Real-space method for calculation of the electric field gradient in systems without symmetry

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Abstract. In this paper we present a new scheme for obtaining the electronic contribution to the electric field gradient at the nucleus in systems which are well represented by a tight-binding Hamiltonian. We show that for close-packed metallic systems the linear muffin-tin orbital method in the recently developed tight-binding representation provides a realistic tight-binding Hamiltonian which can be used in this context.

The scheme is based on the recursion method and can be applied to systems without symmetry such as amorphous metals, where k-space methods cannot be used.

Test calculations were done for HCP Zr with the z axis of the coordinate system taken along the c axis of the crystal and also along an arbitrary direction. The results are independent of the choice of the system, showing that the procedure works in absence of symmetry. When compared with the experimental results for HCP Zr, our calculations give the correct sign and a reasonable value for the magnitude. Considering the approximations made when obtaining the Hamiltonian and the subtlety of the effect, the results are very encouraging.

In the following paper, other HCP metals are studied. A comparison between real-space and k-space calculations in these metals gives a good idea of the advantages and limitations of the proposed real-space scheme.

1. Introduction

Lately there has been great interest in the behaviour of the electric field gradient (EFG) at the nucleus in non-periodic systems due to the local character of this information. A large number of experiments have been performed to study the EFG in transition-metal alloys including amorphous systems in order to obtain clues about the local environment and chemical ordering.

On the other hand, theoretical understanding of the EFG in transition metals has been slow and only recently have reliable calculations of these quantities, even for simple periodic systems, become available (Blaha *et al* 1988). For non-periodic systems, the situation is much worse. There is a good description of the so-called lattice contribution to the EFG based on a point-charge model (Cjzek *et al* 1981), which is often used to interpret the experiments (Michaelsen *et al* 1986, Aubertin *et al* 1985). However, in transition-metal alloys the lattice contribution is small and the EFG is dominated by the contribution of the valence electrons close to the nucleus, which is totally ignored in the point-charge model (Das and Schmidt 1986). To understand the behaviour of the EFG, we need a good description of the electronic structure and, even though progress has

been made (Guenzburger and Ellis 1987), for non-periodic systems this is no simple task. Only recently, within a very simple model and with the help of supercells, have such calculations been attempted in amorphous metals (Levy Yeyati *et al* 1988).

In this paper we develop a scheme which allows us to obtain the EFG by means of a real-space procedure which requires no translational symmetry. A similar real-space calculation, with a much simpler Hamiltonian which included only the non-dominant d contributions, was used before to estimate the EFG of an Fe impurity in HCP Zr (Petrilli and Frota-Pessôa 1985). In this previous calculation, we used symmetry to guarantee that the EFG was given by a diagonal matrix and to avoid the calculation of the more difficult off-diagonal terms. Here, in § 2, we generalise the real-space recursion scheme to include s and p orbitals and to calculate the full EFG tensor. This scheme, implemented in real space, can be used in the absence of symmetry to obtain the EFG for any system which is well described by a tight-binding Hamiltonian. In addition, we show in § 3 how the procedure can be used in connection with the linear muffin-tin orbital (LMTO) method in the tight-binding representation (Andersen and Jepsen 1984, Andersen *et al* 1985). This representation provides the framework for calculations of the electronic structure of non-periodic systems, based on a realistic tight-binding Hamiltonian. We also discuss the approximations that were made when obtaining the Hamiltonian used in the present calculations. Finally in § 4 we present our conclusions.

2. The electric field gradient tensor

The EFG at the nuclei is given in terms of the electronic wavefunctions ψ_E and the electrostatic potential $V(r)$ as a tensor V_{ij} given by (Amaral *et al* 1984):

$$V_{ij} = 2 \int^{E_F} \left\langle \psi_E \left| \frac{\partial^2 V(r)}{\partial x_i \, \partial x_j} \right| \psi_E \right\rangle dE \tag{1}$$

where $x_i = x, y, z$ and E_F is the Fermi energy.

The tensor V_{ij} is traceless and symmetric and has in general only five independent components. We can always reduce the tensor to a diagonal form by chosing coordinate axes along the principal axes. In that case we have three non-zero components V_{zz}, V_{xx} and V_{yy} but, since the tensor is traceless, only two of them are independent. It is standard in the literature to define the z axis along the direction of maximum EFG so that, when the tensor is written in terms of the principal axes, V_{zz} is chosen as the component with the largest absolute value.

In a system with axial symmetry the direction of maximum EFG coincides with the symmetry axis. If we choose the z axis along this direction, the V_{ij} tensor is diagonal. In amorphous metals and other non-symmetric systems the direction of maximum EFG varies from site to site. The V_{ij} tensor for each site is in general non-diagonal and the choice of the local principal axes is done through tensor diagonalisation. Therefore, if we define V_{zz} by chosing the z axis along the direction of maximum EFG, this choice will be local and the direction of z will vary from one nucleus to the other.

In a previous paper (Petrilli and Frota-Pessôa 1985) we have developed a scheme based on the recursion method (Haydock 1980) which allows us to obtain the EFG in systems with axial symmetry for which the V_{ij} tensor is diagonal for the natural choice of coordinates.

