

From ultrasoft pseudopotentials to the projector augmented-wave method

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(Received 6 July 1998)

The formal relationship between ultrasoft (US) Vanderbilt-type pseudopotentials and Blöchl's projector augmented wave (PAW) method is derived. It is shown that the total energy functional for US pseudopotentials can be obtained by linearization of two terms in a slightly modified PAW total energy functional. The Hamilton operator, the forces, and the stress tensor are derived for this modified PAW functional. A simple way to implement the PAW method in existing plane-wave codes supporting US pseudopotentials is pointed out. In addition, critical tests are presented to compare the accuracy and efficiency of the PAW and the US pseudopotential method with relaxed core all electron methods. These tests include small molecules (H_2 , H_2O , Li_2 , N_2 , F_2 , BF_3 , SiF_4) and several bulk systems (diamond, Si, V, Li, Ca, CaF_2 , Fe, Co, Ni). Particular attention is paid to the bulk properties and magnetic energies of Fe, Co, and Ni.

[S0163-1829(98)00848-0]

I. INTRODUCTION

First-principles Kohn-Sham density-functional methods (see, e.g., Refs. 1 and 2) employing a plane-wave basis set and the pseudopotential (PP) approximation are currently among the most successful techniques in computational chemistry and computational material science.³⁻⁵ The biggest merit of these methods is their formal simplicity, but unfortunately this simplicity has a price: first-row elements, transition metals, and rare-earth elements are computationally demanding to treat with standard norm-conserving pseudopotentials.⁶ Therefore, various attempts have been made to generate soft pseudopotentials, and the most successful approach to date is the concept of ultrasoft PP introduced by Vanderbilt.⁷ Blöchl⁸ has further developed the US-PP concept by combining ideas from pseudopotential and LAPW (linearized augmented-plane-wave) methods in a conceptually elegant framework, called the projector augmented-wave method (PAW). Although Blöchl has indicated in his work that similarities between ultrasoft PP's and his method exist, no formal relationship was established. In the present work, we will derive this relationship, which shows that the only difference between Vanderbilt's and Blöchl's approach are simple one-center terms. We will also indicate a simple way to implement the PAW method in existing plane-wave codes that use norm-conserving or ultrasoft pseudopotentials.

Norm-conserving pseudopotentials were first introduced and used by Hamann, Schlüter, and Chiang.⁶ In their scheme, inside some core radius, the all-electron (AE) wave function is replaced by a soft nodeless pseudo- (PS) wave function, with the crucial restriction that the PS wave function must have the same norm as the all-electron wave function within the chosen core radius; outside the core radius the PS and AE wave function are identical. It is now well established that good transferability requires a core radius around the outermost maximum of the AE wave function, because only then

the charge distribution and moments of the AE wave functions are well reproduced by the PS wave functions (see, e.g., Ref. 9). Therefore, for elements with strongly localized orbitals (like first-row, $3d$, and rare-earth elements) the resulting pseudopotentials require a large plane-wave basis set. To work around this, compromises are often made by increasing the core radius significantly beyond the outermost maximum in the AE wave function. But this is usually not a satisfactory solution because the transferability is always adversely affected when the core radius is increased, and for any new chemical environment, additional tests are required to establish the reliability of such soft PP's.

An elegant solution to this problem was proposed by Vanderbilt.⁷ In his method, the norm-conservation constraint is relaxed and to make up for the resulting charge deficit, localized atom-centered augmentation charges are introduced. These augmentation charges are defined as the charge density difference between the AE and the PS wave function, but for convenience they are pseudized to allow an efficient treatment of the augmentation charges on a regular grid. The core radius of the pseudopotential can now be chosen around half the nearest-neighbor distance— independent of the position of the maximum of the AE wave function (see Ref. 10). Only for the augmentation charges a small cutoff radius must be used to restore the moments and the charge distribution of the AE wave function accurately (for details see Ref. 11). The pseudized augmentation charges are usually treated on a regular grid in real space, which is not necessarily the same as the one used for the representation of the wave functions. The relation between the ultrasoft PP method and other plane-wave-based methods was discussed in detail by Singh.⁵

