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Abstract. Eight schemes for the reconstruction of the true aspherical wavefunctions from the pseudowavefunctions in a crystal are developed. The schemes are distinguished by four different choices of the boundary conditions for the self-consistent solution of the Kohn–Sham equation for the true wavefunction in a reconstruction sphere (the boundary conditions being supplied by the pseudopotential calculation) and by two different ways of solving the Kohn–Sham equations (numerically or by the use of a basis set). The methods are tested by calculating the electric field gradients in hexagonal metals and on atoms near a vacancy in Na. The comparison with all-electron calculations and with experiments demonstrates that the reconstruction schemes represent powerful tools for the calculation of electric field gradients within the framework of the pseudopotential methods for situations with moderate or large electric field gradients. Altogether, the reconstruction schemes extend the applicability of the pseudopotential method to situations where the nodal structure of the true wavefunctions of the valence electrons in the core regime is essential.

1. Introduction

The numerical methods of the *ab-initio* electron theory of solids may be subdivided into two classes. In the first class of methods the wavefunctions are represented by basis functions which are to some extent adapted to the oscillations of the wavefunctions near the nuclei, for instance the augmented-plane-wave (AWP) method [1, 2], the Korringa–Kohn–Rostocker (KKR) method [3, 4], the linear methods (linearized-augmented-plane-wave (LAPW) [5, 6], linear-muffin-tin-orbital (LMTO) [5], augmented-spherical-wave (ASW) [7] methods) and the linear-combination-of-atomic-orbitals (LCAO) methods (see, e.g., [8]). The second class encompasses the large variety of pseudopotential methods (see, e.g., [9–12]), which produce nodeless valence pseudowavefunctions that are nearly identical with the real valence wavefunctions outside the core region, i.e. in the bonding area between the atoms of the solid. The tightly bound core states which respond very weakly to the presence of neighbouring atoms are described within the frozen-core approximation by the core states of the respective free atoms.

The pseudopotential methods have been most extensively used in the past for the investigation of defects in solids, sometimes in combination with molecular-dynamics techniques [13], yielding highly accurate information about the structural relaxation of defect energetics. On the other hand, there are applications (e.g. the calculation of hyperfine parameters) where real valence wavefunctions instead of pseudowavefunctions are required

and also those where in addition the frozen-core approximation must be abandoned. For instance, the magnetic contact hyperfine field at a nucleus is determined by the spin density at the nucleus which consists of a valence contribution, which is not adequately described by valence pseudowavefunctions, and a contribution due to the polarization of the cores by the valence spin density, which is the dominant contribution in many magnetic materials [14]. Another example consists of the electric field gradients (EFGs) experienced by nuclei at non-cubic lattice sites, for instance close to structural defects. In most cases these quantities are mainly determined by the valence charge densities close to the nuclei, whereas the core contributions are rather small [15]. They may be measured by a variety of experimental techniques [16] and play the role of fingerprints of the structural defects which may be used to identify the defects by comparing the experimental data with the theoretical predictions for certain types of defect. Because the pseudowavefunctions do not correctly describe the valence charge densities close to the nuclei, calculations of the EFG so far have been performed mostly by the LAPW [15], LMTO [17, 18], the ASW [19] and the KKR [20] all-electron methods. The application of the pseudopotential method was only possible in cases where the dominant angular momentum contributions of the wavefunctions of the EFG correspond to nodeless valence states, e.g. the nodeless 2p states which determine the EFG at atoms near a vacancy in BCC Li, but it has already failed for the case of Na [21]. Because forces on atoms can most conveniently be calculated with the pseudopotential method, this method is nevertheless extensively used for a study of defects including the structural relaxation effects. In order to obtain from these calculations properties which depend on the valence charge densities near the nuclei, one has to reconstruct the real valence wavefunctions ψ_{kj} from the valence pseudowavefunctions $\tilde{\psi}_{kj}$. In the present paper, two methods for such a reconstruction are developed (section 2). The methods are tested by comparing the results for the EFGs with those obtained by the full-potential LAPW and LMTO methods (section 3).

2. Formalism

2.1. Basic idea

We start with some comments on the pseudowavefunctions $\tilde{\psi}_{kj}$ which are the basic ingredients of the reconstruction scheme. The non-local (i.e. angular-momentum-dependent) ionic pseudopotentials are constructed in such a way that they reproduce the scattering properties of the real ionic core (nucleus plus core electrons) of a free atom nearly exactly outside the core radius $r_{c,l}$ for the single-particle atomic valence wavefunctions of angular momentum l and single-particle energy ε_l. The radius $r_{c,l}$ thereby is located between the outermost node and the outermost maximum of the real valence wavefunction and is very often smaller than the physical radius of the ionic core. The accuracy is only limited by the fact that, in many pseudopotential construction methods, smooth pseudopotential cut-off functions are used so that the pseudowavefunction is not identical with the real wavefunction already at $r = r_{c,l}$ but approaches the real wavefunction very rapidly for $r > r_{c,l}$. When the so-constructed ionic pseudopotentials are transferred to a solid, the accuracy by which the pseudopotential reproduces the scattering properties of the real potential is limited for the following reasons.

   (i) The energy of the valence wavefunction in the crystal is different from ε_l, for which the pseudopotential was constructed. This problem can be reduced, for instance, by using norm-conserving pseudopotentials [9–11] which guarantee a good transferability of the pseudopotential with respect to the energy.

(ii) The angular-momentum dependence is taken into account only up to a maximum angular momentum l_{max}, whereas the wavefunctions contain components of all l.

(iii) The unscreening procedure at the end of the pseudopotential construction provides only an approximate subdivision [9–11, 22] into ionic core and valence states.

In spite of these problems, the scattering properties of the real ionic cores outside the core radius $r_{c,l}$ are generally reproduced with very high accuracy also in the solid, so that we assume in the following for simplicity that the pseudowavefunction is exactly identical with the true wavefunction outside the cores of radius $r_{c,l}$ and corresponds to the same energy. The above-discussed limitations, however, should be taken as a reminder that the accuracy of the reconstructed true wavefunctions is principally limited by the accuracy of the pseudopotential method, in addition to slight inaccuracies introduced by the reconstruction method itself.

