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1990 J. Phys.: Condens. Matter 2 149

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## Real-space method for calculation of the electric field gradient: comparison with $k$ -space results

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Received 24 April 1989, in final form 23 June 1989

**Abstract.** Results for the electric field gradient (EFG) in eight HCP metals are obtained using the linear muffin-tin orbital (LMTO) atomic sphere approximation (ASA) method and a recently proposed LMTO ASA recursion scheme. In all cases the  $k$ -space LMTO ASA results for the EFG agree well with those obtained using the real-space procedure and a first-order LMTO ASA tight-binding Hamiltonian with interactions limited to first neighbours. This is remarkable considering that the EFG is determined by differences between partial occupation numbers, which are of order of a hundredth of an electron and shows that the first-order Hamiltonian is very reliable. A comparison with more precise full-potential linear augmented plane-wave calculations and experimental values shows reasonably good agreement. This opens the way for predictions of the EFG in more complicated and disordered systems.

### 1. Introduction

The preceding paper (Petrilli and Frota-Pessôa 1990) has presented a method for calculation of the electric field gradient (EFG), based on the recursion method (Haydock 1980) and the linear muffin-tin orbital (LMTO) tight-binding (TB) formalism (Andersen and Jepsen 1984), which does not require symmetry and can be applied to amorphous materials. It was shown that the recursion method has enough precision to give meaningful results for the EFG. Reasonable results were obtained for the EFG of HCP Zr using a first-order approximation to the LMTO TB Hamiltonian and direct inversion for the structure constant  $\mathbf{S}$ . In this paper we investigate in a systematic manner whether this approach gives a useful description of the EFG. The usefulness of the LMTO TB recursion scheme hinges on two questions.

- (i) How well can the LMTO method, in the atomic sphere approximation (ASA) (Andersen 1975) for the potential, reproduce the EFG?
- (ii) What is the effect of the additional simplifications which make it possible to use the recursion method?

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As test cases, we have used the third- and fourth-row HCP metals with the exception of Co (which is magnetic). In this way we can compare the results with the thorough full-potential (FP) linear augmented plane-wave (LAPW) calculations of Blaha *et al* (1988) for the same materials.

The aim of the present work is to develop a scheme which lies between full-blown expensive calculations and simple unrealistic models based on Sternheimer factors (Kaufmann and Vianden 1979), but which is applicable to amorphous as well as crystalline systems. In the absence of a better scheme, the point-charge model, which is appropriate for non-metallic systems, is often used to interpret experimental results. However, it is evident from the results of Blaha *et al* (1988) that this approach is unsuitable for metals, where the lattice contribution is small. These LAPW results will be used here as a control to verify that the present real-space formalism is capable of giving the correct signs and order of magnitudes for the EFG in metals. It will also give a clear idea of the limitations of the method. Of course we do not expect to reproduce the accuracy of the FP LAPW calculations using a real-space formalism and a simple LMTO ASA TB Hamiltonian but, if the correct trends are well reproduced and the limitations well understood, the real-space formalism can be used to study the behaviour of the EFG in complex systems, for which very little is known and more exact methods are extremely costly or not applicable.

For later reference, we summarise the results of the FP LAPW calculations for the HCP metals. The EFG is determined almost completely by the charge distribution near the nucleus (*i.e.* lattice contributions of the type used in point-charge models are negligible). The EFG separates into p-p, d-d and s-d contributions according to the angular momentum character of the wavefunction close to nucleus. The s-d term is always very small. The p-p term dominates and is about three to five times larger than the d-d term even for transition metals. This can be traced to the larger amplitude of the p partial wave near the nucleus. However, there is a relevant cancellation of p-p and d-d terms in some cases. Finally, it was found that core and semi-core states make only small contributions.

Since the EFG is mainly determined by the shape of the charge density near the nucleus, it makes sense to explore the possibility of deriving the EFG from LMTO ASA calculations. For these, the output charge density near the nucleus (including non-spherical terms) is quite accurate even if a spherically symmetric input potential is used (Andersen *et al* 1986). In § 2 we present a detailed analysis of the problem for HCP Zr. Section 3 presents results for other HCP metals. Conclusions are presented in § 4.