In this section we generalise the procedure to obtain the EFG to the case where the V_{ij} tensor may be non-diagonal for the given coordinate system.

As before (Petrilli and Frota-Pessôa 1985), we use the tight-binding approach and expand the wavefunction $|\psi_E\rangle$ in terms of a set of local energy-independent basis functions $|\varphi_{m,R}\rangle$, where R is a vector indicating the position of the site and m indicates the orbital. Then we have

$$|\psi_E\rangle = \sum_R \sum_{m=1}^{9} a_{m,R}(E)|\varphi_{m,R}\rangle. \tag{2}$$

Here we take nine (s, p and d) orbitals for each site, the functions $|\varphi_{m,R}\rangle$ are chosen to be real and the nine orbitals are designated by $s, x, y, z, xy, xz, yz, x^2 - y^2$ and $3z^2 - r^2$. When this set of basis functions is used, the Hamiltonian matrix in real space is symmetric because its matrix elements are real. Therefore the coefficients $a_{m,R}(E)$ are eigenvectors of a symmetric matrix and can be taken to be real.

To obtain the tensor V_{ij} at a given site R, we neglect, as we have done previously (Petrilli and Frota-Pessôa 1985), the contributions from local orbitals with index $R' \neq R$, which should be small. This assumption was confirmed by recent linear augmented plane-wave (LAPW) calculations (Blaha *et al* 1988). Neglecting these terms, we write

$$V_{ij} = 2 \sum_{m=1}^{9} \sum_{m'=1}^{9} n_{m,m'} \left\langle \varphi_{m,R} \left| \frac{\partial^2 V(r)}{\partial x_i \, \partial x_j} \right| \varphi_{m',R} \right\rangle \tag{3}$$

where

$$n_{m,m'} = \int^{E_F} a_{m,R}^*(E) a_{m',R}(E) \, dE. \tag{4}$$

From here on we drop the index R indicating the site, which is always the one being considered and use only one index in $n_{m,m'}$ whenever the two orbital indices happen to be equal. In the Appendix we show the expressions obtained for the six components of V_{ij} using the above notation. The integrals I_{pp} and I_{dd} associated with the p and d contributions to the EFG are given by the averaged value of r^{-3} with respect to the normalised radial part of the p and d basis functions respectively. The integral I_{sd} is similar but involves the integral over all space of r^{-3} multiplied by the product of the radial parts of s and d basis functions. As we shall see, the p contribution is dominant and depends on the value of I_{pp} given explicitly by

$$I_{pp} = \int_0^\infty \frac{|\varphi_p(r)|^2 \, dr}{r}. \tag{5}$$

As I_{pp}, I_{dd} and I_{sd} are related to the average value of the radial part of the tensor V_{ij}, the fractions multiplying the several $n_{m,m'}$ in the expressions of V_{ij} are results of the average over the respective angular parts.

The integrals for the radial parts are not difficult to evaluate. Therefore the values of V_{ij} depend essentially on $n_{m,m'}$ which are related to the coefficients $a_m(E)$. To obtain these values, we have to know the electronic structure for the system in question, and depending on the object of study this may not be an easy task.

To obtain $n_{m,m'}$, we may use the recursion method (Haydock 1980). As we have shown before (Petrilli and Frota-Pessôa 1985), when $m = m'$, n_m is given directly by the occupation number per spin associated with the local orbital m:

$$n_m = \int^{E_F} |a_m(E)|^2 \, dE = \int^{E_F} \rho_m(E) \, dE. \tag{6}$$

Here $\rho_m(E)$ is the local density of states per spin, projected on the orbital m, which

Table 1. Values of the elements of the EFG tensor for the p, d and s–d contributions in the rotated case, before diagonalisation.

	V_{xx} (10^{13} esu cm^{-3})	V_{yy} (10^{13} esu cm^{-3})	V_{zz} (10^{13} esu cm^{-3})	V_{xy} (10^{13} esu cm^{-3})	V_{xz} (10^{13} esu cm^{-3})	V_{yz} (10^{13} esu cm^{-3})
p	−7.22	−27.07	34.29	0.0	36.01	0.0
d	−1.90	−7.87	9.77	0.0	9.62	0.0
s–d	0.0224	0.0857	−0.1081	0.0	−0.1113	0.0

can be obtained from the diagonal element of the Green function using the standard recursion procedure.

To obtain $n_{m,m'}$, we need the off-diagonal terms of the Green function, which can be calculated using the slightly more complicated procedure (Haydock 1980), described below. We perform two different recursion calculations, one taking as the starting orbital $|u_{m+m'}\rangle$ and the other $|u_{m-m'}\rangle$. These initial orbitals are defined in terms of the original local basis as

$$|u_{m \pm m'}\rangle = (1/2^{1/2})(|\varphi_m\rangle \pm |\varphi_{m'}\rangle). \qquad (7)$$

These calculations give $\rho_{m+m'}(E)$ and $\rho_{m-m'}(E)$, the local densities of states associated with the orbitals $|u_{m \pm m'}\rangle$. If we compare the expansions of $|u_{m \pm m'}\rangle$ as basis functions, we obtain a relation between the expansion coefficients which gives us $n_{m,m'}$ as

$$n_{m,m'} = \frac{1}{2} \int^{E_F} [\rho_{m+m'}(E) - \rho_{m-m'}(E)] \, dE \qquad m \neq m'. \qquad (8)$$

As we have values for $n_{m,m'}$ the expressions in the Appendix can be used to obtain the EFG tensor in the general case of systems which lack symmetry.