For the reconstruction of the true wavefunctions ψ_{kj}, the pseudowavefunctions $\tilde{\psi}_{kj}$ which have been obtained from a pseudopotential calculation for the system under consideration and the true wavefunctions ψ_{kj} to be constructed are expanded with respect to cubic harmonics $K_{lm}(\hat{r})$ ($r = |r|$, $\hat{r} = r/r$):

$$\tilde{\psi}_{kj}(r) = \frac{1}{\sqrt{N}} \sum_{lm} \tilde{\chi}_{lm}^{kj}(r) K_{lm}(\hat{r}) \tag{1}$$

$$\psi_{kj}(r) = \frac{1}{\sqrt{N}} \sum_{lm} \chi_{lm}^{kj}(r) K_{lm}(\hat{r}) \tag{2}$$

where N denotes the number of unit cells. Because according to the above discussion the pseudowavefunctions agree with the true wavefunctions for $r > r_{c,l}$ the reconstruction may be achieved by replacing the expansion coefficients $\tilde{\chi}_{lm}^{kj}(r)$ by the coefficients $\chi_{lm}^{kj}(r)$ inside a reconstruction sphere of radius $r_{rec} \geqslant r_{c,l}$ for all l (when using smooth pseudopotential cut-off functions, a reconstruction radius r_{rec} slightly larger than the largest $r_{c,l}$ must be used). The various reconstruction schemes differ by using different approximations for the determination of $\chi_{lm}^{kj}(r)$. In the first class of reconstruction schemes these expansion coefficients are calculated by solving the aspherical Kohn–Sham [23] equations for $\psi_{kj}(r)$ inside the reconstruction sphere numerically and self-consistently with the pseudopotential replaced by the electrostatic potential of the nucleus plus the core electrons and subject to appropriate supplementary conditions supplied by the pseudopotential calculation (section 2.2). In the second class of reconstruction schemes the radial functions $\chi_{lm}^{kj}(r)$ are represented approximately by a small number of suitably constructed basis functions (section 2.3).

2.2. Reconstruction by a numerical solution of the aspherical Kohn–Sham equations

In this reconstruction scheme the real wavefunction ψ_{kj} inside the reconstruction sphere is obtained from a self-consistent solution of the Kohn–Sham [23] equation

$$\left(-\frac{\hbar^2}{2m} \Delta + V_{eff}(r) \right) \psi_{kj}(r) = \varepsilon_{kj} \psi_{kj}(r). \tag{3}$$

Thereby $V_{eff}(r)$ is the true effective potential of the solid given by the Coulomb potentials of the nuclei and the Hartree potential V_H and the exchange–correlation potential V_{xc} of the core electron density n_c and the valence electron density n_v:

$$V_{eff}(r) = -\sum_{T,\alpha} \frac{Z_\alpha e^2}{|r - T - R_\alpha|} + V_H[n_c + n_v] + V_{xc}[n_c + n_v]. \tag{4}$$

Here α denotes the basis atoms in the unit cell, $Z_\alpha e$ the nuclear charge and T the translation vectors. Expanding ψ_{kj} into cubic harmonics $K_{lm}(\hat{r})$ according to equation (2) with $R_{lm}^{kj}(r) := r\chi_{lm}^{kj}(r)$, which gives

$$\psi_{kj}(r) = \frac{1}{\sqrt{N}} \sum_{lm} \frac{R_{lm}^{kj}(r)}{r} K_{lm}(\hat{r}) \tag{5}$$

the Kohn–Sham equation (3) transforms into a system of coupled ordinary second-order differential equations for the radial wavefunctions $R_{lm}^{kj}(r)$:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2}\right)\right] R_{lm}^{kj}(r) + \sum_{LM} \int K_{lm}(\hat{r}) V_{eff}(r) K_{LM}(\hat{r}) \, d^2\Omega \, R_{LM}^{kj}(r)$$
$$= \varepsilon_{kj} R_{lm}^{kj}(r). \tag{6}$$

This set of equations has to be solved self-consistently in an iteration cycle together with equation (4), because the valence electron density n_v occurring in equation (4) is given by

$$n_v(r) = \frac{1}{N} \sum_{kj} f_{kj} \sum_{L'M',LM} \frac{R_{LM}^{kj}(r)(R_{L'M'}^{kj}(r))^*}{r^2} K_{LM}(\hat{r}) K_{L'M'}(\hat{r}). \tag{7}$$

The core electron density n_c is given by the superposition of frozen atomic core densities. Apart from constant factors, the solutions $R_{lm}^{kj}(r)$ of equation (6) which are regular at $r = 0$ are totally determined for each iteration step by ε_{kj}. The constant factors may be obtained, for instance (see below), from the values of $R_{lm}^{kj}(r)$ at $r = r_{rec}$. Because within the limitations discussed above the energy of the pseudowavefunction is identical with the energy of the true wavefunction for $r \geqslant r_{rec}$, the true wavefunction inside the sphere may be constructed from the solution of equations (4), (6) and (7) with the supplementary conditions given by fixing ε_{kj} and $R_{lm}^{kj}(r_{rec})$ to the values obtained by the pseudopotential calculation, i.e. $R_{lm}^{kj}(r_{rec}) = \tilde{R}_{lm}^{kj}(r_{rec})$.

For a free atom the effective potential $V_{eff}(r)$ is spherically symmetric and the set of coupled equations (6) reduces to decoupled equations for the $R_l^j(r)$. Then $R_l^j(r)$ inside the core may be constructed from the solution of the respective equation with the information about ε_j and $R_l^j(r_{rec})$ or $(d/dr)R_l^j|_{r_{rec}}$ obtained by the pseudopotential calculation for the atom, as discussed already by Gardner and Holzwarth [24]. For an aspherical potential in a solid the whole set of equations (6) has to be considered.

There are two problems which arise when the general reconstruction scheme outlined in this section is transformed to a practical implementation scheme for the computer. The first problem is the coupling of an infinite number of differential equations (6). The second problem concerns the supplementary conditions and arises from the approximations involved in the pseudopotential scheme and from those introduced for the approximate solution of the coupled differential equations (6).

