Calculation of shape-truncation functions for Voronoi polyhedra

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Abstract. We develop a new efficient method for calculating the shape-truncation functions of arbitrary Voronoi polyhedra by combining analytical and numerical techniques. Applications are presented for cells of cubic symmetry as well as for hexagonal close-packed (HCP) atomic polyhedra with different values of the c/a ratio. We also discuss an efficient way for performing three-dimensional integrations in electronic-structure calculations (e.g. solve Poisson's equation) using shape functions.

1. Introduction

In realistic electronic-structure calculations employing cellular methods considerable effort has been made recently for evaluating three-dimensional multi-centre integrals without imposing any shape approximation on the potential and charge density [1–3]. Indeed in a self-consistent scheme, within the density functional theory for instance, an effective potential must be constructed from the local charge density at each iteration. This task involves three-dimensional integrations of a site-centred expanded charge density within the, in general non-periodic, whole system. The same problem also occurs in total-energy calculations, where it is important to avoid shape approximation on the potential and charge density in order to obtain the desired accuracy [4, 5].

One approach to the multi-centre integration problem initially involves partitioning of space among the atoms where a certain portion of the space in the shape of a polyhedron is attached to each atom. These polyhedra are variously known as Dirichlet regions, Voronoi polyhedra, Wigner–Seitz cells etc. We will use here the name 'Voronoi polyhedra'. In mathematical language we say that a point r belongs to the Voronoi cell V_n of atom n located at position R_n if it is closer to n than to any other atom m of the system:

$$r \epsilon V_n \Leftrightarrow |r - R_n| \leqslant |r - R_m| \qquad \forall m. \tag{1}$$

Thus, a Voronoi polyhedron is defined by the closest planes that are perpendicular bisectors of the lines joining the central atom and its neighbours. Numerous algorithms for the automatic construction of these polyhedra exist in the literature [6–10]. The definition of Voronoi cells and their geometrical construction is not restricted to equal

atomic volumes, but can be easily generalized [10]. The generalization allows for a realistic partitioning of the space among atoms of different size, in the case of lattice relaxation, interstitial impurities, interfaces etc.

Several methods have been suggested in the literature for performing the three-dimensional integrals over the Voronoi polyhedra. A straightforward numerical integration using rapidly convergent Gaussian product formulae has been developed to a high degree of sophistication in the works of Boerrigter *et al* [1] and of Averill and Painter [3]. An interesting scheme has been proposed by Becke [2]. In his method the system is not divided into conventional discrete cells, but into fuzzy, overlapping, analytically continuous cells. This is done in the following way. Integration within a Voronoi cell can be performed by multiplying the integrand with a unit step function, $\Theta(\sigma(\hat{r}) - r)$ where $\sigma(\hat{r})$ is the distance of the cell surface from the origin, in the direction defined by the solid angle $\hat{r}$. The so-called shape function, which is equal to one for points r lying inside the Voronoi polyhedron and vanishes outside of it, is replaced with an appropriate continuous analogue, resembling, e.g., the finite-temperature Fermi function.

We should also mention here the methods originating from the work of Ellis [11] and Ellis and Painter [12] on the use of Diophantine integration [13, 14] in solid-state and molecular electronic-structure calculations. This integration method, however, as shown by Boerrigter *et al* [1], behaves poorly as the number of mesh points increases and is therefore unsuitable for high accuracy integrations. Monte-Carlo integration techniques also exhibit a similar slow convergence [15, 16] and are not recommended for routine use in the evaluation of the numerous integrals occurring in electronic-structure calculations.

It has been suggested several times that the computation of these integrals within Voronoi cells can be simplified by fitting the potential and/or charge density with Gaussians [17–24], plane waves [25] or Hankel functions [26] and by performing the required integrals with the fitting functions numerically. Here, also the use of a numerical technique for three-dimensional integration is involved.

