

Transferability of pseudopotentials

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Pseudopotentials have become an important tool for the calculation of electronic and structural properties of molecules and solids. The extensive experience with pseudopotentials shows that they accurately describe the properties of matter. It remains to be understood, however, why the same pseudopotential can describe atoms in different chemical environments. We show that this transferability is related to the existence of a region around the nuclei where the charge density is practically independent of the chemical environment.

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INTRODUCTION

Modern chemistry is based on the classification of the elements in the periodic table. Elements which are in the same column have similar chemical properties even though their number of core electrons varies widely. This observation was the motivation for the construction of pseudopotentials or pseudoatoms which have only the relevant valence electrons. The purpose of this paper is to elucidate the reasons why pseudopotentials work so well and to show trends across the periodic table.

Many proposals have been put forward to construct pseudopotentials and research is still very active in this field. A review was recently given by Pickett [1].

Pseudopotentials are extremely useful for the following reasons.

(1) The number of electrons in the calculation is reduced.

(2) It is not necessary to include basis functions in the basis set capable of describing strongly localized oscillations, since there are no core orbitals and since the pseudo wave functions do not have the strong oscillations of the true wave functions in the core region, required by orthogonality to the core orbitals.

(3) The numerical noise is reduced. In all-electron calculations the contribution from the core electrons to the total energy is much larger than the contribution from the valence electrons. Small relative errors in the core orbitals can therefore spoil the result and introduce considerable errors into the chemically important energy differences which are smaller than typical valence electron energies. This problem is avoided in the frozen-core approximation, whose validity is a necessary requirement for all pseudopotential theories. Experience shows that this approximation is very well satisfied. A theoretical discussion can be found in Ref. [2].

An important contribution was made by Bachelet, Hamann, and Schlüter [3], who provided a table with the pseudopotentials for all the elements of the periodic table and thus made pseudopotentials available to a wide community of users. Their paper was entitled "Pseudopotentials That Work" and it indeed turned out that they work very well. This is quite surprising, since the pseudopoten-

tial for a given atom is constructed for a specific electronic reference configuration. Therefore it remains to be understood why this pseudopotential is really a property of the element independent of its electronic configuration and can therefore describe the element in all chemically reasonable configurations. This transferability problem will be investigated in the present paper. Since the pseudopotentials of Bachelet, Hamann, and Schlüter are the most frequently used, the following discussion will be given within the framework of these norm-conserving pseudopotentials. The conclusions, however, are valid in general. Furthermore, the local-density approximation (LDA), which is reviewed in Ref. [4], will be used throughout the paper.

All pseudopotential theories have one important thing in common. They define a cutoff parameter r_c (which may be angular momentum dependent) beyond which the potential is identical to the true (all-electron) potential and beyond which the pseudo wave function is identical to the true wave function. We will show that the maximal radius r_c , which still gives good transferability, is a quantity characteristic of the atom.

REQUIREMENTS FOR A GOOD PSEUDOPOTENTIAL

A good pseudopotential must be able to describe the valence orbitals of an atom in any kind of chemical environment. It must, for instance, describe the free atom as well as the atom in a solid and it must describe the atom in a covalent as well as in an ionic bond (i.e., Cl in Cl_2 or NaCl). How can we translate those requirements in mathematical terms? Let us assume we did a self-consistent all-electron calculation for a periodic solid, i.e., we know the self-consistent potential. We then solve Schrödinger's one-particle equation for all valence orbitals using the corresponding pseudopotential constructed for this reference configuration. The pseudopotential will well reproduce the eigenvalues and the eigenfunctions in the valence region (beyond r_c) if its energy versus logarithmic derivative curve at r_c is sufficiently close to the true energy versus logarithmic derivative curve in the range of eigenvalues we are interested in. This range of

energies is typically of the order of the width of the valence band. We will call this requirement "conservation of scattering properties." The central quantity for the conservation of scattering properties is therefore the energy versus logarithmic derivative curve. There is a one-to-one correspondence between this curve and the potential inside the sphere of radius r_c , i.e., the energy versus logarithmic derivative curve must change if the potential in the sphere changes. Conservation of scattering properties is well obeyed in norm-conserving pseudo-

potentials [3] since for the reference configuration (and therefore by the self-consistency for the reference potential) the energy versus logarithmic derivative curve and its derivative at the reference energy (usually the energy of the atomic eigenvalue) have the correct values.