## 2. Computational details and results for Zr

To calculate the EFG for a given crystalline structure, two approaches are possible. In the first approach, a self-consistent band-structure calculation is done to obtain the electronic charge density. By solving the Poisson equation for the total (electronic plus nuclear plus core) density, the electrostatic potential is obtained. The leading terms of the  $l = 2$  components of this potential near the nucleus determine the EFG. In general, a  $3 \times 3$  matrix must be diagonalised to obtain the  $zz$  component  $V_{zz}$  of the field gradient tensor. For systems with axial symmetry (such as HCP) it is enough to consider the leading term of the (2.0) component of the electrostatic potential:

$$V_{zz} = A \lim_{r \rightarrow 0} \frac{V_{20}(r)}{r^2} = A \frac{8\pi}{5} \int Y_{20}(\hat{r}) \rho(r) \frac{1}{r^3} dr \quad (1)$$

where the integral runs over all space excluding the nucleus in question,  $\rho(r)$  is the total

charge density,  $V_{20}$  is the radial part of the  $(l, m) = (2, 0)$  component of the electrostatic potential felt by the nucleus, and  $A$  is a constant. (We use atomic units so that the Poisson equation is  $\nabla^2 V = -8\pi\rho$ .) This procedure was followed by Blaha *et al* (1988) using the FPLAPW method to generate the charge density. To do the same in the LMTO ASA method, we exploit the fact that, to a good approximation, the integral can be replaced by an integral over a reasonably large sphere around the nucleus. This is another statement of the fact that lattice contributions do not matter for the HCP metals. The wavefunction  $\psi$  is expressed as a one-centre expansion around the nucleus and  $\rho = |\psi|^2$  is evaluated. The decomposition of the EFG into p-p, d-d and s-d terms results from selection rules for the Clebsch-Gordan coefficients which enter in this step. The EFG contributions depend only weakly on the sphere radius, so that our results (obtained for Wigner-Seitz spheres) can be compared directly with those of Blaha *et al* (for muffin-tin spheres). The only modification to a standard LMTO ASA needed for this procedure is to accumulate the full non-spherical output charge density. Finally, one can try to improve the LMTO ASA results by including combined corrections (CCs). Without CCs the integrals entering the Hamiltonian and overlap matrices are approximated by integrals over atomic spheres. If CCs are included, the integrals are evaluated for the correct Wigner-Seitz cell, albeit for a potential defined differently in the overlap and interstitial regions. The effect of CCs is to shift the energies of the bands slightly, which leads to changes in the asymmetry of the occupation numbers. These changes may be important in EFG calculations.

The second way to obtain the EFG, presented in the companion paper (Petrilli and Frota-Pessôa 1990), is suitable for the TB schemes. The procedure can be applied to any lattice but, if the system has axial symmetry, the p-p and d-d contributions can be obtained from a simple weighted sum of the partial occupancies of the p or d states, multiplied by a structure-independent radial integral of the corresponding basis function. As was shown in the companion paper, the contributions are of the form

$$V_{zz}^{pp} = C \frac{1}{5} I_{pp} (\frac{1}{2} N_x + \frac{1}{2} N_y - N_z) \quad (2)$$

$$V_{zz}^{dd} = C \frac{1}{7} I_{dd} (N_{x^2-y^2} + N_{xy} - \frac{1}{2} N_{xz} - \frac{1}{2} N_{yz} - N_{3z^2-r^2}) \quad I_{ll} = \int_0^R \frac{\varphi_l^2}{r^3} r^2 dr.$$

As in the previous paper,  $N_x$  and similar terms are occupation numbers and the quantities in the parentheses will be denoted as the *charge asymmetries*  $\Delta N_p$  and  $\Delta N_d$ . To obtain  $V_{zz}$  in  $10^{13}$  esu  $\text{cm}^{-3}$ , with the  $I_{ll}$  given in table 4 later, the constant  $C$  should be taken as 1296. The occupancies are obtained by filling the calculated partial densities of states (DOSS) up to the Fermi level and the integrals of the radial functions are calculated for the first-order LMTO ASA TB basis.