We have used the procedure described above to evaluate the EFG of Zr. To perform the calculations, we have chosen an atom at the centre of a cylindrical cluster of radius R and height h, containing 1249 atoms distributed on a HCP array with the experimental lattice parameters $a = 3.23$ Å and $c/a = 1.59$. To maximise the distance from the central atom to the surface for a given number of atoms, we have used $h \simeq 2R$. If we chose the z axis along the c axis of the HCP lattice, V_{ij} will be a diagonal tensor and the EFG can be easily obtained (Petrilli and Frota-Pessôa 1985). However, here we wish to illustrate a more general procedure, which can be applied in absence of symmetry to calculate a general non-diagonal V_{ij}. So we have chosen a second coordinate system for which the z axis makes an angle of 30° with the c axis. In this coordinate system the axial symmetry is broken and the tensor is non-diagonal. Of course the direction of maximum EFG should still be along the c axis, and this will be a further test for our results.

To parametrise our real-space Hamiltonian, we have used the LMTO atomic sphere approximation (ASA) tight-binding formalism (Andersen and Jepsen 1984, Andersen et al 1985) to first order as described in the next section. We note that this formalism can also be applied to treat non-periodic binary alloys (Frota-Pessôa 1987, Fujiwara 1984).

We obtain the tensor V_{ij} at the site of the central Zr atom by using the recursion method and the procedure described before, which allows us to obtain $n_{m,m'}$ for every pair of orbitals at the site. Because the tensor is symmetric, it is completely characterised by six components. In table 1 we show these components for the p, d and s–d contributions, before diagonalisation. We then diagonalise the tensor and identify the largest

Table 2. Values of the d, p and s–d contributions and of the total electronic contribution to the EFG for a HCP Zr lattice for a coordinate system whose z axis is parallel to the c axis and for another system where the z axis is rotated by 30°. The full-potential LAPW results of Blaha *et al* are also shown for comparison.

	d–d contribution (10^{13} esu cm^{-3})	p–p contribution (10^{13} esu cm^{-3})	s–d contribution (10^{13} esu cm^{-3})	Total EFG (10^{13} esu cm^{-3})
z parallel to c axis	14.09	55.12	−0.175	69.0
z rotated 30°	15.19	55.09	−0.173	70.1
LAPW	32	123	—	143

component in magnitude with V_{zz}. From the eigenvectors we can also identify the direction of the principal axes associated with V_{zz}. In our calculation this direction for every contribution (p, d and total) to the EFG agrees to within a degree with the direction of the c axis, as was to be expected.

We have also calculated the EFG at the central site using a coordinate system for which the z axis coincides with the c axis and for which V_{ij} is diagonal automatically. In this case, $V_{xx} = V_{yy}$ by symmetry and, because the EFG tensor is traceless, the value of V_{zz} (table 2) determines all the elements. The idea is to determine the order of magnitude of the errors which are inherent in the recursion method, such as the use of terminators. If the results for V_{zz} in the two coordinate systems are consistent, the recursion procedure is giving a meaningful result. In table 2 we show the results of the procedures starting with firstly z parallel to the c axis and secondly with z rotated by 30°. In all cases, the recursion chain was terminated at $LL = 20$ and the terminator used by Beer and Pettifor (1984) was used to obtain the density of states. The partial densities of states were then integrated to obtain the occupation numbers. We note that the terminator can introduce sharp peaks into the density of states at the band edges. We have to be aware of that fact when performing the integrations. This problem may be avoided in the future if one uses the Gaussian quadrature method (Nex 1978) to obtain the integrated quantities.

The agreement between the results obtained using the two different coordinate systems is quite good in value and direction, showing that the procedure can be used to find V_{zz} when the direction of maximum EFG is not known *a priori*. We have noted that the d contribution is more sensitive to the terminator (figure 1), probably because of the larger value of the d density of states near the Fermi level. This may be the cause of the slightly larger discrepancy observed between the values of the d contribution in table 2. Our results show that, in agreement with the results of Blaha *et al*, also shown in table 2 for comparison, the p contribution dominates the EFG, but we note that our results for the EFG of HCP Zr are roughly a factor of 2 smaller than those obtained using the more exact full potential LAPW formalism. In the companion paper (Methfessel and Frota-Pessôa 1990), we trace this difference to the use of the ASA approximation.