Vanderbilt's approach is now adopted quite widely,¹¹⁻¹⁹ and especially for the $3d$ transition-metals savings in the computer and improvements in the accuracy can be significant.²⁰ But the success of the method is partly hampered by the rather difficult construction of the pseudopotentials.

tials, i.e., too many parameters (several cutoff radii) must be chosen and therefore extensive tests are required in order to obtain an accurate and highly transferable PP.

Some of these disadvantages are avoided in Blöchl's PAW method. Blöchl introduces a linear transformation from the PS to the AE wave function and derives the PAW total energy functional in a consistent manner applying this transformation to the KS functional. The construction of PAW datasets is easier because the pseudization of the augmentation charges is avoided, i.e., the PAW method works directly with the full AE wave functions and AE potentials. This is achieved using radial support grids around each atom instead of regular grids. The decomposition into radial grid and regular grid is complete, insofar that no cross term between the grids must be evaluated. Despite these advantages, the method is not yet used very often, and in addition to Blöchl's own implementation of the method we are aware of only one second program supporting the PAW method.^{21,22} This is partly due to the fact that the PAW approach was introduced a few years after Vanderbilt's method, but another reason is that—apart from its formal elegance—it was not obvious at the time that the PAW method has significant advantages over other frozen core approaches like the US-PP approach. There are also some aspects in Blöchl's work that deviate so significantly from conventional pseudopotential methods, that the implementation and testing of the method seems to be fairly difficult. In this work, we will rewrite the PAW total energy functional so that it resembles more closely the usual expressions used in pseudopotential programs and we will establish the exact formal relationship between both the US-PP and the PAW method. Our results show that only very few additional terms must be evaluated in order to implement the PAW method in programs supporting US-PP's.

The paper is organized as follows: Section II derives the rearranged PAW total energy functional. Then we establish the formal relationship between the PAW and the US-PP method (Sec. II F). The Hamilton operator and the forces for the modified PAW functional are obtained in Sec. III, and in Sec. IV the construction of our PAW datasets is discussed. Several critical tests for dimers, small molecules, and bulk systems (including magnetic Fe, Co, and Ni) are presented in Sec. V. Discussions and conclusions are at the end.

II. THE PAW TOTAL ENERGY FUNCTIONAL

A. Basic PAW formalism

As a first step, we derive a modified form of the PAW total energy functional. We do that in order to obtain a functional that resembles closely the functional for US-PP. Our derivation follows Blöchl's work closely,⁸ but the decomposition of the Hartree energy—the treatment of the core valence interaction particularly—and the treatment of the exchange correlation differ somewhat. Although it would be possible to start immediately from the final expression of the PAW total energy functional in Ref. 8, we have decided to rederive the modified PAW functional directly from the Kohn-Sham density functional, because this makes the derivation more concise and easier to follow. The exact Kohn-Sham density functional is as usually given by

$$E = \sum_n f_n \langle \Psi_n | -\frac{1}{2} \Delta | \Psi_n \rangle + E_H[n + n_Z] + E_{xc}[n]. \quad (1)$$

$E_H[n + n_Z]$ is the Hartree energy of the electronic charge density n and the point charge densities of the nuclei n_Z , $E_{xc}[n]$ is the electronic exchange-correlation energy, and f_n are orbital occupation numbers. We will first give a brief summary of the basics of the PAW method (see Ref. 8; in general we also adopt the notation of Ref. 8). In the PAW method, the AE wave function Ψ_n is derived from the PS wave function $\tilde{\Psi}_n$ by means of a linear transformation:⁸