To see whether the LMTO method can predict field gradients and to monitor the effect of the approximations leading to the LMTO TB recursion scheme, we have performed four calculations for the EFG of Zr with different degrees of accuracy. In order of increasing degree of approximation, the procedures are as follows: procedure (a), LMTO ASA in  $k$ -space using an spd basis with CCs included; procedure (b), the same without CCs; procedure (c), first-order LMTO TB Hamiltonian in  $k$ -space with LMTO TB structure constant  $\mathbf{S}$  obtained by direct matrix inversion (see companion paper); procedure (d), the same Hamiltonian in connection with the recursion method. For procedures (a) and (b), the EFG was obtained from the full output charge density as described above. Hereby the one-centre expansion of the wavefunction was truncated at  $l = 2$ . With CCs included, the standard practice of renormalising the wavefunction was not followed when determining the charge density, since this treats the density near the nucleus more correctly.

**Table 1.** Comparison of calculated EFGs for Zr for different approximations to the Hamiltonian. FPLAPW refers to the results of Blaha *et al* (1988). The total EFG includes the s-d terms and (for the LAPW calculation) the lattice and semi-core contributions. The experimental value is  $123 \times 10^{13}$  esu  $\text{cm}^{-3}$ .

		EFG ( $10^{13}$ esu $\text{cm}^{-3}$ )				
	FPLAPW	LMTO + CCS (a)	LMTO ASA (b)	LMTO TB, <i>k</i> -space, (c)	LMTO TB, recursion, (d)	
Total	143	160	90	69	78	
p-p	123	124	60	49	62	
d-d	32	36	31	20	16	

For procedures (c) and (d), the EFG was evaluated using the partial charges and radial integrals. Procedure (d) is the method which can be applied to amorphous systems. For Zr as well as the other HCP metals, a standard self-consistent LMTO ASA potential was used as input. The present calculations are non-relativistic, since we have found that relativistic effects have a small influence on the EFG for the metals considered in this paper. The same potential was used for all four procedures (a)–(d). For the *k*-space results, 484 *k*-points in the irreducible part were used for Brillouin zone integrations. In all our calculations, semi-core and lattice contributions were neglected. For procedures (c) and (d) the same first-order LMTO TB nearest-neighbour Hamiltonian was used. As was described in the preceding paper, this two-centre LMTO TB Hamiltonian can be written in terms of the TB structure constant  $\mathbf{S}$  and potential parameters  $\mathbf{C}$  and  $\mathbf{\Delta}$ . In the present calculations we have generated  $\mathbf{C}$  and  $\mathbf{\Delta}$  from the standard potential parameters *C*, *Q* and  $\Delta$  associated with the self-consistent ASA potential of procedures (a) and (b). We note that these parameters are slightly different from those tabulated in the literature, which were used in the companion paper. The structure constant matrix  $\mathbf{S}$  was obtained by direct inversion using clusters of 19 atoms. The real-space calculation of procedure (d) was performed on a cylindrical cluster of 1249 atoms and a cut-off parameter  $LL = 20$  was used for the recursion chain. As in the preceding paper, the terminator used by Beer and Pettifor (1984) was employed to obtain the density of states.

Using the FPLAPW results as benchmarks, the following sources of error are possible as one goes from procedure (a) to (d). Firstly, all our calculations use an ASA potential as opposed to the FP used by Blaha *et al*. This explains the error in procedure (a). Secondly, by comparing procedures (a) and (b) we see the effect of ignoring the CCS, thereby going over to a less sophisticated description of the crystal potential. Thirdly, procedure (c) has transformed the Hamiltonian to the LMTO TB representation (which is an exact transformation) but has then taken only the first-order terms and has truncated to nearest-neighbour interactions. Finally, procedure (d) has used the same Hamiltonian in the recursion method. This causes errors due to finite cluster size, surface effects and choice of terminator.

From table 1, it can be seen that the error caused by the ASA potential is very small. This is unexpected, since the EFG depends very sensitively on the charge distribution. On the other hand, the CCS are important for obtaining good agreement; without them, the results are halved. As will be seen in § 3, this situation is typical for HCP metals near

**Table 2.** Calculated partial charges and charge asymmetries for Zr for procedures (a)–(d). For procedure (a), there is a small interstitial charge which is not tabulated.