Conservation of scattering properties, however, must not only be fulfilled for the reference configuration but it should hold for all chemical environments. If this is the case the pseudopotential is said to be transferable. Transferability is easily tested by doing calculations for

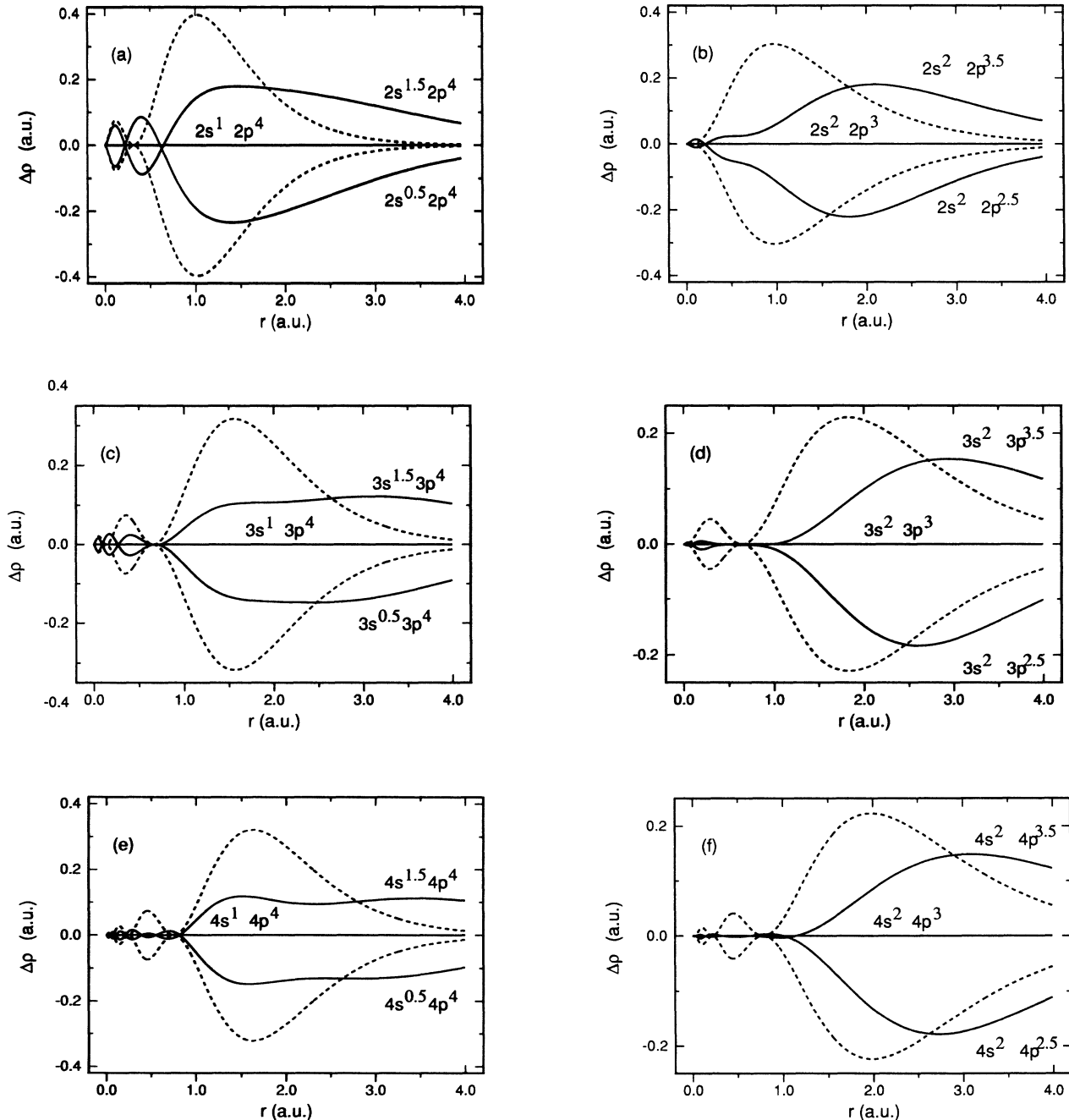


FIG. 1. The difference in the radial charge $4\pi r^2\rho$ for different ionic configurations of N [(a), (b)], P [(c), (d)], and As [(e), (f)]. The solid lines are differences of the self-consistent all-electron charge densities. The dotted line is what one would obtain by adding or subtracting an orbital of the atomic reference configuration without allowing the whole system to relax to self-consistency.

the atom in different ionized and excited states using the pseudopotential constructed for the reference configuration (which is usually the neutral atomic ground state) and comparing the result with the self-consistent all-electron results.

OPEN QUESTIONS

Good transferability is obtained for the Bachelet-Hamann-Schlüter pseudopotentials but it is not obvious why. On the contrary, at a first glance it seems unlikely that the conservation of scattering properties can be fulfilled for different self-consistent potentials in the sphere around the atom. If the self-consistent potential in the sphere changes in different chemical environments the scattering properties will also change. The pseudopotential, however, remains the same and it is therefore not guaranteed that it will also correctly reproduce the scattering properties for a self-consistent potential different from the reference potential.

Another question to be asked is the following: The construction of the pseudopotential is based on the con-

servation of the eigenvalues and the scattering properties, but the total energy never comes into play. Why is the pseudopotential nevertheless useful for total energy calculations?

THE CHARGE DENSITY IN THE CORE REGION IN DIFFERENT CHEMICAL ENVIRONMENTS

As we mentioned above, transferability can be tested by doing pseudopotential calculations for different ionized and excited atomic states. For comparison we have first done all-electron calculations with an atomic LDA program. In Fig. 1 we show the change in the all-electron radial charge density as we go to different configurations. The radial charge density is given by $4\pi r^2 \rho(r)$, where $\rho(r)$ is the angular averaged charge density. This charge density integrated over the surface of the sphere is the relevant quantity for the total energy, which is calculated from a three-dimensional integral. There is clearly a fairly well-defined region where the charge density does not change very much and if it changes then only in an oscillatory way. This region will