The first problem is removed by assuming that the asphericity of the effective potential in the sphere of radius r_{rec} is very weak, so that the effective potential can be replaced by the spherically averaged effective potential $V_{eff}^{(a)}(r)$:

$$V_{eff}^{(a)}(r) = \frac{1}{4\pi} \int V_{eff}(r) \, d^2\Omega. \tag{8}$$

Due to the orthonormality relations of the cubic harmonics, the set of coupled differential equations (6) then reduces to a set of decoupled differential equations

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2}\right) + V_{eff}^{(a)}(r)\right] R_{lm}^{kj}(r) = \varepsilon_{kj} R_{lm}^{kj}(r). \tag{9}$$

It should be noted that the situation is still much more complicated than in the case of a free atom, because there the true wavefunction and the pseudowavefunction have a well defined angular-momentum character l, so that only one equation of type (9) has to be solved. In contrast, the wavefunctions in a solid in principle contain all l, m components so that, for each eigenstate (kj), many equations of type (9) must be solved with different supplementary conditions, e.g. $R_{lm}^{kj}(r_{rec}) = \tilde{R}_{lm}^{kj}(r_{rec})$ for different l, m. It would be extremely hard to justify the neglect of the asphericity of the effective potential in the reconstruction sphere by analytical arguments. Therefore, in the present paper the procedure is justified *a posteriori* by the very good agreement between the EFG obtained in the present results and that found in all-electron calculations for a variety of different situations (section 3). Obviously, the asphericity of the wavefunctions in the reconstruction spheres is nearly exclusively determined by the aspherical boundary conditions, whereas the asphericity of the effective potential is negligibly small in the reconstruction spheres at least for metallic systems without covalent bonds. The results of section 3 show that this general statement is true, independent of the symmetry of the considered atomic site. The agreement with the all-electron data is equally good for the HCP materials and for the atoms near a vacancy in Na, which exhibit a different symmetry. In the meanwhile, we have also performed calculations of the EFG near a vacancy in Al, using a large supercell which contains many different sites with different symmetries, respectively. The agreement between the results of our reconstruction method and the data of an all-electron calculation is very good for all sites.

The second problem is related to the approximation involved in the whole procedure. If the pseudopotential calculations yielded the exact eigenvalues and the exact eigenfunctions for $r \geqslant r_{rec}$, and if equations (4), (6) and (7) were solved exactly, we could use any combination of two from the following set:

$$R_{lm}^{kj}(r_{rec}) = \tilde{R}_{lm}^{kj}(r_{rec}) \tag{10}$$

$$\frac{\mathrm{d}}{\mathrm{d}r} R_{lm}^{kj}(r_{rec}) = \frac{\mathrm{d}}{\mathrm{d}r} \tilde{R}_{lm}^{kj}(r_{rec}) \tag{11}$$

$$\varepsilon_{kj} = \tilde{\varepsilon}_{kj} \tag{12}$$

as supplementary conditions which determine the radial functions uniquely and all combinations would be equivalent. Instead of the energy ε_{kj} we can also prescribe the logarithmic derivative

$$L_{lm}^{kj} = \left(\frac{\mathrm{d}}{\mathrm{d}r} R_{lm}^{kj} \right) \Big/ R_{lm}^{kj} \tag{13}$$

at $r = r_{rec}$, i.e.

$$L_{lm}^{kj}(r_{rec}) = \tilde{L}_{lm}^{kj}(r_{rec}) \tag{14}$$

which, together with the number of nodes of the wavefunction ψ_{kj} (in the following we understand that equation (14) is always considered in combination with the number of nodes) uniquely determines the energy in equation (9). Because of the approximations involved in the pseudopotential calculation, however, none of these relations is fulfilled exactly. Furthermore, the decoupling of equations (6) via the assumption of a spherically symmetric effective potential for $r < r_c$ generates small errors in R_{lm}^{kj}, so that the reconstructed wavefunctions (5) calculated with these radial functions do not exactly correspond to the true eigenvalues ε_{kj}. As a result, the various possible combinations of supplementary conditions are no longer equivalent, and the question arises as to which of these combinations accounts for the various approximations in a most suitable way. For instance, because when

calculating the radial functions from the decoupled equations (9) the asphericity of ψ_{kj} *within the reconstruction sphere arises exclusively from the imposed boundary conditions* for $R_{lm}^{kj}(r)$, it seems to be reasonable to fix the values for the radial functions and their derivatives according to equations (10) and (11). Equations (9) then yield slightly different values for ε_{kj} for different l, m. Releasing the energy in this way might possibly, to some extent, correct the errors introduced by the spherical approximation for the effective potential inside the sphere. Finally, it should be noted that during the iteration cycle for the self-consistent solution of equations (4), (7), (8) and (9) the true effective potential is approached only gradually, and as a result not all supplementary conditions (10)–(12) can be fulfilled simultaneously. One of the consequences is that during the iteration cycle the number of electrons in the reconstruction sphere is not correct, giving rise to numerical instabilities via corresponding errors in the Hartree potential and the exchange–correlation potential. It therefore turns out to be extremely helpful to use the norm conservation for each l, m channel as one supplementary condition, i.e.

$$\int_0^{r_{rec}} |R_{lm}^{kj}(r)|^2 \, \mathrm{d}r = \int_0^{r_{rec}} |\tilde{R}_{lm}^{kj}(r)|^2 \, \mathrm{d}r. \tag{15}$$

When working with a norm-conserving pseudopotential [9–11] it is guaranteed that for a spherically symmetric situation the norm is conserved for each l channel which, however, does not necessarily mean that it is conserved also for each l, m channel in an aspherical situation. If we do not use equation (15) as one of the supplementary conditions, according to our experience we must at least correct the norm of the total wavefunction in each iteration step according to

$$\sum_{l,m} \int_0^{r_{rec}} |R_{lm}^{kj}(r)|^2 \, \mathrm{d}r = \sum_{l,m} \int_0^{r_{rec}} |\tilde{R}_{lm}^{kj}(r)|^2 \, \mathrm{d}r \tag{16}$$

in order to avoid numerical instabilities. This is achieved by multiplying all the radial functions R_{lm}^{kj} obtained by the same factor in such a way that equation (16) is fulfilled.

Altogether, it is not possible to select an optimum from the set of possible combinations of two out of equations (9)–(12) in an unambiguous way. It might even be that, for various situations, various optimum combinations apply. Choosing one set of combinations yields solutions for R_{lm}^{kj} and ε_{kj} which do not necessarily fulfil those equations from (10)–(12), (14) and (15) which were not explicitly used as supplementary conditions. The deviations can be considered as a test for the success and quality of the chosen reconstruction scheme. In our explicit calculations we have used the following combinations of supplementary conditions:

Reconstruction scheme 1: logarithmic derivative (14) and norm conservation for each l, m channel (15);

Reconstruction scheme 2: value of $R_{lm}^{kj}(r_{rec})$ and $(\mathrm{d}/\mathrm{d}r)R_{lm}^{kj}(r_{rec})$ according to (10) and (11) (in each iteration step the correct total norm is guaranteed by additionally imposing equation (16));

Reconstruction scheme 3: value of ε_{kj} (12) and norm conservation for each l, m channel (15);

Reconstruction scheme 4: value of ε_{kj} (12) and $R_{lm}^{kj}(r_{rec})$ (10) (in each iteration step the correct total norm is guaranteed by imposing in addition equation (16)).

