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# Modelling the valence electronic structure of the core region of an atom in a solid within a local-density approximation pseudopotential framework: reintroduction of the full nodal form

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**Abstract.** A method for calculating all-electron wavefunctions within the pseudopotential framework is presented. The phase-shift technique is used to construct valence wavefunctions with the proper node structure in a core region, matching the self-consistent partial pseudo-charge density that has been yielded by pseudopotential calculation in a solid. Making use of the total pseudo-charge density and the electrostatic potential of the pseudopotential calculation, the atomic-like all-electron calculation is performed.

Pseudopotentials, eliminating the need to include core electrons and strong potentials, greatly simplify *ab-initio* electronic structure calculations and *ab-initio* calculations of the structural properties of solids (see, e.g., [1–6]). They produce nodeless valence wavefunctions—pseudo-functions—providing the correct description of bonding within pseudopotential formalism and reproducing all-electron electronic structure calculations with a high degree of accuracy.

On the other hand, for many applications, where matrix elements between core and valence states are necessary, the nodeless pseudo-functions (eigenfunctions of the pseudo-Hamiltonian) cannot be directly employed [7, 8]. The first way of getting round this problem has already been introduced by Van de Walle and Blöchl [7]. In this paper, we present a procedure making it possible to include the proper node structure of originally nodeless valence pseudo-wavefunctions together with the core states in a fully consistent way and to gain the all-electron information from pseudopotential quantities.

The method is based on the following. If the pseudopotential is generated for the cut-off radius  $R_C$ , then the self-consistent pseudopotential quantities are correct outside a sphere of radius  $R_C$  surrounding an atom, and they can be used as boundary conditions to calculate the corresponding atom-like quantities inside this sphere. Moreover, if the pseudopotential is norm conserving, then the amount of pseudo-charge inside the sphere is correct, which yields a simple normalization condition for reconstructed valence wavefunctions with the proper node structure.

The present procedure consists in accomplishing two steps. First, we perform the self-consistent pseudopotential calculation of the pseudo-charge density  $\rho^{\text{PS}}(\mathbf{r})$  in a crystal and determine the spherical average of angular-momentum  $l$ -components  $\rho_l^{\text{PS}}(r)$  with respect to each atom, for  $r \leq R_C$ , where the number of  $l$ -components corresponds to the number of

angular-momentum components of atomic pseudopotential. It is obvious that the sum of  $\rho_i^{\text{PS}}(r)$  taken into account should be nearly equal to  $\rho^{\text{PS}}(r)$  for  $r \leq R_C$ . In the second step, we perform the self-consistent atomic-like calculation using the  $\rho_i^{\text{PS}}(r)$  as the boundary and normalization condition mentioned above. It differs from the standard LDA calculation of electronic states of an atom in three points:

- (i) determining the boundary condition for valence radial wavefunctions,
- (ii) calculating the valence charge density and
- (iii) solving the Poisson equation.

(i) Let  $\Phi_i^{\text{PS}}(r)$  denote the radial pseudo-function corresponding to the spherical average of the partial charge density which is related to a given atom:

$$\Phi_i^{\text{PS}}(r) = [\rho_i^{\text{PS}}(r)]^{1/2} = \left( \sum_{m=-l}^l \langle \psi^{\text{PS}} | Y_{lm} \rangle \langle Y_{lm} | \psi^{\text{PS}} \rangle \right)^{1/2} \quad (1)$$

where  $|\psi^{\text{PS}}\rangle$  is a self-consistent pseudo-function in a crystal and  $|Y_{lm}\rangle$  denotes spherical harmonics. We require the atomic-like valence wavefunctions  $\psi_l(r)$  to match  $\Phi_i^{\text{PS}}$  at the radius  $R_A$ , the 'augmentation' radius, which we suppose to be equal to  $R_C$ . By means of the logarithmic derivative, this requirement is

$$(d/dr)\{\ln[r\psi_l(r)]\} = (d/dr)\{\ln[r\Phi_i^{\text{PS}}(r)]\}|_{r=R_A} \quad (2)$$

and it replaces the boundary condition of the radial Schrödinger equation. Since applying this condition is not possible directly because of numerical instabilities, the phase-shift technique [9] is used to calculate the radial wavefunction satisfying this boundary condition and having the correct number of nodes. The normalization condition for  $\psi_l(r)$  given by

$$\int_0^{R_A} |\psi_l(r)|^2 r^2 dr = \int_0^{R_A} [\Phi_i^{\text{PS}}(r)]^2 r^2 dr \quad (3)$$

is a consequence of the norm-conserving property of the pseudopotential. As regards the core electronic states, there is no difference from the standard atomic calculation; the core wavefunctions are normalizable in the usual way.

