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LETTER TO THE EDITOR

Optimized and transferable densities from first-principles local density calculations

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Abstract. From *ab initio* pseudopotential calculations of the solid we extract atomic-like electron densities which, when overlapped in the crystal, reproduce the self-consistent density except for those components for which the structure factor is zero. We demonstrate the universality of the optimized densities for different crystal structures at varying volumes. These densities are the optimized choice for the Harris functional, and we compare our result with the Finnis contraction of the free atom density and with the effective medium theory *ansatz* of embedding an atom in a homogenous electron gas.

There has been a renewed interest in non-self-consistent total energy calculations since the advent of the Harris functional introduced independently by Harris [1] and by Foulkes and Haydock [2]. These workers exploited the stationary property [3, 4] of this new energy functional and demonstrated its success in molecular systems. Polatoglou and Methfessel [5] and, later, Read and Needs [6] studied bulk systems, showing that the cohesive energies, lattice constants, phonon frequencies and bulk moduli can be accurately determined by using overlapping free atomic densities as the input to the Harris functional. A well known problem using this *ansatz* for the input density, however, is the complete failure to determine surface energies [6]. Finnis [7] resolved this difficulty by a two-parameter variation of the input density until the stationary value of the Harris functional was attained which gave the correct surface energy compared with the self-consistent result. The long-wavelength components of the density are especially important for the surface because of the long-range nature of the Coulomb interaction, so the Finnis procedure, which results in a contraction of the charge density, had evidently addressed this issue albeit in an *ad hoc* way.

The main aim of this letter is to present a means of determining optimized atomic-like densities from first-principles calculations of the crystalline solid that are transferable to different chemical environments, and in so doing we investigate the success of the Finnis contraction for the surface problem. The concept of a transferable density is central in the effective medium theory (EMT) [8] where the atom is renormalized by embedding it in a homogenous electron gas. We show that this procedure takes into account to good measure the proper screening of the ion in the solid state environment since the result compares well with our optimized density.

The total density ρ_{tot} in a crystal of overlapping free atomic densities ρ_{atom} is given by

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_{\mathbf{R}_\mu} \rho_{\text{atom}}(\mathbf{r} - \mathbf{R}_\mu) \quad (1)$$

where R_μ is the set of lattice vectors, and we consider only one type of atom for convenience. We formulate the problem in reciprocal space where our arguments are most transparent. The corresponding expression in Fourier space is

$$\rho_{\text{tot}}(\mathbf{G}) = S(\mathbf{G})\rho_{\text{atom}}(\mathbf{G}) \quad (2)$$

where \mathbf{G} is a reciprocal lattice vector, and $S(\mathbf{G})$ is the structure factor [9]. This density may be used to construct the input potential for the iteration of the Kohn-Sham equations [10, 11] to a self-consistent density $\rho_{\text{tot}}^{\text{sc}}$. From this result, we can extract an atomic-like density ρ_{op} (optimized) which is related to $\rho_{\text{tot}}^{\text{sc}}$ by the structure factor as in equation (2). This optimized density depends on the crystal structure and volume, and is only determined on the discrete set of reciprocal lattice vectors for which the structure factor is non-zero. Overlapping such densities in the solid is designed to reproduce the correct density only for those components for which the structure factor is non-zero; it is not possible to retrieve all the properties of a system from overlapping atomic-like densities, for example the Friedel oscillations associated with a metallic surface are inherently non-atomic-like. Also, the well known occurrence of the 'forbidden' $\mathbf{G} = (2, 2, 2)$ reflection in the diamond structure [12] results from the covalent bonding of the atoms and cannot be reduced to any atomic-like spherical density.