The numerical effort thereby is considerably larger when releasing the energy than when fixing the energy.

It remains to evaluate the given pseudowavefunction into spherical harmonics (appendix A) in order to provide the information on $\tilde{R}_{lm}^{kj}(r_{rec})$ and $(\mathrm{d}/\mathrm{d}r)\tilde{R}_{lm}^{kj}(r_{rec})$ entering the supplementary conditions (10), (11), (15) and (16) and to calculate the effective potential $V_{eff}^{(a)}(r)$ given by equations (4) and (8) for each iteration step (appendix B). Finally, the Kohn–Sham equations (9) are solved by the predictor–corrector method of Adams, Bashforth and Moulton (see, e.g., [25]).

It should be noted that Vackář and Šimunek [26] solved the spherical Kohn–Sham equation for the spherically averaged effective potential $V_{eff}^{(a)}(r)$ in the reconstruction sphere with boundary conditions obtained from the spherical average of the l component of the pseudocharge density of the crystal. In this way, they obtained the 'averaged' l-dependent node structure of all crystal orbitals, but of course they were not able to describe correctly the asphericity of the charge density in the reconstruction sphere which is needed for a calculation of the EFG.

2.3. Reconstruction by suitably constructed basic functions

Instead of calculating the expansion coefficients $\chi_{lm}^{kj} = R_{lm}^{kj}/r$ by integrating the Kohn–Sham equations numerically in a reconstruction sphere subject to appropriate supplementary conditions, we can also choose appropriate trial functions for χ_{lm}^{kj}. To do this, the $\chi_{lm}^{kj}(r)$ are represented by a set of radial basis functions $B_{l,n}(r)$:

$$\chi_{lm}^{kj}(r) = \sum_n C_{lm,n}^{kj} B_{l,n}(r). \tag{17}$$

Analogously, we can expand $\tilde{\chi}_{lm}^{kj}(r)$ into a set of radial basis functions $\tilde{B}_{l,n}(r)$:

$$\tilde{\chi}_{lm}^{kj}(r) = \sum_n \tilde{C}_{lm,n}^{kj} \tilde{B}_{l,n}(r). \tag{18}$$

The sets may be complete, for instance the all-electron atomic single-particle eigenfunctions $\{\phi_{l,n}(r)\}$, the atomic pseudowavefunctions $\{\tilde{\phi}_{l,n}(r)\}$ or the Bessel functions $\{j_l(|k+G_n|r)\}$ used in equation (A3), and they may be even over-complete, for instance a mixed basis [27, 28] $\{j_l(|k+G_n|r), f_{0l}(r)\}$, where $f_{0l}(r)$ is a function localized at the basis atom under consideration for the reconstruction. For practical reasons, however, the representations (17) and (18) must be terminated at a finite value of $n = n_{max}$.

In the reconstruction scheme presented in this section we use the (in principle) overcomplete set $\{j_l(|k+G_n|r), f_{0l}(r)\}$ according to equation (A3) for the representation of the expansion coefficients $\tilde{\chi}_{lm}^{kj}(r)$ of the pseudowavefunction. Inside the reconstruction sphere we then replace $\tilde{\chi}_{lm}^{kj}$ by an approximation for χ_{lm}^{kj} based on a representation of type (17) with just two basis functions:

$$\chi_{lm}^{kj}(r) = C_{lm,1}^{kj} \phi_l(E) + C_{lm,2}^{kj} \dot{\phi}_l(E). \tag{19}$$

Here, $\phi_l(E)$ is the solution of the Kohn–Sham equation

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} \right) + V_{eff}^{(a)}(r) \right] \phi_l(E) = E\phi_l(E) \tag{20}$$

for a prescribed energy E, normalized in the reconstruction sphere, i.e.

$$\int_0^{r_{rec}} |\phi_l(r)|^2 \, \mathrm{d}r = 1. \tag{21}$$

$\dot{\phi}_l(E)$ is the derivative of $\phi_l(E)$ with respect to the energy, $\dot{\phi}_l(E) = (\mathrm{d}/\mathrm{d}E)\phi_l(E)$, and can be obtained from the equation

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} \right) + V_{eff}^{(a)}(r) \right] \dot{\phi}_l(r) = E\dot{\phi}_l(r) + \phi_l(r). \tag{22}$$

Thereby, $V_{eff}^{(a)}$ denotes the spherically averaged effective potential as in section 2.1, which has to be calculated according to appendix B in each iteration step. These two basis functions are well known from the APW [2, 5, 6] and the LMTO [5] method. They may be evaluated at the centre $\tilde{\varepsilon}_l$ of the respective l band in the crystal, as in the LAPW [5, 6] and in the LMTO [5] methods, or at the eigenvalue $\tilde{\varepsilon}_{kj}$ of the pseudowavefunction $\tilde{\psi}_{kj}(r)$ which is considered for the reconstruction, as in the APW method of Soler and Williams [2]. Note that in both cases we just fix the energy for the construction of the two basis functions which, of course, does not mean that the energy of the wavefunction ψ_{kj} of equation (2) reconstructed by the use of equation (19) does coincide with this prescribed energy for the basis functions. We therefore can again use any combination of two out of the set of supplementary conditions (10)–(12) and (15) to determine the coefficients $C_{lm,1}^{kj}$ and $C_{lm,2}^{kj}$ of equation (19). We have used the following combinations of supplementary conditions:

Reconstruction scheme 5: logarithmic derivative (14) and norm conservation for each l, m channel (15) (basis functions evaluated at $\tilde{\varepsilon}_{kj}$);

Reconstruction scheme 6: value of $R_{lm}^{kj}(r_{rec})$ and $(\mathrm{d}/\mathrm{d}r)R_{lm}^{kj}(r_{rec})$ according to (10) and (11) (basis functions evaluated at $\tilde{\varepsilon}_{kj}$; in each iteration step the correct total norm is guaranteed by additionally imposing equation (16));

Reconstruction scheme 7: supplementary conditions as in reconstruction scheme 5, with basis functions evaluated at $\tilde{\varepsilon}_l$;

Reconstruction scheme 8: supplementary conditions as in reconstruction scheme 6, with basis functions evaluated at $\tilde{\varepsilon}_l$.

