have destroyed the periodicity of the lattice of nuclear charges. Second, including the nuclear charges in the charge density means that the largest $\vec{k}$-vectors which appear in the sum are in the order of $2\pi/r_n$, where r_n is the nuclear radius. It would be much better to exclude the nuclear charges altogether from the summation and to carry out a lattice sum over point charges with the nuclear charge Z. In two dimensions, the nuclei would be infinitely thin circular discs anyway, which produce an electric field like that of a point charge at large (atomic spacing) distances. Then it suffices to treat $\vec{k}$-vectors up to $2\pi/r_\mathrm{e}$ where r_e denotes the typical size of a core electron wave function. The total electronic charge would then be non-zero. This tantamounts to include $\vec{k} = 0$ in the summation. One could, of course, use positive ion cores (with assumed charges based on chemical valence) instead of bare nuclei in the point charge summation and introduce Sternheimer factors. Then we are back to the point-charge-plus-undulatory-background model of Hewitt and Taylor [3], but in two dimensions. Clearly, we are still far away from a physical situation because we cannot satisfy quantum mechanics with s, p, d etc. wavefunctions for the electrons in two dimensions. Hence, we require a simple extension to include the z-dimension.

3. EFGs in Layers

The simplest assumption would be a charge density which can be factorized into a function $f(x, y)$ and another function $g(z)$. A Gaussian exp($-0.5r^2/\sigma^2$) would just do the job. Hence, we assume for the following $g(z)$ to be Gaussian. To simplify matters, only $V_{zz}(0)$ will be calculated, i. e. we assume axial symmetry. The extension to the general case of non-axial symmetry is straightforward. First, we calculate the influence of a pair of identical slab-shaped layers separated by a distance $2c$ with the charge density as defined in (1) but **not** including the origin. In other words, we integrate from $c - \varepsilon$ to $c + \varepsilon$ instead of $-\varepsilon$ to $+\varepsilon$. The result is:

$$\begin{aligned} V_{zz}(0) &= -4\pi \sum_{\vec{k}} n_{\vec{k}} e^{-ck}\left(e^{-\varepsilon k} - e^{+\varepsilon k}\right) \\ &\approx 8\pi \sum_{\vec{k}} n_{\vec{k}} e^{-ck} \varepsilon k. \end{aligned} \tag{9}$$

Since we are interested in very thin slabs only, the $\sinh(\varepsilon k)$ is approximated by εk. Now we have to sum over all slabs – including the central slab containing the origin – weighted by the Gaussian $g(z)$:

$$\begin{aligned} V_{zz}(0) = 4\pi \Bigg\{ & \frac{n(0)}{3} \\ & + \sum_{\vec{k}} n_{\vec{k}} \Big(- e^{-\varepsilon k} \sum_{l} e^{-0.5(l\varepsilon/\sigma)^2} e^{-l\varepsilon k} \Big) \Bigg\} \\ \approx -\frac{8\pi}{3} n(0) & + 8\pi \sum_{\vec{k}} n_{\vec{k}} \varepsilon k \sum_{l} e^{-0.5(l\varepsilon/\sigma)^2} e^{-l\varepsilon k}. \end{aligned} \tag{10}$$

The second line is an approximation for small ε for the term from the central slab. Instead of carrying out the sum we carry out an integral, form the quadratic complement for the integrand and finally arrive at

$$\begin{aligned} V_{zz}(0) = & -\frac{8\pi}{3} n(0) \\ & + 8\pi \sum_{\vec{k}} n_{\vec{k}} k\sigma \sqrt{\frac{\pi}{2}} e^{k^2\sigma^2/2} \operatorname{erfc}\left(k\sigma/\sqrt{2}\right) \\ = & -\frac{8\pi}{3} n(0) \\ & + 8\pi \sum_{\vec{k}} n_{\vec{k}} \left(1 + \sum_{m=1}^{\infty} (-1)^m \frac{(2m-1)!!}{(k\sigma)^{2m}}\right). \end{aligned} \tag{11}$$

Here, we have made use of a series expansion of the complementary error-function. The double exclamation mark denotes the factorial of odd integers. This series shows that the terms decrease rapidly with the power $2m$ of the variable $k\sigma$, i. e. the size parameter of the Fourier-transformed $g(z)$. While σ is in the order of halve an interatomic spacing, k could go up to $2\pi/r_{\mathrm{e}}$ provided the sum over the nuclear charges is carried out separately (see above). For the nuclei, instead of point-charges with an infinite number of Fourier-coefficients of equal strength, non-overlapping spherically symmetric charge distributions can be considered, as has been pointed out by Bertaut, with a small number of Fourier-coefficients only [8]. Hence, again we note that even for the extension to the third dimension we require only the leading terms in the expansion of the charge density. This is, of course, a consequence of the fact that we assumed a charge density which is factorizable into $f(x, y)$ multiplied by a Gaussian $g(z)$, i. e. we assumed the **same** $f(x, y)$ in every slab.