In many electronic-structure calculations the charge densities and potentials are given in an angular-momentum representation. It is then convenient to describe the shape of the Voronoi cells by a Heaviside step function, $\Theta(\sigma(\hat{r}) - r)$ being equal to one in the cell and zero outside. The three-dimensional multi-centre integration is then formally reduced to a sum of one-dimensional radial integrals of the angular-momentum components of the integrands, multiplied with the appropriate Gaunt coefficients [27, 28]. For that, one needs to calculate the angular-momentum components of the shape function $\Theta(\sigma(\hat{r}) - r)$. Once evaluated for a given cell shape, they can be used when truncation by that boundary is needed. Since they scale with the size of the cell they need only be calculated once for each geometry. The shape functions have been introduced by Andersen and Woolley [29], who also described a technique for their analytic evaluation when the cell boundary is a set of planes. This results in complicated analytical expressions, and numerical calculations seem to be more efficient. Morgan [27] has computed the components up to $l = 8$ for FCC and BCC cells by numerical integration using a direct product of two Gaussian quadratures. In the same paper unpublished results of a computation of these function by Janak, using the Gilat–Raubenheimer method, are presented. The use of Brillouin zone integration techniques has also been suggested by Christensen [30]. Recently, Stefanou *et al* [28] proposed a new method for the calculation of these functions for cubic and other high symmetry cells by combining analytical and numerical techniques. In this paper

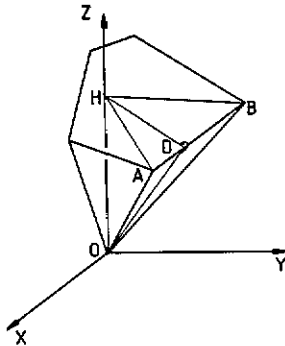we develop a generalization of this method to calculate shape functions for arbitrary Voronoi polyhedra.

Figure 1. Division of a rotated pyramid into elementary tetrahedra.

2. Calculational method

We expand the shape function in a real-spherical-harmonic basis:

$$\Theta(\sigma(\hat{r}) - r) = \sum_{l,m} \Theta_{lm}(r) Y_{lm}(\hat{r}). \tag{2}$$

The angular-momentum components $\Theta_{lm}(r)$ are given by

$$\Theta_{lm}(r) = \int_0^{2\pi} \int_0^{\pi} \mathrm{d}\varphi \, \mathrm{d}\vartheta \, \sin \vartheta \Theta(\sigma(\vartheta, \varphi) - r) Y_{lm}(\vartheta, \varphi) \tag{3}$$

where the shape function in the integral truncates the integration to those angles for which the surface of the sphere $(0, r)$ lies inside the Voronoi polyhedron. We divide the polyhedron into N pyramids with the centre of the polyhedron as common vertex and its faces as bases, and rotate each pyramid through the Euler angles $\alpha_n, \beta_n, \gamma_n$ so that its base becomes perpendicular to the z-axis. Such a rotated pyramid is shown in figure 1. Then, equation (3) takes the form:

$$\Theta_{lm}(r) = \sum_{n=1}^{N} \sum_{m'=-l}^{l} \mathcal{D}_{m'm}^{(l)}(\alpha_n, \beta_n, \gamma_n) \int \int_{\Omega_n} \mathrm{d}\varphi \, \mathrm{d}\vartheta \, \sin \vartheta \Theta(\sigma(\vartheta, \varphi) - r) Y_{lm'}(\vartheta, \varphi)$$

$$\tag{4}$$

where $\mathcal{D}_{m'm}^{(l)}$ transforms real spherical harmonics under three-dimensional rotations [31] and Ω_n denotes the solid angle integration boundaries of the nth rotated pyramid. The base of each rotated pyramid is a convex polygon. It is divided into triangles with vertices being those of the polygon and with a common vertex being the intersection of the base with the z-axis. This point may lie inside or outside the polygon. In the latter case the polygon can also be obtained as a superposition of such triangles, if the contribution of the triangles lying entirely outside are subtracted. In this way we define

a subdivision of the nth pyramid into $T(n)$ elementary tetrahedra and equation (4) is written:

$$\Theta_{lm}(r) = \sum_{n=1}^{N} \sum_{m'=-l}^{l} \mathcal{D}_{m'm}^{(l)}(\alpha_n, \beta_n, \gamma_n)$$

$$\times \sum_{t=1}^{T(n)} S_t \int \int_{\Omega_t} \mathrm{d}\varphi \, \mathrm{d}\vartheta \, \sin\vartheta \Theta(\sigma(\vartheta,\varphi) - r) Y_{lm'}(\vartheta,\varphi) \qquad (5)$$

where $S_t = -1$ if the entire tetrahedron t lies outside the polyhedron and $S_t = 1$ otherwise. The efficiency and accuracy of our method relies on the fact that we first analytically integrate over ϑ and only the remaining φ-integration is done numerically, for instance by Simpson's method. As detailed in [28], this means we have to evaluate

$$I(p,q,\vartheta) = \int \mathrm{d}\vartheta \, \sin^p \vartheta \cos^q \vartheta \qquad (6)$$

for which we have given recurrence relations [28]. Recent closed form expressions for $I(p,q,\vartheta)$ have also been obtained by Szalay [32].