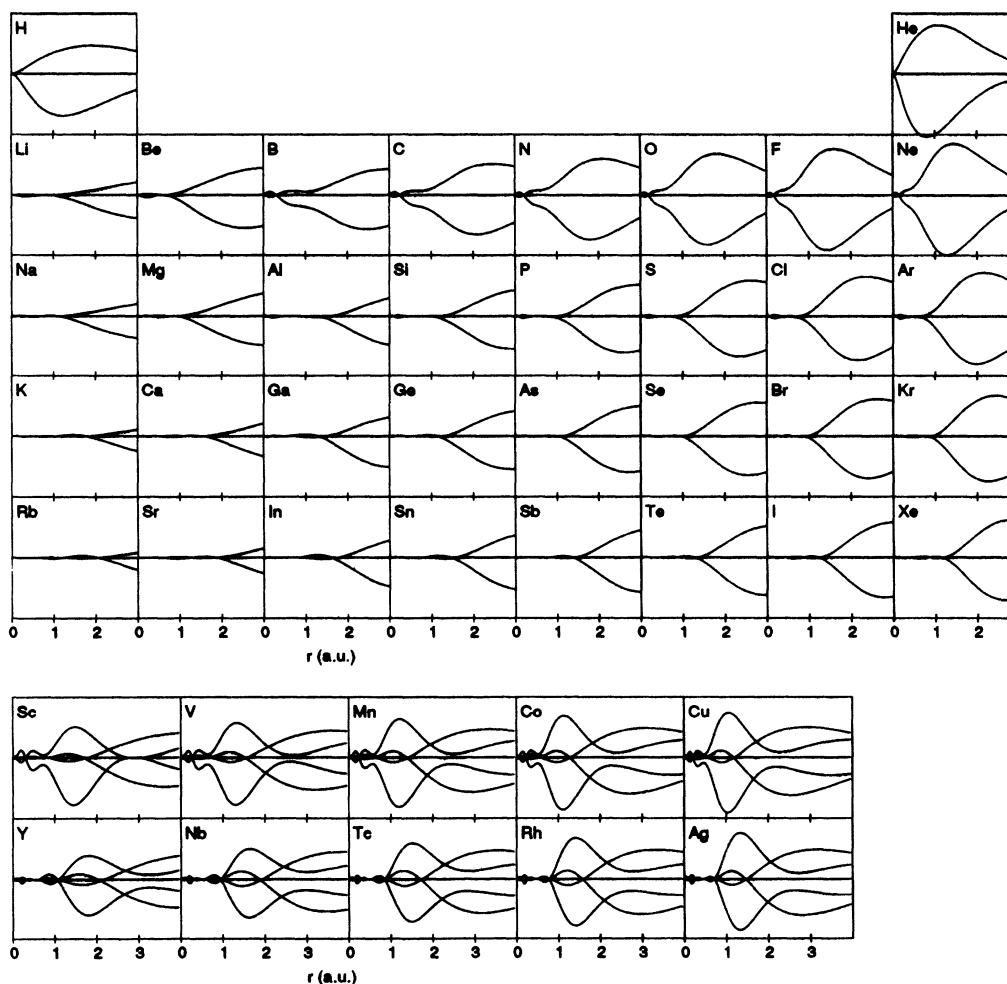


FIG. 2. The difference in the self-consistent radial all-electron charge density across the periodic table if one changes the occupancy of the most weakly bound orbital by half an electron. For the case of the transition metals changes of the occupancy of both d and s electrons are shown, since both are very weakly bound. The former give rise to changes of the charge density close to the nucleus while the latter change it further away from the nucleus.

in the following be called the "inert region." It coincides fairly well with the core region. The number of oscillations increases as one goes to heavier elements with more filled shells. Due to screening, the change of the charge in the inert region is much smaller than what one would obtain by simply adding or removing an unrelaxed valence orbital. We emphasize that changes of the charge density in the core region are not small because the valence charge density in the core region is already small, but because of this screening effect illustrated in Fig. 1. In Fig. 2 we show the behavior across the periodic table. It can be seen that the screening effect is most pronounced in normal metal atoms, where the inert region becomes particularly large and well defined. This explains the empirical observation that pseudopotentials are particularly soft for normal metal atoms. The same inert region is found when one compares atoms in different excited states or atoms confined to different volumes. Since we have discussed the radial charge density, our findings are not in contradiction to NMR experiments which are based on the changes of the true charge density near the nucleus. In Fig. 3 we present the pseudo charge densities for two of the configurations of Fig. 1. The results were obtained with the pseudopotentials of Bachelet, Hamann, and Schlüter. The pseudo charge has