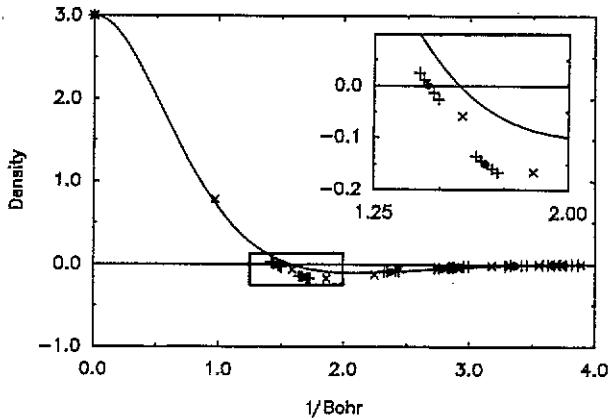


Figure 1. The pseudoatomic charge density $\rho_{\text{atom}}(\mathbf{k})$ for atomic Al (full curve) and the optimized density $\rho_{\text{op}}(\mathbf{G})$ for Al in the FCC lattice $a_0 = 3.96 \text{ \AA}$ (●) showing the discrete shells in reciprocal space that equation (2) samples. The pluses indicate the evolution (see inset) of the components of $\rho_{\text{op}}(\mathbf{G})$ for lattice constants in the range 3.85 to 4.05 \AA , and the crosses show the components for Al in the diamond structure ($a_0 = 5.91 \text{ \AA}$).

The construction of $\rho_{\text{op}}(\mathbf{r})$ therefore first requires an analytical continuation in reciprocal space of $\rho_{\text{op}}(\mathbf{G})$ to $\rho_{\text{op}}(\mathbf{k})$, where \mathbf{k} is a continuous variable, before inversion to real space—but there is obviously no unique prescription for doing this. In figure 1 we show $\rho_{\text{atom}}(\mathbf{k})$ for atomic Al for which we have only considered the pseudovalence electron density [13, 14]. Also presented is $\rho_{\text{op}}(\mathbf{G})$ which shows the discrete shells in reciprocal space that the FCC lattice ($S(\mathbf{G}) = 1$ for all \mathbf{G}) samples, and which indicates the degree of deviation of the self-consistent density from the free

atomic density. Charge conservation fixes the $G = 0$ term, and the short-wavelength components converge rapidly to the atomic value of zero so that the essential physics of bulk Al is determined in the intermediate-wavelength region. Varying the lattice constant produces a different result, and figure 1 shows the evolution of the components of the optimized densities for various volumes about the equilibrium value. We note that the curves traced out in this manner remain remarkably parallel to the free atomic density (see inset) which justifies the success of using overlapping such densities in calculating the elastic properties and phonon frequencies of the bulk [6, 15]. We have also included in the figure the result for Al in a hypothetical diamond structure to investigate the structure dependence of the optimized density. The challenge is to engineer the long-wavelength components to deal appropriately with the surface problem which we consider next.

We first observe that for a lattice with a basis of *dissimilar* atoms, as is the case in a surface unit cell, it is not possible to resolve atomic-like densities for each atom—an analytical continuation of $\rho_{\text{tot}}(G)$ will correspond to a real-space density that is localized on the Wigner-Seitz cell which, when overlapped in the lattice, produces the self-consistent density. We studied the Al(111) ideal surface in a supercell geometry oriented along the z direction with four atomic layers and two vacuum layers. We made the simplifying assumption that all four Al atoms in the supercell are identical so that we extract a representative atomic-like density for the surface problem—this is consistent with Finnis's contraction of all the atoms in the surface unit cell, i.e. including the atoms in the bulk. We will see that this works well largely because the surface and bulk are decoupled in reciprocal space, with the main contribution to the surface energy being the long-wavelength components which are not present in the bulk.

We have plotted in figure 2(a) the spherically averaged $\rho_{\text{op}}(G)$ which we extracted from the Al(111) surface calculation and, for the sake of clarity, we consider separately the contribution from those components perpendicular to the surface. We note that the short-wavelength components for the surface relax to the bulk result in reciprocal space—which they must be able to recover in real space the bulk-like properties away from the surface. The components perpendicular to the surface are surface sensitive and mark significant deviations away from the free atom result in the long-wavelength region. We now numerically continue $\rho_{\text{op}}(G)$ using a cubic spline, incorporating the surface-sensitive long-wavelength components and the bulk information in the short-wavelength region, as shown in figure 2(a).