If we use the real-space formalism, the p, d and s–d contributions can each be expressed as a product of two terms: the radial integral I_{ll}, and the rest which includes the angular contribution. Here, as explained in the next section, for the radial part $\varphi_l(r)$ we have used values obtained from LMTO ASA calculations for Zr. Using these functions we obtained $I_{pp} = 95.6$ Å^{-3}, $I_{dd} = 12.2$ Å^{-3} and $I_{sd} = 0.085$ Å^{-3}. Localised d atomic wavefunctions are often used to evaluate I_{dd} (Levy Yeati *et al* 1988, Petrilli and Frota-Pessôa 1985). We verified that these results for I_{dd} are in reasonable agreement with
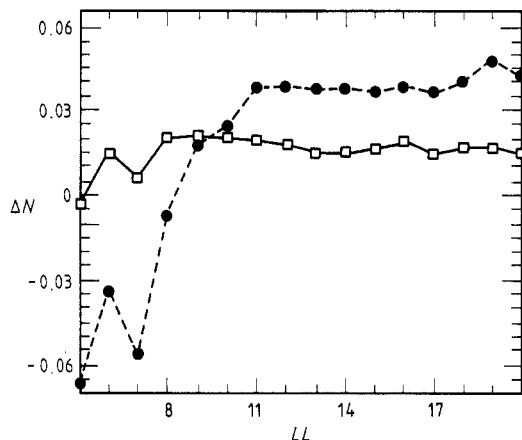
Figure 1. Variation in the angular asymmetries ΔN_p ($\square$) and ΔN_d ($\bullet$) as functions of the recursion's chain cut-off parameter LL.

those obtained by LMTO ASA calculations. We note that this is not the case if the more delocalised p atomic wavefunctions are used. For I_{pp} they give values which are much smaller than the correct ones. If we divide the values of the d, p and s–d contributions given in the Appendix by the radial part, we obtain 1.15, 0.58 and 2.06, respectively. Therefore the part that comes from angular deviations and which is calculated by the recursion procedure is smaller for the p bands. That and the fact that a simple evaluation of I_{pp} using atomic wavefunctions gives a much smaller value for this quantity explain why for a long time it was thought that the d contributions were dominant in transition metal where the d shell is not filled.

The magnitude of the EFG is strongly dependent on the radial integrals I_{pp} and I_{dd} but the sign of the EFG is completely determined by the angular asymmetry. For example, if the system has cubic symmetry, the occupancy of all orbitals would be degenerate and the EFG would be zero. We follow Blaha *et al* (1988) and define the angular asymmetry for p and d electrons by

$$\Delta N_p = \tfrac{1}{2}(N_x + N_y) - N_z$$
$$\Delta N_d = (N_{d_{xy}} + N_{d_{x2-y2}}) - \tfrac{1}{2}(N_{d_{xz}} + N_{d_{yz}}) - H_{d_{3z2-r2}}. \tag{9}$$

Here we use the capital N_i to denote twice the occupation number per spin n_i.

If we choose our coordinate systems to coincide with the principal axis, we get, for Zr (taking $LL = 20$), $\Delta N_p = 0.015$ and $\Delta N_d = 0.042$. (We note that our values for ΔN_p and ΔN_d cannot be directly compared with those of Blaha *et al* because the sizes of their muffin-tin sphere and our ASA sphere are different.) These values are extremely small and could depend on the energy resolution of the density of states. Therefore it is important to verify the dependence of the results on the value of LL, the number of terms that we keep in the recursion chain. This dependence is shown in figure 1. We see that the values of ΔN vary strongly for small values of LL. Both contributions change sign, ΔN_d at $LL \simeq 8$ and ΔN_p at $LL \simeq 5$, but in both cases ΔN tends to stabilise around a final value, at LL greater than 11. Cutting the recursion chain at $LL = 20$ seems to give satisfactory results.

3. The LMTO ASA tight-binding approach

In the last section we have described a real-space scheme to obtain the EFG for a system specified by a tight-binding Hamiltonian and corresponding wavefunctions in real space.

It is well known that the regular tight-binding formalism is not suitable for calculating the electronic structure of delocalised s–p bands in metals, which are essential to obtain a good description of the EFG in metals. In this section we show how the LMTO tight-binding formalism in the ASA can be used to obtain a more suitable Hamiltonian and we discuss the form of the corresponding wavefunctions. The main advantage of having a formalism to guide us is that we know exactly which are the approximations involved. Therefore it is always possible to improve on the Hamiltonan and wavefunctions if it is needed. It would be very hard to improve on the understanding of the problem if, for example, the tight-binding Hamiltonian had been derived from numerical fits to more exact bands.

We also note that it is straightforward to apply the procedure described here to close-packed non-periodic systems, including amorphous transition-metal alloys.

The LMTO ASA tight-binding formalism is well known and has been described in several papers (Andersen and Jepsen 1984, Andersen *et al* 1985). Therefore we shall be brief in our discussions, mainly outlining the procedure and stating the approximations being used in our present calculations.

In the LMTO ASA formalism, space is filled with Wigner–Seitz spheres of radius s, centred at all atomic sites. The potential is assumed to have spherical symmetry in each sphere. The problem of solving for the electronic structure is then divided in two parts. The first part involves finding the solution of the radial Schrödinger equation inside the sphere of radius s, with given boundary conditions, to obtain the values of the potential parameters which are used to construct the Hamiltonian. The second part of the problem is to find the structure constant matrix, which depends only on the relative position of the atoms. The method is a linear method and the LMTO ASA solutions are valid for energies close to a given energy E_ν.