For a given argument r the integral in equation (5) is non-vanishing only within certain limits for the ϑ- and φ-integration, which are determined by the surface part of the sphere $(0,r)$ that lies inside the elementary tetrahedron. These ϑ- and φ-limits are functions of the radius r, which at some critical points can have discontinuous derivatives due to the geometry of the Voronoi polyhedron. Critical points occur either when the sphere $(0,r)$ passes through a vertex of the polyhedron or when it is tangent to an edge or to a face. At these points the derivatives of the shape function components are also, in principle, discontinuous. Thus, integrals involving $\Theta_{lm}(r)$ must be calculated with a suitable radial mesh in order to avoid numerical errors. Such a radial mesh may be constructed by dividing the mesh points into different intervals within which the derivative of the shape function remains continuous.

For each elementary tetrahedron, the ϑ- and φ-angle limits can be determined by simple geometrical considerations. In general one has to consider a sum of P integrals over those parts of the spherical angle Ω_t which correspond to the different parts of the sphere $(0,r)$ that lie inside the elementary tetrahedron. Let OHAB be an elementary tetrahedron of height $OH = r_o$ with $OA = (r_A, \vartheta_A, \varphi_A)$, $OB = (r_B, \vartheta_B, \varphi_B)$, oriented so that $\varphi_A < \varphi_B$, and $OD = (r_D, \vartheta_D, \varphi_D)$ be perpendicular to the edge (AB), as shown in figure 1. The ϑ- and φ-angle limits are then defined as follows.

(i) For $r \leqslant r_0$, $P = 1$ and

$$\varphi_1^{\min} = \varphi_A \qquad \varphi_1^{\max} = \varphi_B \qquad \vartheta_1^{\min} = 0 \qquad \vartheta_1^{\max} = \vartheta_D. \qquad (7)$$

(ii) For $r_0 \leqslant r \leqslant r_D$, $P = 1$ and

$$\varphi_1^{\min} = \varphi_A \qquad \varphi_1^{\max} = \varphi_B \qquad \vartheta_1^{\min} = \arccos r_0/r \qquad \vartheta_1^{\max} = \vartheta_D. \qquad (8)$$

(iii) For $r_D \leqslant r$, $P = 2$ and

$$\varphi_1^{\min} = \varphi_A \qquad \varphi_1^{\max} = \varphi_K \qquad \vartheta_1^{\min} = \arccos r_0/r \qquad \vartheta_1^{\max} = \vartheta_D \qquad (9)$$

$$\varphi_2^{\min} = \varphi_L \qquad \varphi_2^{\max} = \varphi_B \qquad \vartheta_2^{\min} = \arccos r_0/r \qquad \vartheta_2^{\max} = \vartheta_D \qquad (10)$$

where

$$\vartheta_D = \arctan \frac{\sqrt{r_D^2 - r_0^2}}{r_0 \cos(\varphi - \varphi_D)} \tag{11}$$

$$\varphi_{\substack{K \\ (L)}} = \varphi_D \mp \arccos \sqrt{\frac{r_D^2 - r_0^2}{r^2 - r_0^2}} \tag{12}$$

subject to the conditions

$$\varphi_{\substack{K \\ (L)}} = \max(\varphi_A, \varphi_{\substack{K \\ (L)}})$$

$$\varphi_{\substack{K \\ (L)}} = \min(\varphi_B, \varphi_{\substack{K \\ (L)}}). \tag{13}$$

are always restricted within the interval (φ_A, φ_B).

3. Applications

We first applied our method to calculate the components of the shape functions up to $l = 16$ for the Wigner–Seitz cells of simple, FCC and BCC lattices. Our results are identical to those obtained by Stefanou *et al* [28]. However, the generality of the present algorithm, which contrary to the previous one [28] does not apply group theory, implies an increase by a factor of approximately eight in computer time. Here it is interesting to note that we calculate the shape-function components which should be equal to zero by symmetry to be about 10^{-10}. This indicates the accuracy of our method.