At this juncture, we consider the possibility of analytically continuing $\rho_{\text{op}}(G)$ from a purely bulk calculation into the long-wavelength region. One possibility is to consider larger lattice constants so as to derive further information in this region—but such cell sizes may be considered unrealistically large. We applied the *ansatz* of norm conservation in reciprocal space which corresponds to fixing the real-space density at the origin to the free atomic value—hence the fixed point assumption (FPA). There is no exact sum rule to justify this procedure, but we assert its usefulness in determining a real-space density $\rho_{\text{op}}(\mathbf{r})$ that is essentially atomic-like. Ideally, one must look at small deviations away from this assumption. We have presented in figure 2(b) the result of applying the FPA to the bulk components (from figure 1) and we note its similarity with the fully optimized density from the surface problem.

We have presented in figure 2(c) the corresponding result for the Finnis contracted atom (using the optimized parameters from [7] applied to our pseudoatom), and in figure 2(d) the EMT *ansatz* of Al embedded in a homogenous electron gas of density

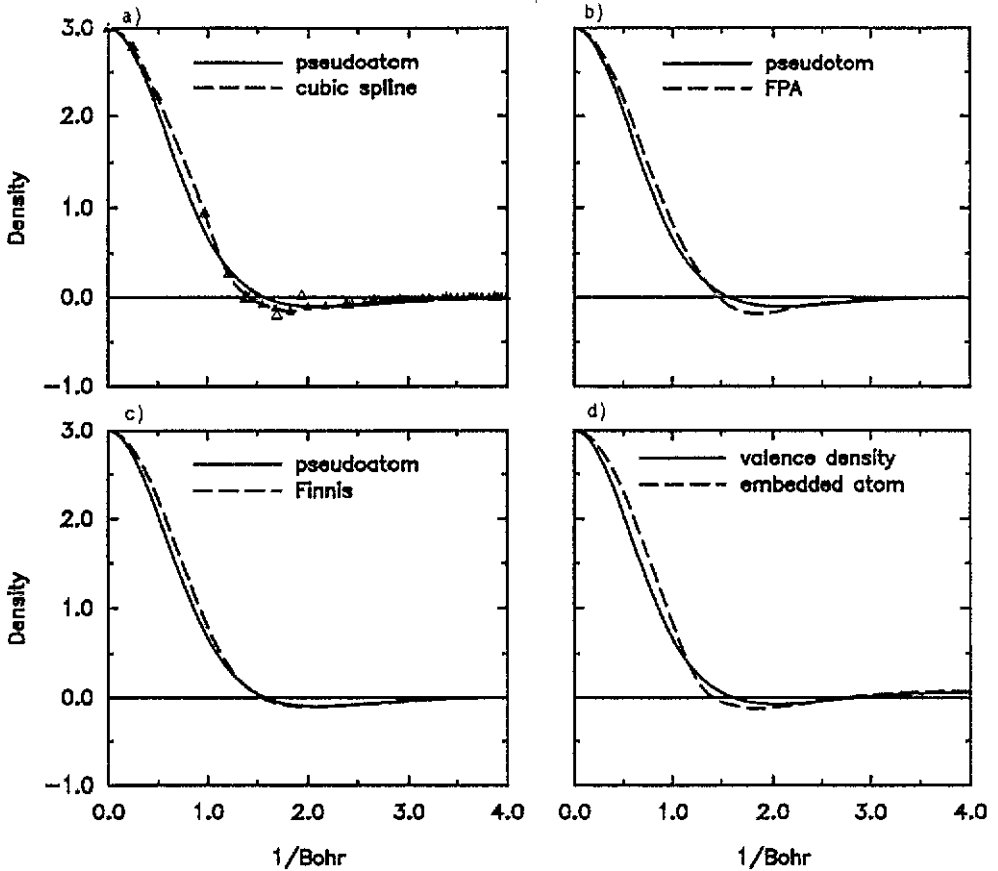


Figure 2. The pseudoatomic charge density $\rho_{\text{atom}}(k)$ for atomic Al (full curve) and (a) the spherically averaged $\rho_{\text{op}}(G)$ for Al(111) ideal surface for $G = (0, 0, G_z)$ (open triangle) and the remaining components (full triangle). The broken curve is the best cubic spline through the components of $\rho_{\text{op}}(G)$. (b) The fixed point assumption (FPA) applied to the bulk components from figure 1 and (c) the Finnis construction applied to $\rho_{\text{atom}}(k)$. (d) The valence charge density $\rho_{\text{atom}}(k)$ for atomic Al (full curve) and the EMT renormalized atom embedded in a homogeneous electron gas of density $r_s = 3.0$.