One characteristic of the LMTO ASA formalism is that the choice of basis set can be done in the most convenient manner. There are three very important basis sets; the standard (Andersen 1975, Skriver 1983), the nearly orthogonal (Andersen 1984), and the tight-binding (also known as the most-localised) basis set (Andersen and Jepsen 1984, Andersen *et al* 1985). The potential parameters C_1, Δ_1, Q_1 and $p_1^{1/2}$ for the nearly orthogonal basis set vary with the material and type of atom considered, and are tabulated for all transition metals (Andersen *et al* 1985). (The potential parameters $C_1 - E_{1\nu}$, Δ_1, Q_1 and $p_1^{-1/2}$ are directly related to the standard parameters $\omega(-)$, $s\Phi^2(-)$, $\Phi(-)$, $\Phi(+)$ and $\langle\Phi^2\rangle^{1/2}$ of Skriver (1983).)

In real space it is very convenient to work in the tight-binding basis set. Therefore to build the Hamiltonian we need the tight-binding potential parameters (for which we used barred quantities) and the tight-binding structure constant. The values $\bar{Q}_s = 0.3485$, $\bar{Q}_p = 0.05303$ and $\bar{Q}_d = 0.01071$, taken to be material independent, can be used to define the LMTO ASA tight-binding representation. Given the above values for $\bar{Q}_1$, the potential parameters $\bar{C}_1$ and $\bar{\Delta}_1$ for energies close to E_ν can be obtained using the tabulated values C_1 and Δ_1 of the nearly orthogonal set and the expressions given below:

$$(\bar{C}_1 - E_{1\nu})/(C_1 - E_{1\nu}) = \bar{\Delta}_1^{1/2}/\Delta_1^{1/2} = 1 - (Q_1 - \bar{Q}_1)(C_1 - E_{1\nu})/\Delta_1. \tag{10}$$

The second part of the problem is to find the structure matrix. In the LMTO ASA tight-binding representation the structure matrix $\bar{\mathbf{S}}$ is of the tight-binding form and is non-zero only for sites i and j which are close neighbours. The correct way of obtaining the tight-binding structure constant matrix $\bar{\mathbf{S}}$ is by direct inversion, starting from the

canonical structure constant matrix **S** (associated with the standard representation) which has a known expression (Skriver 1983) and using the definition

$$\bar{\mathbf{S}} = \mathbf{S}(\mathbf{I} - \bar{\mathbf{Q}}\mathbf{S})^{-1}. \tag{11}$$

Here **I** is the unit matrix and $\bar{\mathbf{Q}}$ is a diagonal matrix with elements $\bar{Q}_1$. To find $\bar{\mathbf{S}}$ we would, in principle, have to invert the large $9N \times 9N$ matrix of equation (11), where N (here equal to 1249) is the number of atoms. In practice, to find the 9×9 matrices associated with $\bar{\mathbf{S}}$ for the on-site term and the hopping to close neighbours at a given site, one can apply equation (11) to a small cluster including only first and second neighbours around the site. This can be done because, owing to the localised nature of $\bar{\mathbf{S}}$, these 9×9 matrices do not change significantly when a larger cluster around the atom is used in the matrix inversion. This surprising fact is well known by users of the inversion programs. For example, if we take 50 atoms around the central atom instead of 19, the terms of interest differ by less than 0.1%. The same behaviour is observed for these matrix elements when amorphous clusters are considered. Of course, if small clusters are used to obtain the on-site and hopping terms, the matrix inversion has to be repeated for each inequivalent site. Given $\bar{\mathbf{S}}$ and the potential parameters $\bar{C}_1$, $\bar{\Delta}_1$ and $\bar{Q}_1$, we have all the ingredients to assemble the LMTO ASA tight-binding Hamiltonian.

In the tight-binding representation the basis functions $\bar{X}_{RL}(r_R)$ are given by (Andersen *et al* 1985)

$$\bar{X}_{RL}(r_R) = \bar{\varphi}_{RL}(r)Y_L(\hat{r}_R) + \sum_{R'L'} \dot{\bar{\varphi}}_{R'L'}(r)Y_{L'}(\hat{r}_{R'})\bar{h}_{R'L',RL} \tag{12}$$

where $\bar{\varphi}_{RL}(r)$ and $\dot{\bar{\varphi}}_{RL}(r)$ are defined inside the sphere of radius s, and given as linear combinations of φ and $\dot{\varphi}$, which are the solutions of the Schrödinger equation and its energy derivative at $E = E_\nu$, as

$$\begin{aligned} \bar{\varphi}_{RL}(r) &= \varphi_{RL}(r) \\ \dot{\bar{\varphi}}_{RL}(r) &= \dot{\varphi}_{RL}(r) + \varphi_{RL}(r)\bar{o}_{RL}. \end{aligned} \tag{13}$$