	LMTO + CCS, (a)	LMTO ASA, (b)	LMTO TB, <i>k</i> -space, (c)	LMTO TB, recursion, (d)
<i>s</i>	0.675	0.681	0.739	0.730
<i>x, y</i>	0.225	0.232	0.221	0.223
<i>z</i>	0.191	0.215	0.208	0.206
<i>xy, x<sup>2</sup> – y<sup>2</sup></i>	0.593	0.559	0.548	0.546
<i>xz, yz</i>	0.472	0.475	0.481	0.482
<i>3z<sup>2</sup> – r<sup>2</sup></i>	0.575	0.572	0.553	0.562
$\Delta N_p$	0.034	0.016	0.013	0.017
$\Delta N_d$	0.138	0.071	0.061	0.049

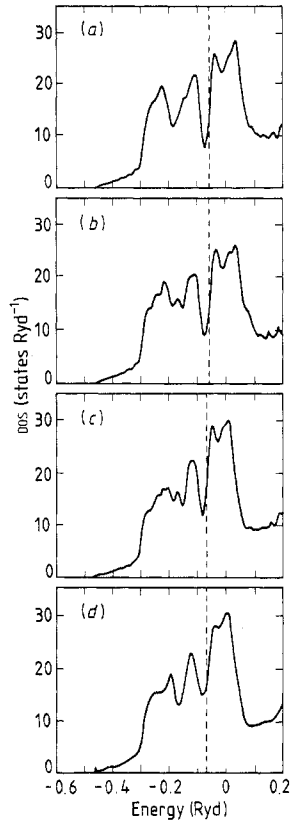
the beginning of the transition series. The effect of the various approximations is most clearly seen from the partial charges in the ASA spheres shown in table 2. One sees that the charge asymmetries  $\Delta N_p$  and  $\Delta N_d$  which determine the EFG are very small quantities. Thus the sensitivity to *details* such as the CCS is understandable. We have also calculated the charges for the muffin-tin radius used by Blaha (1988) for procedure (a) and have found good agreement with his values. This fact, together with table 2, clearly shows that the most drastic step is to ignore the CCS, which changes the partial charges by up to 0.03 electrons.

The most interesting result from tables 1 and 2 is that going over to the nearest-neighbour first-order Hamiltonian (procedure (c)) and use of the recursion method (procedure (d)) lead to errors which are small. Thus, it is adequate to work with a simple short-range Hamiltonian and a unit-matrix overlap. The success of the recursion method in this context arises because the partial charges are integrated quantities, which are known to be easily calculated. Errors in the partial charges for the p and d channels introduced by the recursion method are of the order of millielectrons. This gives a measure for the numerical noise which can be expected in the present scheme.

The conclusions presented above are confirmed by the DOSS for the four cases shown in figure 1. There is quite a large difference between the DOSS for procedures (a) and (b), showing that the CCS are of importance. The DOSS for procedures (b), (c) and (d) are very similar. The most noticeable effect is that the peak to the right of the Fermi energy is slightly higher and narrower for procedures (c) and (d). These cases use the first-order Hamiltonian, which is known to compress the DOS at energies which lie high above the range of interest (Andersen *et al* 1985).

We note that equation (2) expressing the EFG using the charge asymmetries and radial integrals can also be used for procedures (a) and (b), giving, for example,  $125 \times 10^{13}$  esu cm<sup>-3</sup> and  $46 \times 10^{13}$  esu cm<sup>-3</sup> for the p–p and d–d contributions for procedure (a). The fact that this works is clear because the partial charges from the standard and first-order LMTO TB method agree to first order in energy. Thus, to a good approximation there is in fact a proportionality between  $\Delta N_p$ ,  $\Delta N_d$  and the EFG contributions even without explicit use of the TB representation.

Finally we compare the results obtained here for Zr with those in the preceding paper, where the Varena parameters (Andersen *et al* 1985) were used to build the



**Figure 1.** Total DOS for Zr calculated using (a) procedure (a), (b) procedure (b), (c) procedure (c) and (d) procedure (d).