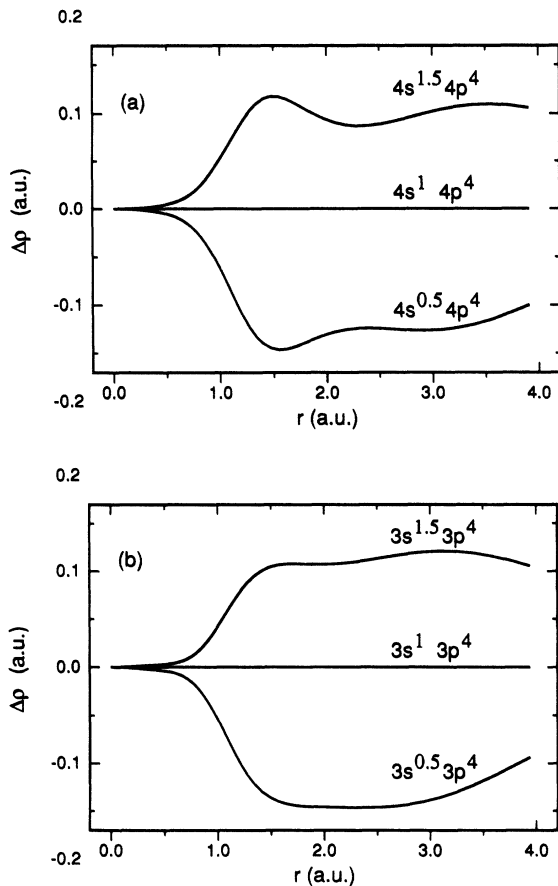


FIG. 3. The difference in the self-consistent radial pseudo charge $4\pi r^2 \bar{\rho}$ for different ionized configurations of P (a) and As (b) as calculated with the pseudopotential of Bachelet, Hamann, and Schlüter.

a similar behavior in the inert region as the true charge, the oscillations found in the all-electron case are, however, smoothed out.

WHY PSEUDOPOTENTIALS WORK

The knowledge about the behavior of the charge density in the core region enables us to answer the questions put forward above. If the radius r_c is chosen inside the inert region, the charge distribution and therefore the self-consistent potential (apart from an unimportant constant which represents the electrostatic potential of the outside region) do not change significantly. Therefore one energy versus logarithmic derivative curve can describe the scattering properties in all chemical environments. In other words transferability is only obtained if r_c is within the inert region.

What about the total energy? The total valence energy in the frozen-core approximation can be written as [5]

$$E_{\text{tot}} = \sum_i E_i - \frac{1}{2} \int \frac{\rho_v(r)\rho_v(r')}{|r-r'|} + \int \epsilon_{\text{xc}}(\rho_v(r)+\rho_c(r)) - \int \mu_{\text{xc}}(\rho_v(r)+\rho_c(r))\rho_v(r) \quad (1)$$

where ρ_v is the valence electron charge density, ρ_c the frozen-core electron charge density, and ϵ_{xc} and μ_{xc} denote the exchange correlation energy and potential. In the pseudopotential formalism, where the core electrons are eliminated, the corresponding expression is

$$\tilde{E}_{\text{tot}} = \sum_i E_i - \frac{1}{2} \int \frac{\bar{\rho}_v(r)\bar{\rho}_v(r')}{|r-r'|} + \int \epsilon_{\text{xc}}(\bar{\rho}_v(r)) - \int \mu_{\text{xc}}(\bar{\rho}_v(r))\bar{\rho}_v(r) \quad (2)$$

where $\bar{\rho}_v$ is the pseudo charge distribution. The first term (sum over all eigenvalues) is (nearly) identical in both expressions since the pseudopotential eigenvalues correctly reproduce the true eigenvalues as was discussed above. The remaining terms, however, are only identical in the region where the pseudo wave function and the true wave function coincide and where the core density is negligible. The error ΔE_{tot} is therefore

$$\Delta E_{\text{tot}} = \left[-\frac{1}{2} \int \frac{\rho_v(r)\rho_v(r')}{|r-r'|} + \int \epsilon_{\text{xc}}(\rho_v(r)+\rho_c(r)) - \int \mu_{\text{xc}}(\rho_v(r)+\rho_c(r))\rho_v(r) \right] - \left[-\frac{1}{2} \int \frac{\bar{\rho}_v(r)\bar{\rho}_v(r')}{|r-r'|} + \int \epsilon_{\text{xc}}(\bar{\rho}_v(r)) - \int \mu_{\text{xc}}(\bar{\rho}_v(r))\bar{\rho}_v(r) \right]$$

where the integrals are taken only over the region of space where the above-mentioned conditions are not fulfilled.