We now compare the numerical effort of the reconstruction schemes outlined in sections 2.1 and 2.2. For reconstruction schemes 1 and 2 or reconstruction schemes 3 and 4 we must solve $\sum_{l=0}^{l_{max}}(2l+1) = (l_{max}+1)^2$ or $l_{max}+1$ radial Kohn–Sham equations (9), respectively, when evaluating the wavefunction up to l_{max}. In the second class of schemes (reconstruction schemes 5–8) we must solve $l_{max}+1$ radial Kohn–Sham equations (20) for ϕ_l and $l_{max}+1$ radial equations (22) for $\dot{\phi}_l$. For $l_{max} = 2$, 3 or 4 this means six, eight or ten calculations. Furthermore, if we represent the reconstructed valence charge density $n_v(r)$ by N wavefunctions ψ_{kj} according to equation (7), we have to repeat these solutions of single-particle equations N times, both in the first class of schemes and in the second class of schemes when evaluating the basic functions at $\tilde{\varepsilon}_{kj}$. However, if we evaluate them always at the centre of gravity $\tilde{\varepsilon}_{kj}$, we do not need to do this. Whereas the computer time spent for the solution of single-particle equations scales like $N(l_{max}+1)^2$ for reconstruction schemes 1 and 2, it scales like $l_{max}+1$ in the second class of schemes when evaluating at $\tilde{\varepsilon}_l$. It will be shown in section 3 that the accuracy of the calculations is nearly unaffected when using $\tilde{\varepsilon}_l$ instead of $\tilde{\varepsilon}_{kj}$, which is to be expected from the success of the LAPW method where the basis functions are also evaluated at $\tilde{\varepsilon}_l$. Finally, it will be demonstrated in section 3 that it is not necessary probably in most cases to iterate the solutions of the Kohn–Sham equations to self-consistency during the reconstruction cycle, but it is sufficient to perform the whole calculation only for the potential $V_{eff}^{(a)}$ obtained from the spherically averaged pseudocharge density or from a superposition of all-electron densities of free atoms.

It should be noted that in the reconstruction scheme described in this section the pseudowavefunction and the reconstructed wavefunction are not handled on equal footing. Whereas the expansion coefficients $\tilde{\chi}_{lm}^{kj} = \tilde{R}_{lm}^{kj}/r$ of the pseudowavefunction are more or less exactly evaluated into Bessel functions according to equation (A3), the corresponding coefficients χ_{lm}^{kj} of the reconstructed wavefunction are approximately represented by the two basis functions ϕ_l and $\dot{\phi}_l$. Van der Walle and Blöchl [29] have circumvented this problem. They made the expansions (17) and (18) for the reconstructed wavefunction and the pseudowavefunction in a completely analogous way using the solutions of the radial Kohn–Sham equations for the isolated atom or for the isolated pseudoatom, respectively, as radial basis functions $B_{l,n}(r)$ and $\tilde{B}_{l,n}(r)$. The expansion coefficients $C_{lm,n}^{kj}$ and $\tilde{C}_{lm,n}^{kj}$ are identical, because the wavefunctions of the atom and the pseudoatom coincide for $r \geqslant r_{c,l}$ (see section 2.1), and they are determined by a projector formalism.

3. Calculation of electric field gradients

In this section the reconstruction schemes 1–8 are tested by calculating the EFGs for regular atomic sites in some hexagonal metals and for atoms near a vacancy in Na.

The electrostatic potential $\phi(r)$ at site r in the crystal is given by the solution of Poisson's equation for the total charge density $\rho(r)$:

$$\rho(r) = e \sum_{T,\alpha} Z_\alpha^{ion} \delta(r - T - R_\alpha) - e n_v(r). \tag{23}$$

Because the core charge densities are spherically symmetric around the nuclear sites they can be replaced by point charges when calculating the potential at a nuclear site. Therefore, by the first term of equation (23) we have described the ionic cores, i.e. the combined effect of the nuclear charges and the core charges by point charges of size $Z_\alpha^{ion} e$. Accordingly, the traceless tensor of the EFG at site $\alpha = 0$ in the unit cell,

$$V_{ij} = \frac{\partial^2 \phi}{\partial x_i \partial x_j}\bigg|_{R_\alpha=0} - \tfrac{1}{3}\delta_{ij}\Delta\phi\bigg|_{R_\alpha=0} \tag{24}$$

consists of an ionic part

$$V_{ij}^{ion} = e \sum_{\substack{T,\alpha \\ \alpha\neq 0 \text{ for } T=0}} Z_\alpha^{ion} \left[\frac{3(T+\cdot R_\alpha)_i \cdot (T + R_\alpha)_j}{|T + R_\alpha|^5} - \frac{\delta_{ij}}{|T + R_\alpha|^3} \right] \tag{25}$$

and a contribution of the valence charge density given by

$$V_{ij}^{val} = -e \int n_v(r') \left(3\frac{x_i' x_j'}{r'^5} - \frac{\delta_{ij}}{r'^3} \right) \mathrm{d}^3 r'. \tag{26}$$

Because the term in large parentheses in equation (26) may be represented by a linear combination of cubic harmonics $K_{2,m}$, we only need the $2, m$ components of $n_v(r)$ (see appendix C), which may be obtained from equation (7) as

$$n_{v,2m}(r) = \frac{1}{N} \cdot \sum_{kj} f_{kj} \sum_{L'M',LM} G_{LM,L'M'}^{2m} \frac{R_{LM}^{kj}(r)(R_{L'M'}^{kj}(r))^*}{r^2} \tag{27}$$

with the Gaunt coefficients

$$G_{LM,L'M'}^{2m} = \int K_{2m}(\hat{r}) K_{LM}(\hat{r}) K_{L'M'}(\hat{r}) \, \mathrm{d}^2\Omega \tag{28}$$

for which $G^{2m}_{LM,L'M'} \neq 0$ for

$$\left.\begin{array}{l} |L - L'| \leqslant l \leqslant L + L' \text{ in steps of } 2 \\ m = \pm M \pm M'. \end{array}\right\} \tag{29}$$

Accordingly, the $2m$ components of $n_v(r)$ are composed of products of angular momentum contributions s–d, p–p, p–f, d–d, d–g, etc, whereby the p–p contributions are dominant in most cases [15].