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi}_n \rangle. \quad (2)$$

The PS wave functions $\tilde{\Psi}_n$ are the variational quantities. The index i is a shorthand for the atomic site \mathbf{R} , the angular momentum numbers $L=l, m$, and an additional index k referring to the reference energy ϵ_{kl} . The AE partial waves ϕ_i are obtained for a reference atom, the PS partial waves $\tilde{\phi}_i$ are equivalent to the AE partial waves outside a core radius r_c^l and match continuously onto $\tilde{\phi}_i$ inside the core radius. The core radius r_c^l is usually chosen approximately around half the nearest-neighbor distance.¹⁰ The projector functions \tilde{p}_i are dual to the partial waves:

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}.$$

Starting from Eq. (2) it is possible to show that in the PAW method, the AE charge density is given by (for details we refer to Ref. 8):

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}), \quad (3)$$

where \tilde{n} is the soft pseudo-charge-density calculated directly from the pseudo-wave-functions on a plane-wave grid [Eq. (15) of Ref. 8]:

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \langle \tilde{\Psi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi}_n \rangle. \quad (4)$$

The onsite charge densities n^1 and \tilde{n}^1 are treated on a radial support grid, that extends up to r_{rad} around each ion. They are defined as [Eq. (16) of Ref. 8]

$$n^1(\mathbf{r}) = \sum_{(i,j)} \rho_{ij} \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle, \quad (5)$$

and [Eq. (17) of Ref. 8]

$$\tilde{n}^1(\mathbf{r}) = \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle. \quad (6)$$

ρ_{ij} are the occupancies of each augmentation channel (i,j) and they are calculated from the pseudo-wave-functions applying the projector functions:

$$\rho_{ij} = \sum_n f_n \langle \tilde{\Psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\Psi}_n \rangle. \quad (7)$$

For a complete set of projectors the charge density \tilde{n}^1 is exactly the same as \tilde{n} within the augmentation spheres. In addition, comparison with the work of Vanderbilt [Eqs.

(18)–(20) of Ref. 7] shows that the definition of the total charge density [Eq. (3)] is in principle equivalent in the PAW and US-PP approach if the projector functions \tilde{p}_i are the same (see Sec. II F). Of course, in practice, the US-PP method always adopts pseudized augmentation charges.

From now on, we shall concentrate on the frozen core case. In order to do that, we restrict the sum over bands in Eqs. (4) and (7) to the valence bands, and the quantities \tilde{n} , \tilde{n}^1 , n^1 , etc. shall denote valence only quantities. In addition, we introduce four quantities that will be used for the description of the core charge density: n_c , \tilde{n}_c , n_{Zc} , \tilde{n}_{Zc} . As n_c we denote the charge density of the frozen core all-electron wave functions in the reference atom. The partial electronic core density \tilde{n}_c is equivalent to the frozen core AE charge density outside a certain radius r_{pc} . r_{pc} lies inside the augmentation region. The partial core density is used in order to calculate nonlinear core corrections in the spirit of Louie *et al.*²³ (see Sec. II C).

With n_{Zc} , we denote the point charge density of the nuclei n_Z plus the frozen core AE charge density n_c :

$$n_{Zc} = n_Z + n_c. \quad (8)$$

Finally, the pseudized core density \tilde{n}_{Zc} is a charge distribution that is equivalent to n_{Zc} outside the core radius and shall have the same moment as n_{Zc} inside the core region:

$$\int_{\Omega_r} n_{Zc}(\mathbf{r}) d^3\mathbf{r} = \int_{\Omega_r} \tilde{n}_{Zc}(\mathbf{r}) d\mathbf{r}, \quad (9)$$

where \int_{Ω_r} stands for the integration on the radial support grid. The total moment of n_{Zc} and \tilde{n}_{Zc} is equivalent to the ionic net charge $-Z_{\text{ion}}$ (by convention, the charge of an electron is $+1$).²⁴ The pseudized core charge \tilde{n}_{Zc} is used in the decomposition of the Hartree energy in the next subsection.