The index $L = l, m$ and the constant $\bar{o}_L$ at the site R does not depend on the value of m and is given by the relation

$$\bar{o}_1 = -(Q_1 - \bar{Q}_1)/(\Delta_1 \bar{\Delta}_1)^{1/2}. \tag{14}$$

As before, unbarred values are tabulated parameters of the nearly orthogonal set. Using the notation of Andersen *et al* (1985), where $|\bar{X}\rangle^\times$ is defined as a row vector with components $|X_{RL}\rangle$, we find that the Hamiltonian $\bar{\mathbf{H}}$ and the overlap $\bar{\mathbf{O}}$ for the LMTO ASA tight-binding basis are matrices of the form

$$\bar{\mathbf{O}} = {}^\times\langle\bar{X}|\bar{X}\rangle^\times = (\mathbf{I} + \bar{\mathbf{o}}\bar{\mathbf{h}})^+(\mathbf{I} + \bar{\mathbf{o}}\bar{\mathbf{h}}) \tag{15}$$

$$\bar{\mathbf{H}} = {}^\times\langle\bar{X}|-\nabla^2 + V|\bar{X}\rangle^\times = (\mathbf{I} + \bar{\mathbf{o}}\bar{\mathbf{h}})^+\bar{\mathbf{h}} + (\mathbf{I} + \bar{\mathbf{o}}\bar{\mathbf{h}})^+E_\nu(\mathbf{I} + \bar{\mathbf{o}}\bar{\mathbf{h}}) \tag{16}$$

where $\bar{\mathbf{h}}$ is a matrix with elements $\bar{h}_{RL,R'L'}$, which appear in equation (12). Very small terms, of the order of $\bar{\mathbf{h}}^+\mathbf{p}\bar{\mathbf{h}}$ with $p_{RL} = \langle\dot{\varphi}_{RL}^2\rangle$, have been neglected in the above expressions.

The matrices $\bar{\mathbf{H}}$ and $\bar{\mathbf{O}}$ generate an eigenvalue problem of the form

$$(\bar{\mathbf{H}} - E\bar{\mathbf{O}})\bar{\mathbf{b}} = 0 \tag{17}$$

where the wavefunction for a given eigenvalue i is given by

$$\psi^i(r) = \sum_{RL}\left(\bar{\varphi}_{RL}(r)Y_L(\hat{r}_R) + \sum_{R'L'}\dot{\bar{\varphi}}_{R'L'}(r)Y_{L'}(\hat{r}_{R'})\bar{h}_{R'L'.RL}\right)\bar{b}_{RL}. \tag{18}$$

Because of the convenient form of the overlap matrix $\bar{\mathbf{O}}$, the eigenvalue problem can be reformulated in terms of a new effective Hamiltonian $\mathcal{H}$ and new vectors c such that $(\mathcal{H} - E)c = 0$. Here $\mathcal{H}$ and c are defined as

$$\mathcal{H} = (\mathbf{I} + \bar{\mathbf{o}}\bar{\mathbf{h}})^{+-1}\bar{\mathbf{H}}(I + \bar{\mathbf{o}}\bar{\mathbf{h}})^{-1} = E_\nu + \bar{\mathbf{h}} - \bar{\mathbf{h}}\bar{\mathbf{o}}\bar{\mathbf{h}} + \bar{\mathbf{h}}\bar{\mathbf{o}}\bar{\mathbf{h}}\bar{\mathbf{o}}\bar{\mathbf{h}} \tag{19}$$

$$c = (\mathbf{I} + \bar{\mathbf{o}}\bar{\mathbf{h}})\bar{\mathbf{b}}. \tag{20}$$

Higher-order terms in $\bar{\mathbf{h}}$ have been neglected because they are of the same order as small terms that have been neglected before.

In our present real-space calculations we have kept only the first-order term in $\bar{\mathbf{h}}$. This is a good approximation for energies close to E_ν and $\bar{\mathbf{o}}$ small. The first-order Hamiltonian $\mathcal{H}^{(1)} = E_\nu + \bar{\mathbf{h}}$ can be written in a simple form in terms of the known quantities $\bar{C}_1$, $\bar{\Delta}_1$ and $\bar{\mathbf{S}}$ as

$$\mathcal{H}^{(1)} = \bar{\mathbf{C}} + \bar{\Delta}^{1/2}\bar{\mathbf{S}}\bar{\Delta}^{1/2}. \tag{21}$$

To establish the solution of the problem in terms of the first-order Hamiltonian $\mathcal{H}^{(1)}$, we should examine the behaviour of the wavefunction $\psi^i(r)$ when this approximation is used. In this first-order approximation we have $\bar{\mathbf{h}}\bar{\mathbf{b}} = (E - E_\nu)\bar{\mathbf{b}}$. We can use this relation and equation (13) to rewrite equation (18) as

$$\psi^i_{(1)}(r) = \sum_{RL} \{\varphi_{RL}(r)Y_L(\hat{r}_R)\bar{b}^i_{RL} + [\dot{\varphi}_{RL}(r) + \varphi_{RL}(r)\bar{o}_{RL}]$$

$$\times Y_L(r_R)(E^i - E_\nu)\bar{b}^i_{RL}\} \tag{22}$$

where the subscript (1) indicates that the expression $\psi^i_{(1)}(r)$ is valid to first order in $E - E_\nu$.

We can now add to equation (22) a second-order term of the form

$$\dot{\varphi}_{RL}(r)\bar{o}_{RL}(E^i - E_\nu)^2\bar{b}^i_{RL}$$

without changing the value of ψ^i to first order.