(ii) Now let us consider calculation of the charge density. For the core states,

$$\rho_{\text{core}}(r) = \sum_{\text{core}} n_i |\psi_i(r)|^2 \quad (4)$$

as in the standard atomic calculation. However, this cannot be used for the valence states, since (owing to the boundary condition (2)) the radial wavefunctions are (generally) divergent beyond the radius  $R_A$ . This is not relevant to calculating the valence wavefunctions themselves, because the charge density outside the sphere of radius  $R_A$  does not affect them at all. Nevertheless, the charge density in this region must be well defined with respect to determining the exchange–correlation potential for calculating the core states, although the effect of the particular shape of the charge density in the outer region upon the core functions is very slight. We use the simple prescription

$$\rho_{\text{val}}(r) = \begin{cases} \sum_{\text{val}} n_i |\psi_i(r)|^2 & r \leq R_A \\ \int \frac{\rho^{\text{PS}}[r(r, \vartheta, \varphi)] \sin \vartheta d\vartheta d\varphi}{4\pi} & R_A < r \leq R_M \\ \rho_{\text{val}}(R_M) & r > R_M \end{cases} \quad (5)$$

where  $R_M$  is some maximum reasonable radius greater than  $R_A$ . It should not be greater than one half of interatomic distance (or the 'muffin-tin' radius), but this point is not crucial at all, for the reasons described above. Since the constant value of the charge density beyond  $R_M$  does not affect any relevant quantity except for the exchange–correlation potential used for calculating the core wavefunctions, which are vanishing in this region anyway, changing this term could result in changing the corresponding eigenvalues only, which is not relevant to further calculations.

(iii) The last question that should be discussed here is calculation of the electrostatic (Hartree) potential  $V_H$ , because we have no boundary condition for solving the Poisson equation in the usual way. Therefore, we make use of the linearity of this equation and split it into the core and the valence parts, solving the Poisson equation for each part separately with different boundary conditions. We calculate the 'core Hartree' potential  $V_{H \text{ core}}$  as a solution of the Poisson equation with  $\rho_{\text{core}}$ , satisfying the boundary condition

$$V_{H \text{ core}}(r) \rightarrow Z_{\text{core}}/r \text{ for } r \rightarrow \infty \quad (6)$$

and the 'valence Hartree' potential  $V_{H \text{ val}}$  as a solution with  $\rho_{\text{val}}$  inside the sphere of radius  $R_A$  matching the spherical average of the electrostatic potential  $V_H^{\text{PS}}(r)$  taken from self-consistent pseudopotential calculation in a solid at the surface of the sphere:

$$V_{H \text{ val}}(r) = V_H^{\text{PS}}(r)|_{r=R_A} \quad (7)$$

where

$$V_H^{\text{PS}}(r) = \int \frac{V_H^{\text{PS}}[r(r, \vartheta, \varphi)] \sin \vartheta \, d\vartheta \, d\varphi}{4\pi} \quad (8)$$

We use  $V_H^{\text{PS}}(r)$  instead of  $V_{H \text{ val}}(r)$  beyond  $R_A$ , i.e. we define

$$V_{H \text{ val}}(r) = V_H^{\text{PS}}(r) \quad \text{for } r > R_A. \quad (9)$$

Finally, we can write the total potential as

$$V(r) = V_{H \text{ core}} + V_{H \text{ val}} + V_{\text{XC}}(\rho_{\text{core}} + \rho_{\text{val}}) \quad (10)$$

where  $V_{\text{XC}}$  denotes the LDA exchange–correlation potential, e.g. the Heddin–Lundqvist term as used in testing the procedure at the end of this paper.