Hamiltonian. The Varena parameters were generated by scalar relativistic LMTO ASA calculations using a basis which included f electrons. These have been tabulated by Andersen *et al* (1985) for all transition metals. The non-relativistic calculations of procedure (b) do not include f electrons. The different approaches used to obtain the potential parameters account for the differences between the results for the EFG of Zr in the two papers. A comparison between the two results shows that the EFG is not very sensitive to the choice of potential parameters.

On the other hand, at least for HCP metals, the results for the EFG are very sensitive to the choice of the structure constant  $\mathbf{S}$ . If the approximate interpolation formula is used (Andersen and Jepsen 1984), an EFG for Zr which is much smaller and has the wrong sign is found. We note that the use of the interpolation formula leads to a Hamiltonian which is quite accurate and is adequate if we wish, for example, to obtain the main features of the DOS in an amorphous alloy. It is only because of the sensitive dependence of the EFG on the partial charges that a more exact treatment is needed here.

### 3. Results for third- and fourth-row HCP metals

In order to determine whether the conclusions of the last section are valid more generally, we have done similar calculations for all third- and fourth-row HCP metals except Co.

**Table 3.** Experimental and theoretical EFGs for eight third- and fourth-row HCP metals. For each element the top entry indicates the total EFG, followed by the corresponding p-p and d-d contributions. In the first column the atomic number and the experimental  $c/a$  ratio which was used in the calculations, are also shown.

		EFG ( $10^{13}$ esu $\text{cm}^{-3}$ )			
	Experimental	FP LAPW	ASA + CCS	ASA	Recursion
Sc	$\pm 13$	32	31	17	25
21		40	35	25	33
1.59		-5	-4	-8	-8
Y	—	93	95	45	40
39		106	100	58	54
1.57		-11	-4	-13	-14
Ti	$\pm 54$	69	85	46	34
22		48	50	19	23
1.59		33	36	27	12
Zr	$\pm 123$	143	160	90	78
40		123	124	60	62
1.59		32	36	31	16
Tc	$\pm 23$	-49	-25	-69	-70
43		-70	-39	-82	-76
1.60		14	14	14	6
Ru	-32	-41	-1	-29	-63
44		-75	-45	-102	-115
1.59		22	45	74	52
Zn	+120	125	95	161	180
30		177	100	197	200
1.86		-32	-7	-38	-20
Cd	+230	284	193	346	272
48		322	178	370	342
1.89		-39	13	-25	-70

Table 3 presents experimental and theoretical EFGs for the HCP metals that we have considered. The materials were sorted by d-band occupancy. The last three columns correspond to procedures (a), (b) and (d) in § 2. Details of the procedure were the same as for Zr. We see that the agreement of the ASA + CCS calculation to the FP LAPW result is very good for Sc, Y, Ti and Zr, but only reasonable for the other four metals. (We point out that, even for the worst case, Ru, the p-p and d-d contributions are correct to within a factor of 2.) Evidently the error caused by the spherical potential approximation correlates with the number of valence electrons. A possible explanation is that the magnitude of the non-spherical terms in the FP calculation is proportional to the number of valence electrons available. These can be either p or d electrons, since both couple to the non-spherical d terms in the potential. Therefore the ASA is a less drastic potential approximation at the beginning of the transition series. This correlation between the number of valence electrons and the importance of the FP should be transferable to other structures such as amorphous systems.



Next, the effect of the CCS is considered. The inclusion of the CCS shifts the energies of the bands slightly and leads to changes in the asymmetry of the occupation numbers as was seen for Zr. The sensitivity to the CCS is influenced to a large extent by how well the Wigner–Seitz sphere approximates the Wigner–Seitz cell. For the HCP metals, this is directly coupled to the  $c/a$  ratio. Table 3 shows that there is indeed a clear correlation between  $c/a$  and the effect of the removal the CCS; for  $c/a$  near 1.6, the EFG becomes more negative while, for  $c/a$  near 1.9, the EFG increases. In both cases the results change by a factor which lies somewhere between 0.5 and 2.