Because V_{ij} is a symmetric tensor, it may be diagonalized, and the components in the new reference frame V^{diag}_{ij} are denoted according to

$$|V^{diag}_{zz}| \geqslant |V^{diag}_{yy}| \geqslant |V^{diag}_{xx}|. \tag{30}$$

Because V_{ij} and V^{diag}_{ij} are traceless tensors, there are only two independent components, for instance V^{diag}_{zz} and the asymmetry parameter

$$\eta = \frac{V^{diag}_{yy} - V^{diag}_{xx}}{V^{diag}_{zz}}. \tag{31}$$

It should be noted that for all systems discussed in section 3 (hexagonal metals; atoms near a vacancy in BCC Na for a 15-atom supercell) the asymmetry parameter is zero *for symmetry reasons. In the meanwhile we have performed calculations for atoms near a vacancy in Al for a larger supercell (the results will be published elsewhere) and there is good agreement for the asymmetry parameters* η *on the various sites between our reconstruction methods and an all-electron calculation.*

3.1. Hexagonal metals

In hexagonal systems the electronic density $n(r)$ exhibits the angular-momentum components $lm = 00$, 20, and higher-order components. According to equations (C1)–(C6), there is only one independent component, and the asymmetry parameter η is zero.

The pseudopotentials for Be, Mg, Ti and Zr are constructed according to Vanderbilt [11]. For Be and Mg a plane-wave basic set, and for Ti and Zr a mixed basis composed of plane waves and five localized d orbitals per atom is applied. For Ti and Zr (Be and Mg) 462 (945) k-points are used in the irreducible part of the Brillouin zone. All calculations are performed for the experimental lattice parameters.

Tables 1, 2, 3 and 4 represent the results for V_{zz} for Be, Mg, Ti and Zr, respectively, obtained from the reconstruction schemes 1–8. The results found when proceeding with the reconstruction up to full self-consistency are compared with the data obtained when the procedure is performed for the potential $V^{(a)}_{eff}$ from the spherically averaged pseudocharge density or from a simple superposition of all-electron atomic charge densities. In the upper (lower) block of each table the results are presented for reconstruction schemes with norm conservation for each l, m channel (norm conservation only for the total charge).

Several tendencies become obvious from tables 1–4.

(i) The values from reconstruction schemes with norm conservation for each l, m channel are slightly smaller than those with norm conservation only for the total charge.

(ii) Reconstruction schemes 3 and 4, which solve the Kohn–Sham equations numerically while fixing the energy seem to produce the least reliable results.

(iii) All the other reconstruction schemes, namely 1, 2 and 5–8 yield very similar values for the EFG.

Table 1. Values of V_{zz} obtained for Be by the reconstruction schemes 1–8. The effective potential in the reconstruction sphere is determined self-consistently (first column), by superposition of atomic densities (second column) or taken from the pseudopotential calculation (third column).

Reconstruction scheme	V_{zz} (10^{13} esu cm^{-3})		
	Self-consistently	From atomic densities	From pseudocharge densities
1	−2.094	−2.070	−2.110
5	−2.094	−2.070	−2.110
7	−2.094	−2.070	−2.110
3	−2.003	−1.976	−2.026
2	−2.170	−2.138	−2.193
6	−2.170	−2.136	−2.191
8	−2.170	−2.136	−2.193
4	−1.950	−1.912	−1.985

Table 2. Same as table 1 for Mg.

Reconstruction scheme	V_{zz} (10^{13} esu cm^{-3})		
	Self-consistently	From atomic densities	From pseudocharge densities
1	1.112	1.111	1.091
5	1.112	1.111	1.091
7	1.107	1.106	1.088
3	1.108	1.107	1.089
2	1.117	1.119	1.097
6	1.118	1.119	1.097
8	1.111	1.112	1.093
4	1.118	1.116	1.106

Table 3. Same as table 1 for Ti.

Reconstruction scheme	V_{zz} (10^{13} esu cm^{-3})		
	Self-consistently	From atomic densities	From pseudocharge densities
1	62.17	61.42	62.85
5	62.20	60.65	62.88
7	61.94	59.92	62.80
3	62.35	57.71	64.49
2	64.31	62.51	66.06
6	64.37	60.95	66.08
8	63.84	59.54	65.95
4	63.69	51.78	72.70

(iv) The EFGs are nearly unaffected when evaluating the basic functions ϕ_l and $\dot{\phi}_l$ at the band centre $\tilde{\varepsilon}_l$ instead of evaluation at ε_{kj}.

(v) The EFGs are also nearly unaffected when performing the reconstruction for the potential $V_{eff}^{(a)}$ obtained from a superposition of all-electron atomic charge densities or from

Table 4. Same as table 1 for Zr.

Reconstruction scheme	V_{zz} (10^{13} esu cm^{-3})		
	Self-consistently	From atomic densities	From pseudocharge densities
1	107.9	109.2	106.9
5	107.6	107.8	106.8
7	106.9	106.5	106.3
3	111.9	113.7	111.0
2	119.6	122.5	117.9
6	119.0	119.9	117.7
8	117.8	117.6	116.9
4	123.2 —	123.3	124.4

pseudocharge densities.

Altogether, this suggests that the fast reconstruction schemes 7 and 8 can be used with a non-self-consistent potential $V_{eff}^{(a)}$ in all situations which do not seem to be extremely critical on physical grounds.