$r_s = 3.0$. The Finnis result tracks very closely the fully optimized density in the long-wavelength region, and the EMT density appears to describe closely both the surface and bulk properties.

In figure 3 (a)–(d), we show the corresponding densities in real space, noting the common feature of the contraction of the density toward the core region compared with the free atom density, and the resulting sharper attenuation of the density details.

The fact that essentially all the calculated $\rho_{\text{op}}(G)$ components fall on a single 'universal' electron density curve indicates a certain insensitivity of the electron density to the details of the surroundings. This sensitivity is, however, not so weak that the free atom density falls on the same curve. Indeed, the pronounced contraction of the charge density of the atoms in a metallic medium and the closeness of the charge density of Al atoms in Al to that of Al in a homogeneous electron gas strongly suggests that the main reason for this contraction is screening of the atomic

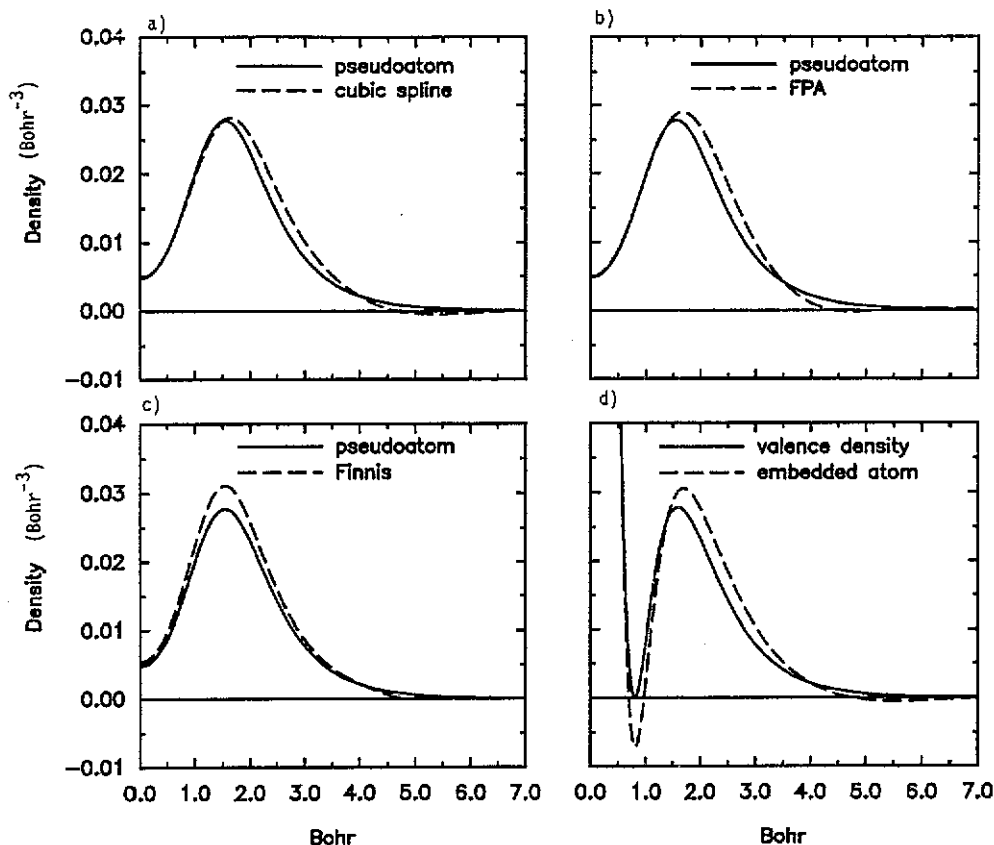


Figure 3. The real-space densities derived from the corresponding reciprocal-space curves in figure 2 for the free pseudoatom (full curves), where the broken curves represent (a) optimized density from Al(111) ideal surface, (b) FPA and (c) Finnis construction. (d) The valence charge density (full) and EMT (broken).