From the preceding, it seems as if the CCS were necessary to obtain accurate results for the HCP metals near the beginning of the transition series, while a FP calculation is needed for the other four metals. However, table 3 shows that, in terms of overall agreement, the ASA without CCS does quite well. While the EFG for Sc, Y, Ti and Zr are too small by a factor of 2, the results for Tc, Ru, Zn and Cd are somewhat better than for ASA + CCS. This is especially clear if the p–p and d–d contributions are considered separately. We note that the LMTO ASA with and without CCS are approximations for the potential which have different shapes. It is conceivable that, through a cancellation of terms, the straightforward ASA is better suited to some cases. This is convenient in the present context since it is much easier to implement the LMTO TB method using recursion if the CCS are not included.

Now we consider the last two approximations leading to the LMTO TB recursion method: substitution by the first-order nearest-neighbour Hamiltonian and use of the recursion method to obtain the partial charges. From the last two columns in table 3, it is seen that these steps introduce small errors compared with the potential approximation. We note that the EFGs obtained from the recursion calculations agree quite well with the LAPW results and with the experimental values. The signs for the total and the partial p–p and d–d EFGs are correct and the magnitudes are incorrect by a factor of no more than 2 in all cases. The trends are well represented and, considering the subtle nature of the EFG, these results are encouraging.

Finally, we have also performed calculations based on the Varenna parameters for all the HCP metals considered here with the exception of Cd and Zn (which were not tabulated by Andersen *et al* (1985)). In all cases, the agreement with the recursion calculations in table 3 is good, both results having the same sign and differing by no more than 20%. Thus, again it seems that the results do not depend sensitively on the input potential parameters. This indicates that reasonable results for other more complicated structures might be obtained from transferable *frozen* potential parameters without iteration to self-consistency. The only other atomic properties then needed are the radial integrals  $I_{ll}$  of equation (2). For completeness, we list these in table 4..

#### 4. Summary and conclusions

The aim of this paper is to find a prescription for constructing the Hamiltonian to use in the recently proposed LMTO TB recursion scheme for the calculation of the EFG in metals. As typical test cases, eight third- and fourth-row HCP metals were considered. Results from  $k$ -space calculations for three different LMTO Hamiltonians and of the recursion method were compared with those of the thorough FP LAPW calculation of Blaha *et al*. In this way, the effects of various approximations to the Hamiltonian could be studied. It turned out that the LMTO ASA calculation with CCS included did very well for transition

**Table 4.** Radial integrals of equation (2) for eight HCP transition metals.

	$I_{pp}$ ( $\text{au}^{-3}$ )	$I_{dd}$ ( $\text{au}^{-3}$ )
Sc	4.79	0.85
Y	9.35	1.13
Ti	6.99	1.39
Zr	14.20	1.81
Tc	20.95	4.19
Ru	20.76	5.17
Zn	5.38	9.57
Cd	8.48	10.39

metals with only a few d electrons but gave only reasonable results for larger d occupations. The LMTO ASA without CCS (which is better suited to use with the recursion method) gave quite good overall agreement with the expensive FP-LAPW results; all signs were predicted correctly, and magnitudes were correct to within a factor of 2. It was found that, by going over to the nearest-neighbour LMTO TB Hamiltonian, only small errors are introduced if the TB structure constants are calculated by direct inversion. However, if the approximate interpolation formula is used instead, the Hamiltonian is not exact enough in the context of the EFG. Finally, it was found that the results were not very sensitive to the potential parameters. This is rather important if we want to apply the method developed here to more complex systems. Given the position of the atoms, the structure constants can be calculated with arbitrary precision for any given system. On the other hand, to obtain exact self-consistent parameters, we would need a convergent calculation, which is exactly what we are trying to avoid. The insensitivity of the results to the potential parameters allows us to use unrelaxed parameters (such as those tabulated in the literature) when applying the real-space method to complex systems. In conclusion, the LMTO TB recursion scheme gives encouraging results for the eight HCP metals that we have considered, indicating that the method should be useful for investigations on more complicated systems.

### Acknowledgments

We wish to thank O K Andersen for useful discussion and M van Schilfgarde for assistance with the LMTO TB structure constants. This work was made possible by funding from the Max-Planck Society and by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

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