We must now distinguish between two cases. In the first case we assume that the core electrons are well local-

ized within the above-defined inert region. The integrals in the expression for ΔE_{tot} must then be taken over this inert region. Since both the all-electron charge density and the pseudo valence charge density do not change significantly, the error ΔE_{tot} is nearly a constant in different chemical environments. Energy differences, which are the important quantities, are therefore well reproduced. Let us illustrate this error cancellation for helium and nitrogen, treated with the Bachelet-Hamann-Schlüter pseudopotential. For helium we do not have any core electrons and the first case clearly applies. The error ΔE_{tot} of 5×10^{-3} hartree is in this case very small, since the pseudocharge is very similar to the true charge in the inert region (number of zeros of wave function and pseudo wave function are identical). The energy difference between $\text{He}(1s^2)$ and $\text{He}(1s^{2.5})$ is, however, reproduced with an error of 3×10^{-4} hartree, which is more than an order of magnitude smaller. For phosphor the total energies given by (1) and (2) are of course completely different (-6.4 and -400 hartree), because the charge densities used to calculate the exchange correlation energies are different. Even though the pseudo valence charge density differs significantly from the true valence charge in the core region, the repulsion energy between the valence electrons of 5.2 hartree is too low by only 2×10^{-2} hartree in the pseudopotential calculation. The energy differences of the ionized states shown in Fig. 1 are, however, again reproduced with a very high precision of less than 1×10^{-3} hartree.

In the second case we assume that the core electrons are extending beyond the inert region. In this case we have no error cancellation of the exchange correlation energy and exchange correlation potential terms in the shell outside the core region where the valence charge density changes already appreciably but where the core charge density has not yet vanished. This problem was discussed in Ref. [6]. There it was shown that in this case it is necessary to include the charge distribution of those extended core orbitals as a frozen background charge density ρ_{BG} in the expressions for the exchange correlation energy and exchange correlation potential. The total energy is then written as

$$\begin{aligned} \tilde{E}_{\text{tot}} = & \sum_i E_i - \frac{1}{2} \int \frac{\tilde{\rho}_v(r)\tilde{\rho}_v(r')}{|r-r'|} \\ & + \int \varepsilon_{\text{xc}}(\tilde{\rho}_v(r) + \rho_{\text{BG}}(r)) \\ & - \int \mu_{\text{xc}}(\tilde{\rho}_v(r) + \rho_{\text{BG}}(r))\tilde{\rho}_v(r) . \end{aligned}$$

ΔE_{tot} is then again nearly a constant in different chemical environments and cancels in energy differences. As we have pointed out, the inert region coincides usually with

the core region. If the r_c radius is therefore chosen such that it contains the entire inert region, this case cannot arise.

ELECTROSTATIC INTERACTIONS

Another important term in total energy calculations is the electrostatic coupling between the core and the valence region. Because of symmetry we can either consider the action of the potential arising from the charge in the valence region on the charge in the inert region or vice versa. We choose the second way. The electrostatic potential in the valence region arising from the charge distribution in the core region is *a priori* not correct, because it was calculated with the pseudocharge. The most important term in this electrostatic interaction, however, is the monopole, which is correct to first order in a norm-conserving pseudopotential. Higher moments from the charge distribution in the inert region will only become important if the inert region becomes very large. In this case terms correcting dipoles and higher moments must be included [7]. If the inert region is chosen according to our prescription above such corrections seem not to be necessary.

CONCLUSIONS

We have shown that the success of the concept of pseudopotential is related to the existence of an inert region where the change in the charge distribution is small in different chemical environments. Transferability can only be obtained if r_c is inside this inert region. This also sets an upper limit to the softness of a pseudopotential. If r_c is chosen larger than the radius of the inert region, the form of the potential in this sphere changes in different chemical environments and the pseudopotential must become configuration dependent [7] (one probably should no longer speak of a pseudopotential in this case). The easiest and best known implementation of this is the linearized augmented plane-wave (LAPW) method [8] where the energy versus logarithmic derivative curve is recalculated in each step of the self-consistent cycle. If, however, the muffin-tin radius is small enough, it is clear that the LAPW method can be implemented as a pseudopotential method. We have recently shown [9] that the resulting LAPW Hamiltonian has very attractive features such as separability of the nonlocal terms.

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