The efficiency and generality of our algorithm is better shown by considering Voronoi cells of lower symmetry. For this reason we calculated the shape functions up to $l = 6$ for the atomic polyhedron of HCP structures with different values of the c/a ratio: $c/a = 1, 1.633, 2$. The geometry of such a Wigner–Seitz atomic polyhedron is determined by the Voronoi construction [6–10]. The Voronoi cell, thus defined around each atom, has a volume equal to $(\sqrt{3}/4)a^2 c$ and is invariant under the rotations of the D_{3h} point symmetry group [33]. The non-zero angular-momentum components of the shape functions are shown in figure 2.

The use of shape-truncation functions is very helpful in obtaining efficient computer codes for electronic-structure calculations, where three-dimensional multi-centre integration is involved. A useful application is, for example, the solution of Poisson's equation. Let us consider the electrostatic potential $V(r)$ created by a charge distribution of density $n(r)$, localized within a Wigner–Seitz cell Ω:

$$V(r) = 2 \int_\Omega dr' \frac{n(r')}{|r - r'|} \tag{14}$$

in Rydberg atomic units. The angular-momentum components of the potential for distances larger than the radius of the circumscribed sphere R_C are given by

$$V_{lm}(r) = \frac{8\pi}{2l+1} r^{-l-1} \left\{ \int_0^{R_{MT}} dr' \, r'^{l+2} n_{lm}(r') + \sum_{l',m'} \sum_{l'',m''} C_{lml'm'l''m''} \right.$$

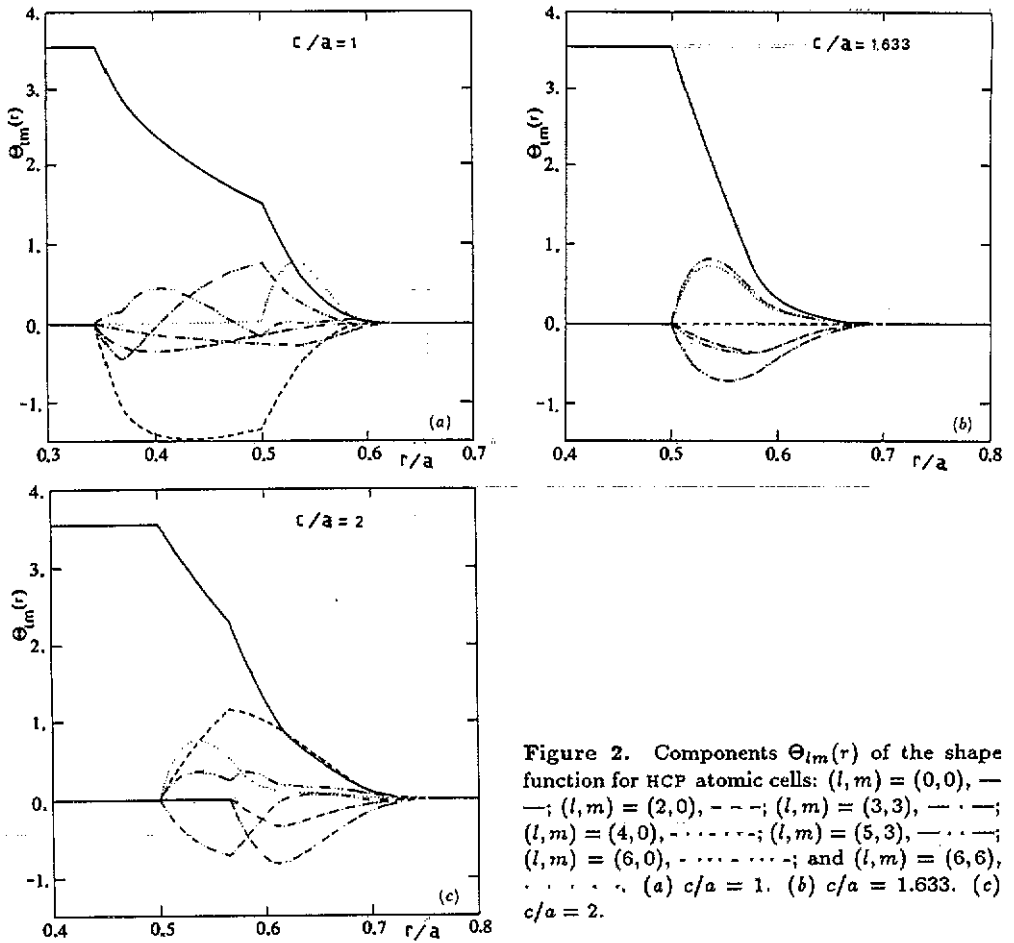$$\left. \times \int_{R_{MT}}^{R_C} dr' \, r'^{l+2} n_{l'm'}(r') \Theta_{l''m''}(r') \right\} \tag{15}$$