In table 5 we compare the results obtained by our pseudopotential calculation and by the reconstruction schemes with those from a full-potential LAPW calculation [15], from our own full-potential LMTO calculation and from experiments. The LMTO calculations are performed with the code described in [30]. The sphere radii are given by the muffin-tin radii, and the highest core states of the respective free atoms are treated via a second κ^2-value in the same band as the other valence states when performing the calculation for the crystal. All the energetically lower-lying states are treated as true core states. The comparison with the LAPW and LMTO calculations should be considered with some caution. First, the convergence with respect to the number of k-points and with respect to the convergence parameters of the various methods is certainly different. For instance, for Mg we used up to 945 k-points in the irreducible Brillouin zone and still were far from convergence, whereas the LAPW result [15] was for 800 k-points. Second, the pseudopotential calculation and the reconstruction schemes are for frozen cores, whereas the highest 'core' states are treated as semicore states in the LAPW calculation and as valence states in the LMTO calculation. In most cases, the contribution of these high-lying 'core' states is small [15], but it amounts to about 10% in Zr. As discussed below, these slight differences in the various calculational methods are not relevant when considering materials such as Ti or Zr with moderate or large EFGs whereas for the systems Be and Mg the EFGs are very small so that extremely accurate calculations, for instance considerably more k-values, would be required in order to obtain consistency with the experiments. Because the primary concern of the paper is not to reproduce the experimental data but to demonstrate the agreement between the results of the reconstruction method and all-electron methods we did not go far beyond the number of k-points used in the FLAPW calculation [15] with which we compare. The comparison with experimental data is even more critical. First, the experimentally measured quantity is the product of V_{zz} and the nuclear quadrupole moment, which exhibits uncertainties in its numerical value of typically 10–20%. Second, the calculations are for lattice parameters at room temperature, but the results should be compared with experimental data at low temperatures, because the effective EFG sometimes strongly depends on the temperature [16]. Thereby the temperature variation in the lattice parameters does not correctly account for this temperature dependence, as has been demonstrated [31] for the case of Zn.

Table 5. Values of V_{zz} for Be, Mg, Ti and Zr as obtained by the reconstruction schemes 1–8 (self-consistent potential) in comparison with values from the pure pseudopotential calculation without reconstruction, from full-potential LMTO and LAPW calculations and from experiments.

	V_{zz} (10^{13} esu cm^{-3})			
	Be	Mg	Ti	Zr
Pseudopotential	−1.95	0.140	19.6	2.45
Rec. scheme 1	−2.09	1.11	62.2	108
Rec. scheme 5	−2.09	1.11	62.2	108
Rec. scheme 7	−2.09	1.11	61.9	107
Rec. scheme 2	−2.17	1.12	64.3	120
Rec. scheme 6	−2.17	1.12	64.4	119
Rec. scheme 8	−2.17	1.11	63.8	118
LMTO	−1.7	1.2	57	133
LAPW [15]	−2.1 [37]	1.6	69	143
Experiments	±1.6 at 77 K [32]	±2.0 at 4.2 K [33]	±54 at 4.2 K [34]	±123 at 4.2 K [35]

Table 6. Values of V_{zz}^{diag} for atoms close to a vacancy in Na as obtained by the pure pseudopotential calculation without reconstruction, by the reconstruction schemes and by the LAPW calculation.

	V_{zz}^{diag} (10^{13} esu cm^{-3})		
	Nearest neighbour	Next-nearest neighbour	Third-nearest neighbour
Pseudopotential	0.27	0.86	0.26
Reconstruction schemes 1–8	8.1–8.2	8.4–8.5	4.1–4.2
LAPW [31]	8.2	8.3	4.1

From table 5 it becomes obvious that the agreement of the reconstructed values with those from LMTO, LAPW and experiments is satisfactory for Ti and Zr, which exhibit moderate to large EFGs. For Be and Mg the values of V_{zz} are very small, and there are stronger discrepancies among the theoretical results and between theory and experiments. For instance, for Mg the reconstructed values agree perfectly with the result of the LMTO calculation which is smaller than the V_{zz}-value of the LAPW calculation (which used even fewer k-points) and considerably smaller than the experimental value. For Be the pure pseudopotential result is nearly identical with the reconstructed value, because the dominant p–p contribution to V_{zz} corresponds to nodeless p wavefunctions. In contrast, for Mg, Ti and Zr the p wavefunctions exhibit nodes and therefore the reconstruction is indispensable.

3.2. Vacancy in Na

We have calculated the EFGs on atoms near a vacancy in BCC Na for a supercell containing 15 atoms by reconstructing the true wavefunctions from the pseudowavefunctions obtained in [21] and, for comparison, by the full-potential LAPW method [36, 31], taking into account the structural relaxation of the atoms around the vacancy. Because of the small supercell size the results cannot be directly compared with experimental data, the emphasis is on the comparison between pure pseudopotential results, reconstructed results and LAPW results.

From table 6 it becomes obvious that the reconstruction of the true wavefunction from the pseudowavefunction is indispensable (see note added in proof to [21]), because the 3p wavefunctions exhibit a node. Furthermore, there is nearly perfect agreement between the reconstructed data and the LAPW data, demonstrating the power of the reconstruction method for the calculation of EFGs near atomic defects.

Acknowledgments

Appendix A

In systems with hard pseudopotentials it is often appropriate [27, 28] to use a basis set of plane waves and a small number of non-overlapping functions $\varphi_{\alpha lm}$ localized at the basis atoms R_α in the elementary unit cells:

$$\tilde{\psi}_{kj}(r) = \frac{1}{\sqrt{\Omega}} \sum_G \tilde{\psi}_G^{kj} \exp[i(k+G)\cdot r]$$
$$+\frac{1}{\sqrt{N}} \sum_{\alpha,l,m} \tilde{\beta}_{\alpha lm}^{kj} \sum_T \exp[ik\cdot(T+R_\alpha)]\varphi_{\alpha lm}(r-T-R_\alpha) \qquad (A1)$$

with

$$\varphi_{\alpha lm}(r') = i^l f_{\alpha l}(r') K_{lm}(\hat{r}') \qquad r' = r - T - R_\alpha \qquad (A2)$$

where T is the translation vector.

Expanding the plane waves into cubic harmonics using the Bessel functions j_l yields inside the reconstruction sphere of the basis atom at R_0:

$$\tilde{R}_{lm}^{kj}(r) = r\tilde{\chi}_{lm}^{kj}(r) = 4\pi i^l \exp(ik\cdot R_0) \qquad (A3)$$
$$\times \left(\frac{1}{\sqrt{\Omega_c}} \sum_G \tilde{\psi}_G^{kj} \exp(iG\cdot R_0) j_l(|k+G|r) K_{lm}(\widehat{k+G}) + \tilde{\beta}_{0lm}^{kj}\frac{f_{0l}(r)}{4\pi}\right)r.$$

Appendix B

In this appendix the calculation of the spherical part $V_{eff}^{(a)}(r)$ of the effective potential given by

$$V_{eff}^{(a)}(r) = -\sum_{T,\alpha} \frac{Z_\alpha e^2}{|r-T-R_\alpha|} + V_H[n_c] + V_H[n_v] + V_{XC}[n_c+n_v] \qquad (B1)$$

is described.