Accomplishing the self-consistent atomic-like calculation using the rules mentioned above, we obtain the atomic-like quantities matching the spherical average of pseudo-quantities taken from self-consistent calculation in a solid at the surface of the sphere of radius  $R_A$ . In particular, we obtain

(1) the valence radial wavefunctions matching the spherical average of the corresponding pseudo-wavefunctions with logarithmic derivatives,

(2) the valence charge density matching the spherical average of the pseudo-charge density,

(3) the potential, the 'valence part' of which matches the spherical average of the self-consistent pseudo-potential in a solid, and

(4) all the corresponding 'core' quantities which are self-consistent with the valence quantities.

It should be noted that the boundary and normalization conditions (2) and (3) for the valence radial wavefunction do not imply that the function  $\psi_l(r)$  matches the 'average' function  $\Phi_l^{\text{PS}}(r)$  continuously and smoothly at  $R_A$ . These conditions ensure just matching the logarithmic derivatives and the same amount of charge inside the sphere. The quantity in question is the partial charge density. If and only if the partial charge density matches the partial pseudo-charge density at some radius  $R_A^0$ , then the result is independent of  $R_A$  in the neighbourhood of  $R_A^0$  and the wavefunctions match smoothly and continuously. This condition has not been taken into account in the present procedure, because the conditions (2) and (3) determine the wavefunctions completely. We use this condition as an independent criterion of relevant approximations, i.e. the very slight dependence of results on  $R_A$  (or the ratio  $\rho_l^{\text{PS}}(R_A)/\psi_l(R_A)^2$ ) indicates the adequacy of using spherical averages for  $V_H^{\text{PS}}$  and  $\rho_l^{\text{PS}}$ .

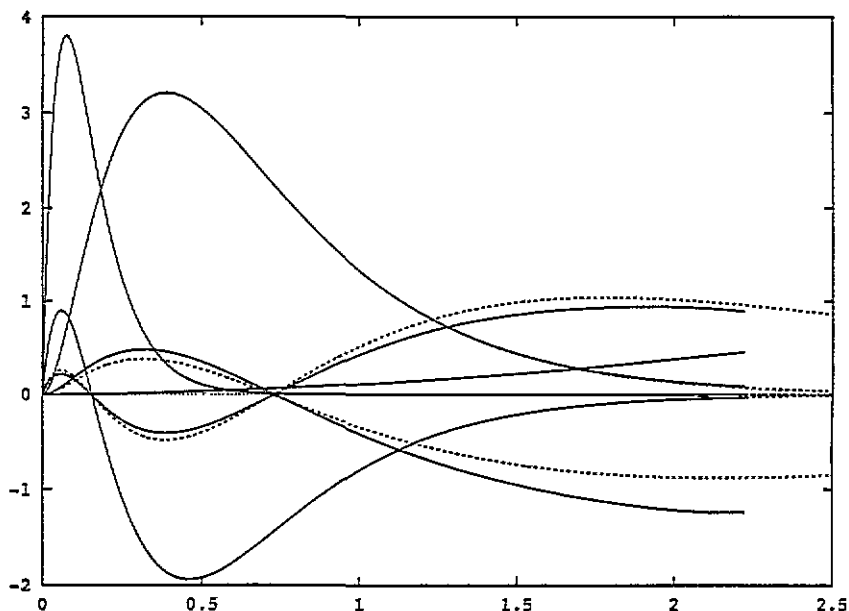


Figure 1. The reconstructed radial wavefunctions with the proper node structure for Si (—). Both the pseudopotential cut-off radius and the augmentation radius are 1.8 au. The reconstructed functions can be compared with the radial wavefunctions of an isolated atom (---) (no atomic function corresponds to the 3d reconstructed function). Both sets of functions are properly normalized with respect to the corresponding charge densities. The radius of 2.22 au corresponds to half the interatomic distance in Si.