4. Discussion and Comparison with Experiment

Such a situation should be a good approximation for a layer of identical atoms and possibly still be reasonable for such a layer "sandwiched" between two layers of atoms of another species, e. g. $\mathrm{TaS_2}$ and $\mathrm{TaSe_2}$. The fact that these layered compounds are built up from X-Ta-X sandwiches, each layer having hexagonal symmetry, repeated along the c-axis, should not matter: the contribution from adjacent sandwiches to the EFG is certainly negligible, not merely because of the larger distance but because this sandwich, being electrically neutral, produces but negligibly small electric fields outside the sandwich (cf. a parallel plate capacitor made of a grid instead of a plate and looked at from a distance large compared to the grid size). In this respect these compounds are nearly two-dimensional, not only because of their electronic and mechanical properties. There are Ta-Ta bonds (called metallic bonds if conducting) and partly covalent Ta-X bonds which should be different for trigonal prismatic (2H-modification) or trigonal antiprismatic (1T-modification, normally called octahedral) coordinated Ta. In order to convert our formulae for the EFG-tensor to SI-units we have to multiply them by $1/4\pi\varepsilon_0 = 8.986 \cdot 10^9$ Vm/As.

The experimental values for V_{zz} at Ta-sites in 2H-$\mathrm{TaS_2}$ and 2H-$\mathrm{TaSe_2}$ at 12 K, averaged over inequivalent Ta-sites due to charge density wave distortions, are –1.58 and –1.51 in units of 10^{22} V/m^2 [9] (the negative sign follows from Mößbauer-data and theory [10]). The corresponding values for the 1T-modification are –1.45 and –1.49 [9]. These numbers can be compared with a simple point-charge calculation assuming effective charges $Z_{\mathrm{Ta}} = +1$ and $Z_{\mathrm{S}} = -0.5$ [10], which gives values around –1.5 for all cases. Here, a Sternheimer factor of $1 - \gamma_{\mathrm{equiv}} = 62$ was used [11]. This might be a fortuitous agreement, and the choice of effective charges is somewhat arbitrary. However, the fact that the Ta-coordination plays a small role only (less than 10%) tells us that apparently the details of the charge density are not very relevant, a situation which is easily understood in the light of the above model. Similar arguments hold also for the mixed metal coordination polytypes $4H_b$ and 6R [9]. Moreover, it is striking that the metal-insulator transition in 1T-TaS2 around 200 K (where the charge density wave locks into a commensurate state) has but a small effect on the **average** EFG. The only significant change is a drastic reduction in the (linear) temperature dependence of the average EFG, indicating a stiffening of the lattice which was explained by interlayer-coupling / localization [9]. This means that the electron density at the nucleus is essentially the same, irrespective of the conductivity. In other words, out of **all** electronic states the ones at the Fermi-energy play little role. This might also be the reason for the observation that very little happens to the EFG when entering the superconducting state. It would be nice to see whether the average isomer shift at Ta-sites in $1T\text{-}TaS_2$ is affected at the metal-insulator transition, but thus far no Mößbauer-data are available for this system. Data are available for $1T\text{-}TaSe_2$ [12], but this system remains metallic at the lock-in temperature [9]. Contrary to Hewitt and Taylor [3], who separated the total charge into ion cores and conduction electrons and identified $n(0)$ with the **average conduction electron** density, $n(0)$ should be identified with the s-electron density of the ion core, with a possible further contribution by the conduction electrons. At present it is not clear whether the "contact-term" plays a leading role in quasi-two dimensional systems or wether the first higher terms of the Fourier-expansion of the charge density distribution are more relevant.

5. Summary

Summing up, the present model for layers or layered materials does not allow to calculate EFGs ab initio, rather the leading terms in the Fourier-expansion of the charge density have to be known in order to make use of the formulae. However, the important information is that for quasi-two-dimensional systems the details, i. e. the higher harmonics, of the charge density do not propagate into the calculation of the EFG.

Blaha [10] carried out ab-initio FLAPW calculations for $2H\text{-}TaS_2$. According to these calculations the main contribution to the EFG comes from the asymmetry counts of the p-p-contribution with an average r^{-3} expectation value of 110 a. u. It is this part of the charge density which should be contained in the leading terms of the Fourier-expansion. Further work will concentrate on more quantitative aspects of the EFG in this system, based on the Fourier-expansion of the calculated charge density for $2H\text{-}TaS_2$.

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Note added in proof

Since the "contact term" is dominated by the s-electron density at the nucleus – even for the lightest atoms and the more for the heavier ones – one should subtract from the total electron density at all atom positions at least the 1s-density (or maybe all spherically symmetric density) at the central nucleus before expanding in a Fourier series; otherwise too many Fourier coefficients are required to model this sharply peaked density. Because of spherical symmetry it would not contribute to the EFG anyway except via the neighbouring atom contributions which can be accounted for by a point charge lattice sum.

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