Therefore $\psi^i_{(1)}(r)$ can be written in the more convenient form

$$\psi^i_{(1)}(r) = \sum_{RL} [\varphi_{RL}(r) + \dot{\varphi}_{RL}(r)(E^i - E_\nu)]Y_L(r_R)[1 + \bar{o}(E^i - E_\nu)]\bar{b}^i_{RL}$$

$$= \sum_{RL} [\varphi_{RL}(r) + \dot{\varphi}_{RL}(r)(E^i - E_\nu)]Y_L(\hat{r}_R)c^i_{RL} \tag{23}$$

where in the last expression equation (20) was used for $\psi^i_{(1)}(r)$. This expression is very similar to equation (2) used to describe the wavefunction in § 2, but now the radial part has a term which is energy dependent. The generalisation of the treatment of § 2 to include the energy dependence of the radial part is trivial. Now, in addition to the contributions listed in the appendix, terms involving integrals of $\varphi(r)$ and $\dot{\varphi}(r)$ as well as the first moments of the partial density of states appear in the expressions for the EFG.

However, these extra contributions, associated with the energy-dependent term of the radial part were found to be always negligible when compared with the contributions due to the energy-independent term which are listed in the Appendix.

When the energy-dependent term is neglected in the radial part and the first-order approximation is used for the Hamiltonian, the eigenvalue problem to be solved is reduced to

$$\mathcal{H}^{(1)}c = Ec \tag{24}$$

with the corresponding wavefunctions $\psi^i_{(1)}(r)$ given by

$$\psi^i_{(1)}(r) = \sum_{RL} \varphi_{RL}(r)Y_L(\hat{r}_R)c^i_{RL}. \tag{25}$$

If we take $\mathcal{H}^{(1)}$ to be our tight-binding Hamiltonian and $\varphi_{RL}(r)$ to describe the radial part of the basis functions, the problem is completely analogous to the regular tight-binding formalism, in the absence of overlap, considered in § 2. Because the LMTO ASA tight-binding formalism does not have the restriction of the regular tight-binding method, we can use the tight-binding expressions given above to treat not only d orbitals but also hybridised s, p and d bands. (We note that, owing to the sum over R', L' in equation (18), the LMTO ASA tight-binding basis function can have a mixed L character. If we go to higher order in $\bar{h}$, this mixed character is not eliminated and the analogy with the regular tight-binding formalism is lost. In this case, V_{zz} can still be obtained from the ρ_{20} component of the charge density in the Wigner–Seitz sphere.)

Finally we wish to make clear which were the approximations used in our present real-space calculations for the EFG in HCP Zr. We note that the LMTO ASA tight-binding approach, if implemented with the exact tight-binding structure constants and higher-order corrections to the Hamiltonian, is just a different representation and must give the same results as the standard LMTO ASA method. However, our real-space calculations in the present form can have errors which may be classified as two different types: firstly, errors that come from the recursion method and, secondly, errors that come from the additional approximations used in the Hamiltonian. The first type is associated with the finite size of the cluster, the cut-off parameter in the recursion chain (here taken at $LL = 20$) and the choice of the terminator. The cluster used here is rather large and the good agreement between the two calculations presented in this paper (z parallel to the c axis and z rotated by 30°) indicate that the other errors introduced by the use of the recursion method are also small. This probably reflects the fact that the results depend on $n_{m,m'}$ which are integrated quantities and therefore well described by the recursion method approach.

The second type of error originates from the approximation that we have made to simplify the Hamiltonian and to make the problem easier to treat. First of all our Hamiltonian is based on the LMTO ASA tight-binding formalism, where the Wigner–Seitz cell is substituted by a sphere of equal volume. This approximation is part of the k-space LMTO ASA formalism and is certainly present in our calculations. In k-space, combined corrections terms can be included to improve the results. If necessary, one could try to implement a similar correction in real space, but this has not been done here. The first-order Hamiltonian $\mathcal{H}^{(1)}$ given by equation (21) was used in our calculations, and we expect the results to be good only for energies close to E_ν. The values of $\bar{C}_1$ and $\bar{\Delta}_1$ were obtained from equation (10) using the tabulated values of C_1, Δ_1, Q_1 and E_ν for Zr. These are self-consistent parameters obtained from scalar relativistic LMTO ASA calculations

using a basis which included f electrons. In the real-space calculations presented here, only s–p and d electrons were included.

The structure constant $\bar{\mathbf{S}}$ was obtained by direct inversion on a cluster of 19 atoms, but only the on-site term and 9×9 matrices connecting the atoms to its 12 nearest neighbours were considered in the calculation. This is not a bad approximation because $\bar{\mathbf{S}}$ gives hopping terms which are well represented by law that predicts an exponential decay with distance (Andersen and Jepsen 1984). Finally, in our calculations, we consider only valence electrons.

Recently, Blaha *et al* (1988) have used a full-potential LAPW calculation to obtain the EFG for a large number of HCP metals, including Zr. Their calculations show that the contributions from the core electrons and from electrons associated with sites other than that being considered are small. Thus the EFG is essentially determined by the shape of the valence charge density close to the nucleus. This justifies in part the approximations that we have made in obtaining equations (3) and (4).