potential by electrons from the surrounding atoms. In linear response theory, the screening length in a homogeneous electron gas of density n varies as $n^{-1/6}$. This gives a relatively weak dependence on n for typical metallic densities, but a large difference between a metallic system and vacuum ($n=0$). In spite of the fact that linear screening is not adequate to describe an Al atom in a metallic system, this explains the observations qualitatively.

The fully optimized density exhibits oscillations in the tail region that are also present in the EMT density, the latter being due to the screening of the atom in the homogeneous electron gas. We observe that the FPA density in figure 3(b) tracks the free atom result for a significant region in the core so that, retrospectively, one concludes that this assumption may be relaxed.

Finally, in table 1, we give results for both bulk and surface Al using the different charge densities as inputs to the Harris functional, and we compare with the self-consistent calculations. Our results corroborate well with previous conclusions that free atom densities constitute good inputs to the Harris functional for the bulk but not for the surface. The optimized density rectifies the problem for the surface; we reiterate that this density does not reproduce the entire self-consistent density

Table 1. (a) Equilibrium lattice constant a_0 , cohesive energy (E) and bulk modulus (B) for Al in the face-centred cubic (FCC), hexagonal close-packed (HCP) and cubic diamond (CD) structures using the self-consistent (SC) and Harris functional methods compared with experiment. (b) Energy of formation (E) of the Al(111) ideal surface using the SC and the various inputs to the Harris functional.

| Structure | Method | a_0 (Å) | E (eV) | B (Mbar) |
|-----------|-------------------------------------|------------------|-------------|---------------|
| (a) | | | | |
| FCC | Experiment [17] | 4.05 | 3.39 | 0.76 |
| | SC | 3.96 | 4.23 | 0.92 |
| | Harris (free atom) | 3.96 | 4.23 | 0.88 |
| HCP | SC | 3.97 | 4.17 | 0.77 |
| | Harris (free atom) | 3.97 | 4.18 | 0.76 |
| CD | SC | 5.91 | 3.42 | 0.45 |
| | Harris (free atom) | 5.91 | 3.42 | 0.43 |
| Structure | Method | E (eV/atom) | | |
| (b) | | | | |
| Al(111) | SC | 0.43 | | |
| | Harris (free atom) | 0.08 | | |
| | Harris (optimized density) | 0.44 | | |
| | Harris (FPA) | 0.45 | | |
| | Harris (Finnis) | 0.43 | | |
| | Harris (embedded atom $r_s = 3.0$) | 0.40 | | |

for reasons enunciated above (zero structure factor, spherical averaging, numerical interpolation, etc), but the stationary property of the Harris functional ensures a good estimate of the total energy. The FPA density is shown also to be a good input to the Harris functional in determining the energy of the Al(111) ideal surface. We note the successful result of using the atom embedded in a homogenous electron gas as an input for the surface calculation.

In summary, the main conclusions of the present work are three fold. (i) We have shown that there is a universal atom-like electron density, which when used as an input density to the Harris functional gives an excellent account of the total energies for bulk and surface problems. (ii) These atom-like densities are contracted relative to the free atom densities. The densities are similar to the optimized densities deduced by Finnis, and give credibility to his approach. (iii) The atom-like densities are also similar to those calculated by embedding the atom in a homogeneous electron gas. This gives a very simple way of understanding the contraction in terms of the screening properties of the surroundings. It also lends support to the basic approximation in the EMT, which is that the total electron density of the system is given by overlapping densities derived by embedding an atom in a homogenous electron gas. We note that in the embedded atom approach [17], which gives a total energy expression similar to that of the simplest version of the EMT, the basic *ansatz* for the electron density is that of overlapping free atoms, an *ansatz* that in itself gives very poor surface energies (cf table 1). The success of the embedded atom method thus stems from a compensation of these errors by the fitting procedures used in deriving the other parameters in the method.

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