In figure 1 and table 1, we present results of testing the procedure on Si, using the pseudopotential generated with the phase-shift technique [9] for  $R_C = 1.8$  au. The independent criterion mentioned above, i.e. the criterion of matching the radial functions at  $R_A$ , is shown in table 1. We define the 'amplitudes' of pseudo-wavefunctions and reconstructed radial wavefunctions,  $\alpha^{\text{PS}}$  and  $\alpha^{\text{R}}$ , respectively:

$$\alpha^{\text{PS}} = \left[ (\Phi_l^{\text{PS}})^2 + \left( \frac{\partial}{\partial r} \Phi_l^{\text{PS}} \right)^2 \right]^{1/2} \Big|_{R_A}$$

**Table 1.** The independent criterion indicating the adequacy of the approximations used. The relation between  $\alpha^{\text{PS}}$  and  $\alpha^{\text{R}}$  corresponds to the relation between the spherical average of the partial pseudo-charge density and the reconstructed partial charge density at the augmentation radius  $R_a$

$R_a$ (au)	$l = 0$		$l = 1$		$l = 2$	
	$\alpha^{\text{PS}}$	$\alpha^{\text{R}}$	$\alpha^{\text{PS}}$	$\alpha^{\text{R}}$	$\alpha^{\text{PS}}$	$\alpha^{\text{R}}$
1.50	1.758	1.748	2.005	1.952	3.137	3.138
1.55	1.662	1.661	1.905	1.869	2.568	2.406
1.60	1.551	1.545	1.808	1.781	2.620	2.542
1.65	1.466	1.459	1.732	1.718	2.426	2.322
1.70	1.389	1.375	1.635	1.616	2.095	1.899
1.75	1.330	1.319	1.565	1.548	2.130	1.991
1.80 ( $R_c$ )	1.274	1.261	1.497	1.479	2.296	2.281
1.85	1.227	1.215	1.441	1.427	2.158	2.113
1.90	1.182	1.166	1.391	1.379	2.041	1.970
1.95	1.142	1.131	1.338	1.322	2.039	1.998
2.00	1.108	1.082	1.294	1.276	1.854	1.739

and

$$\alpha^{\text{R}} = \left[ (\psi_l)^2 + \left( \frac{\partial}{\partial r} \psi_l \right)^2 \right]^{1/2} \Big|_{R_A}$$

The ratio  $\alpha^{\text{PS}}/\alpha^{\text{R}}$ , for several augmentation radii  $R_A$ , corresponds to the factor by which the function  $\psi_l$  would have to be renormalized in order to match  $\Phi_l^{\text{PS}}$  smoothly and continuously (at the cost of losing the norm-conserving property, of course).

In figure 1, we show the reconstructed radial wavefunctions with the proper node structure, for  $R_A = R_C = 1.8$  au, together with radial wavefunctions of isolated atom. For other radii  $R_A \in (1.6, 2.0)$  au, the curves are identical within the thickness of the line.

We also tested the present procedure using the BHS [2] pseudopotential for the self-consistent band-structure calculation of Si. Although the BHS pseudopotential has no sharp cut-off radius, the relative difference  $(\alpha^{\text{PS}} - \alpha^{\text{R}})/\alpha^{\text{PS}}$  does not exceed 5% for optimum  $R_A$ .

So far, the total crystal pseudo-charge density and the spherical average of its  $l$ -component has been used. Consequently, we obtain the 'averaged'  $l$ -dependent node structure for all crystal orbitals which are effectively infinite in number. In principle, however, the same procedure can be used for any general  $k$ -dependent crystal orbital if we use a multipole expansion of  $\rho^{\text{PS}}(\mathbf{r})$  instead of its spherical average. This full expansion of  $\rho^{\text{PS}}(\mathbf{r})$  and the  $k$ -dependent reconstruction of the node structure of each crystal pseudo-function  $|\psi^{\text{PS}}(\mathbf{k}, \mathbf{r})\rangle$  forms, within the pseudopotential framework, an approach analogous to the full-potential linearized augmented-plane-wave technique.

We conclude that the present approach, which makes it possible to reconstruct the proper node structure of pseudo-functions in the core region, will allow us not only to evaluate the transition matrix elements of both the core and the valence states but also to go beyond the frozen-core approximation by constructing the 'all-electron pseudopotentials' which take into account the response of core states and actual s,p,d, ... electron configuration of atoms in solid.

The computer codes are available from the authors on request.

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