Because of the spherical charge distribution, the potential V^{ion} generated outside the sphere around the entire core by the nuclear charge and by the core charge density n_c inside the sphere (the first two terms in (B1)) is identical with the potential generated by the ionic pseudopotential outside the sphere. Therefore, the ionic pseudopotential at the surface of the sphere (which is provided by the pseudopotential calculation) may serve as Dirichlet's boundary condition for the solution of Poisson's equation inside the sphere. It should be cautioned, however, that in a pseudopotential calculation a homogeneous negative

background charge density $-(e/\Omega_c)\sum_\alpha Z_\alpha^V$ is added to the sum of the nuclear and the electronic core charge density, where eZ_α^V is the charge of the nucleus plus electronic charge and α denotes the basis atoms in the unit cell of volume Ω_c. This homogeneous background density compensates the average positive nuclear and electronic core density n_c which would generate a singular potential everywhere. Analogously, a homogeneous positive background charge density of the same magnitude is added to the electronic valence charge density n_v to compensate the average negative valence charge density. In order to match the potentials inside the sphere correctly to those at the sphere boundary obtained by the pseudopotential calculation, we must add the same background charge densities also for the solution of Poisson's equation inside the sphere during the reconstruction, i.e. we must solve Poisson's equation

$$\Delta V^{ion} = 4\pi e^2 Z_{\alpha=0}\delta(r - R_{\alpha=0}) - e^2 n_c(r) - \frac{e^2}{\Omega_c}\sum_\alpha Z_\alpha^v. \tag{B2}$$

The whole procedure, however, is only meaningful if the sphere includes all the core charge density. Because the extension of the ionic core in many cases is larger than the maximum $r_{c,l}$ and hence larger than r_{rec}, it is necessary to use a sphere with a sufficiently large radius r_{match} for the calculation of V^{ion}.

For frozen cores the potential V^{ion} has to be calculated only once at the beginning of the whole reconstruction cycle. In contrast, $V_H[n_v]$ must be evaluated for each iteration step from the valence electron density of the preceding step. Again, $V_H[n_c]$ is determined by solving Poisson's equation

$$\Delta V_H[n_v] = -4\pi e^2 n_v(r) + \frac{4\pi e^2}{\Omega_c}\sum_\alpha Z_\alpha^v \tag{B3}$$

subject to appropriate boundary conditions determined by the pseudopotential calculation. The Hartree potential at the surface of the sphere thereby is determined by the valence charge density in the sphere and outside the sphere. Outside the spheres the pseudowavefunction is identical with the true wavefunction and thus yields the same contribution to the Hartree potential at the surface. Inside the sphere the corresponding charge densities are different, yielding different potentials. However, because the number of electrons in the sphere is conserved in the pseudopotential calculation, the monopole contribution $V_H^{l,m=0}$ of the representation of V_H in terms of cubic harmonics, which defines the spherically averaged potential $V_H^{(a)}[n_v]$, is also conserved. This quantity therefore is calculated from the $l, m = 0$ part of Poisson's equation (B3) with the $l, m = 0$ component of the Hartree potential obtained by the pseudopotential calculation as Dirichlet's boundary condition.

The exchange–correlation potential $V_{xc}[n_c + n_v]$ is directly calculated at any site.

Altogether, the spherically averaged effective potential $V_{eff}^{(a)}(r)$ in the sphere α is given by

$$V_{eff}^{(a)}(r) = -\frac{e^2 Z_{\alpha=0}}{r} - 4\pi e^2 \left(\int_0^r \frac{r'^2}{r} n^{(a)}(r')\,dr' + \int_r^{r_{rec}} r' n^{(a)}(r')\,dr' \right)$$
$$+ V_{boundary} + V_{xc}^{(a)}[n^{(a)}] \tag{B4}$$

with

$$V_{boundary} = \frac{e^2(Z_{\alpha=0} - Z_{match}^c)}{r_{match}} - \frac{e^2 Z_{rec}^v}{r_{rec}} + \frac{4\pi}{6}\frac{e^2}{\Omega_c}\sum_\alpha Z_\alpha^V (r_{match}^2 - r_{rec}^2)$$
$$+ 4\pi e^2 \int_{r_{rec}}^{r_{match}} r' n_c(r')\,dr' + V_H^{(a)}(r_{rec}) + V_{ion}^{(a)}(r_{match}) \tag{B5}$$

$$n^{(a)}(r) = n_c(r) + n_v^{(a)}(r) \tag{B6}$$

$$Z_{rec}^{v} = 4\pi \int_{0}^{r_{rec}} r'^{2} n_{v}^{(a)}(r')\,dr' \tag{B7}$$

$$Z_{match}^{c} = 4\pi \int_{0}^{r_{match}} r'^{2} n_{c}(r')\,dr'. \tag{B8}$$

Appendix C

From equation (26) the following expressions for the tensor V_{ij} are obtained:

$$V_{xx} = -e\sqrt{\frac{4\pi}{5}} \int \frac{n(r')}{r'^{3}}(-K_{20}(\hat{r}') + \sqrt{3}K_{22}(\hat{r}'))\,d^{3}r' \tag{C1}$$

$$V_{yy} = -e\sqrt{\frac{4\pi}{5}} \int \frac{n(r')}{r'^{3}}(-K_{20}(\hat{r}') - \sqrt{3}K_{22}(\hat{r}'))\,d^{3}r' \tag{C2}$$

$$V_{zz} = -e\sqrt{\frac{4\pi}{5}} \int \frac{n(r')}{r'^{3}}2K_{20}(\hat{r}')\,d^{3}r' \tag{C3}$$

$$V_{xy} = -e\sqrt{\frac{12\pi}{5}} \int \frac{n(r')}{r'^{3}}K_{2\,-2}(\hat{r}')\,d^{3}r' \tag{C4}$$

$$V_{xz} = -e\sqrt{\frac{12\pi}{5}} \int \frac{n(r')}{r'^{3}}K_{21}(\hat{r}')\,d^{3}r' \tag{C5}$$

$$V_{yz} = -e\sqrt{\frac{12\pi}{5}} \int \frac{n(r')}{r'^{3}}K_{2\,-1}(\hat{r}')\,d^{3}r'. \tag{C6}$$

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