Figure 2. Components $\Theta_{lm}(r)$ of the shape function for HCP atomic cells: $(l,m) = (0,0)$, —
—; $(l,m) = (2,0)$, - - -; $(l,m) = (3,3)$, — · —; $(l,m) = (4,0)$, - · · · · · -; $(l,m) = (5,3)$, — · · —; $(l,m) = (6,0)$, - · · · - · · · -; and $(l,m) = (6,6)$, · · · · ·. (a) $c/a = 1$. (b) $c/a = 1.633$. (c) $c/a = 2$.

Similar formulae, valid for $0 \leqslant r \leqslant R_{\mathrm{MT}}$ and for $R_{\mathrm{MT}} \leqslant r \leqslant R_{\mathrm{C}}$, R_{MT} being the radius of the muffin-tin sphere, are given in [28].

As shown there the l-convergence of the shape functions is slow. However, this does not seem to be a problem in electronic-structure calculations where, in any case, a restricted l-basis is used for the expansion of wavefunctions, charge densities, potentials etc. Indeed, the angular-momentum cut-offs l_V and l_n in the expansions of the potential and the charge density, respectively, determine a cut-off l_Θ for the shape functions through the Gaunt-coefficients. Selection rules for these coefficients [31] impose the condition that $l_\Theta \leqslant l_V + l_n$.

In electronic-structure calculations the charge density is a smooth and slowly varying function in the interstitial region and the computational effort to solve Poisson's equation can be reduced by fitting the charge density components, as has been suggested by many workers [4, 5, 17, 18, 26]. For this fitting, one can use a relatively restricted basis of fitting functions $f^{(i)}(r)$:

$$n_{lm}(r) = \sum_i b_{lm}^{(i)} f^{(i)}(r) \qquad R_{\mathrm{MT}} \leqslant r \leqslant R_{\mathrm{C}}. \tag{16}$$

Constrained least-squares-fit methods subject to functional continuity or (and) charge-

conservation constraints can also be applied. This leads to integrals of the type

$$J_{l;l'm'}^{(i)}(r) = \int_{R_{\mathrm{MT}}}^{r} \mathrm{d}r' \, r'^{l} f^{(i)}(r') \Theta_{l'm'}(r') \qquad R_{\mathrm{MT}} \leqslant r \leqslant R_{\mathrm{C}} \tag{17}$$

which are smooth functions of r and, for a specific choice of $f^{(i)}$, depend only on the geometry of the cell. Thus, they must be calculated only once and can be stored for further use when solving a problem with this geometry.

4. Conclusion

We have developed a new accurate method for calculating the shape-truncation function of an arbitrary Voronoi polyhedron. Its angular-momentum components are calculated by an effective solid-angle integration within all the appropriate elementary tetrahedra into which the polyhedron is divided. The ϑ-integral is evaluated analytically, so that just a one-dimensional φ-integration must be performed numerically.

We applied the method to cells of cubic symmetry as well as to HCP atomic polyhedra with c/a ratios: 1, 1.633, 2. Our results for cubic cells are identical to those obtained by our previous method [28]. Both methods combine high accuracy with numerical efficiency. The present one needs somewhat longer computer time, but works easily for arbitrary Voronoi polyhedra. It is recommended for low symmetries where the effective solid-angle integration limits needed in our previous method [28] are hard to establish explicitly.

The shape of any atomic polyhedron is described fully by the angular-momentum components of the corresponding truncation function. Thus, volume integration within a cell or spatial truncation of a function by the boundary planes of a polyhedron can be expressed in terms of these shape-truncation functions. Their use is very helpful in obtaining efficient computer codes for solid-state and molecular electronic-structure calculations, where three-dimensional multi-centre integrations (e.g. solution of Poisson's equation) are required.

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