It is interesting to compare our present results with those obtained by the above-mentioned more exact calculations, which reproduce the existing experimental data well. Our results for p and d contributions have the correct sign but both, when compared with those of Blaha *et al*, are too small by a factor of 2. We note that the EFG is a local and very subtle quantity so that extreme care has to be taken. As we have shown (equation (9)), it depends on differences in occupancy of the order of a hundredth of an electron between orbitals of different symmetry. Considering the approximations which were made when building the Hamiltonian and the subtlety of the effect, the results are very encouraging.

In the companion paper (Methfessel and Frota-Pessôa 1990) the real-space procedure is applied to obtain the EFG for several other HCP metals. A detailed comparison between real-space and k-space calculations in these metals gives a good idea of the advantages and limitations of the proposed real-space scheme.

4. Conclusions

We have proposed a real-space procedure based on the recursion method which allows us to obtain the EFG for systems which can be described by a Hamiltonian of the tight-binding form. This real-space procedure can be used to obtain the EFG for materials which lack translational symmetry and cannot be treated by the usual k-space methods. We show that, in the case of close-packed metallic systems, a simple and adequate tight-binding Hamiltonian is provided by the LMTO ASA tight-binding formalism, taken to first order in $E - E_\nu$.

To verify that the proposed real-space procedure works in the absence of symmetry, we have applied it to HCP Zr, first taking the coordinate system to coincide with the principal axis and then using a coordinate system for which the axial symmetry is not preserved. The results for the EFG were independent of choice of coordinates as expected, showing that the recursion method has enough precision to treat the problem correctly.

Our results for HCP Zr show that, in agreement with the results of Blaha *et al*, the p contribution dominates the EFG. We also find the correct sign for the p and d contributions but the magnitudes are smaller than those obtained by Blaha *et al* by a factor of roughly 2. Considering that the EFG is a very subtle quantity which depends on differences in occupancy of the order of a hundredth of an electron between orbitals of different symmetries, the results were very encouraging.

Finally, the procedure developed here can be directly used to study trends for the EFG in amorphous metallic alloys, for which very little is known. Since the real-space procedure is linear in the number of non-equivalent atoms, it is also possible to treat the EFG of complex metallic systems with large numbers of atoms per unit cell, where the application of more exact k-space methods is limited by the size of the facilities or the cost.

Appendix. Theoretical expressions for the V_{ij} components in MKS units using the notation in equation (4)

The theoretical expressions for the V_{ij} components using the notation in equation (4) are as follows:

$$V_{xx} = A\{(I_{dd}/7)[2n_{yz} + n_{3z^2-r^2} - n_{xy} - n_{xz} - n_{x^2-y^2} + (6 \times 3^{1/2}/3)n_{x^2-y^2,3z^2-r^2}]$$
$$+ (I_{pp}/5)(n_y + n_z - 2n_x) + I_{sd}(5^{1/2}/5)(n_{s,3z^2-r^2} - 3^{1/2}n_{s,x^2-y^2})\}$$

$$V_{yy} = A\{(I_{dd}/7)[2n_{xz} + n_{3z^2-r^2} - n_{xy} - n_{yz} - n_{x^2-y^2} - (6 \times 3^{1/2}/3)n_{x^2-y^2,3z^2-r^2}]$$
$$+ (I_{pp}/5)(n_x + n_z - 2n_y) + I_{sd}(5^{1/2}/5)(n_{s,3z^2-r^2} + 3^{1/2}n_{s,x^2-y^2})\}$$

$$V_{zz} = A[(I_{dd}/7)(2n_{xy} + 2n_{x^2-y^2} - n_{xz} - n_{yz} - 2n_{3z^2-r^2}) + (I_{pp}/5)(n_x + n_y - 2n_z)$$
$$- I_{sd}(2 \times 5^{1/2}/5)n_{s,3z^2-r^2}]$$

$$V_{xy} = A\{(I_{dd}/7)[(6 \times 3^{1/2}/3)n_{xy,3z^2-r^2} - 3n_{yz,xz}] - I_{pp}\tfrac{3}{5}n_{x,y} - I_{sd}(15^{1/2}/5)n_{xy,s}\}$$

$$V_{yz} = A\{3(I_{dd}/7)[n_{yz,x^2-y^2} - n_{xy,xz} - (3^{1/2}/3)n_{yz,3z^2-r^2}] - I_{pp}\tfrac{3}{5}n_{y,z}$$
$$- I_{sd}(15^{1/2}/5)n_{yz,s}\}$$

$$V_{xz} = A\{-3(I_{dd}/7)[n_{xy,yz} + n_{xz,x^2-y^2} + (3^{1/2}/3)n_{xz,3z^2-r^2}] - I_{pp}\tfrac{3}{5}n_{x,z}$$
$$- I_{sd}(15^{1/2}/5)n_{xz,s}\}$$

The constant $A = e/\pi\varepsilon_0$ where e is the proton's charge; I_{pp}, I_{dd} and I_{sd} are radial integrals.

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