In the following sections, quantities like n_c , \tilde{n}_c , n_{Zc} , \tilde{n}_{Zc} , \tilde{n}^1 , n^1 , and \hat{n} will be used in the following way: on a plane-wave grid a sum over all ions is implicitly assumed, whereas on the radial grids only terms deriving from the local ion are taken into account.

B. Hartree energy

The Hartree energy is treated rather similar as in Ref. 8; but because we want to derive a total energy functional that resembles that of the US-PP method, the core valence interaction is handled slightly different. The first step works along the same lines as in Ref. 8, i.e., the total charge density n_T is decomposed into three terms:

$$n_T = n + n_{Zc} = \underbrace{(\tilde{n} + \hat{n} + \tilde{n}_{Zc})}_{\tilde{n}_T} + \underbrace{(n^1 + n_{Zc})}_{n_T^1} - \underbrace{(\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc})}_{\tilde{n}_T^1}. \quad (10)$$

This particular decomposition into three terms was chosen by Blöchl to allow an efficient treatment of the long-range electrostatic interactions. The crucial step is the introduction of a compensation charge \hat{n} , which is added to the soft

charge densities $\tilde{n} + \tilde{n}_{Zc}$ and $\tilde{n}^1 + \tilde{n}_{Zc}^1$ in order to reproduce the correct multipole moments of the AE charge density $n^1 + n_{Zc}$ that is located in each augmentation region. Because n_{Zc} and \tilde{n}_{Zc} have exactly the same monopole ($-Z_{\text{ion}}$) and vanishing multipoles, the compensation charge \hat{n} must be chosen so that

$$\tilde{n}^1 + \hat{n}$$

has the same moments as the AE valence charge density n^1 within each sphere (this definition is somewhat different from that of Blöchl). We will come back to our particular choice for the compensation charge in Sec. II E. We also want to point out that similar schemes relying on soft compensation charges are used for instance in the LAPW method to handle the long-range electrostatic effects.²⁵

Even without complicated algebra it is easy to anticipate that \tilde{n}_T describes the electrostatic interaction between different augmentation spheres and between the augmentation and the interstitial regions exactly. Only for on-site terms (i.e., terms within one sphere) errors are introduced that must be corrected. We show this briefly here: for the Hartree energy one obtains

$$\begin{aligned} \frac{1}{2}(n_T)(n_T) &= \frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) + (n_T^1 - \tilde{n}_T^1)(\tilde{n}_T) \\ &+ \frac{1}{2}(n_T^1 - \tilde{n}_T^1)(n_T^1 - \tilde{n}_T^1), \end{aligned} \quad (11)$$

where we have used a shorthand for the electrostatic energy between two charge distributions $a(\mathbf{r})$ and $b(\mathbf{r})$:

$$(a)(b) = \int d\mathbf{r} d\mathbf{r}' \frac{a(\mathbf{r})b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (12)$$

Because $(n_T^1 - \tilde{n}_T^1)$ has by construction of \hat{n} vanishing moments within each individual sphere and is zero in the interstitial region the second and the third terms contribute only within each augmentation sphere. However, the second term in Eq. (11) is problematic because it involves quantities defined on the plane-wave grid \tilde{n}_T and terms only calculated on the radial grid $(n_T^1 - \tilde{n}_T^1)$. To simplify the calculations Blöchl⁸ made one crucial approximation that we adopt here too: it is convenient to replace \tilde{n}_T in the second term by \tilde{n}_T^1 , i.e., the pseudo-charge-density is replaced by its on-site approximation. This is only exact for a complete set of projectors, and introduces an error in other cases, which is evidently given by

$$(n_T^1 - \tilde{n}_T^1)(\tilde{n}_T - \tilde{n}_T^1). \quad (13)$$

This error is discussed in Sec. VII C [Eq. (108)] of Ref. 8. Using this approximation one obtains for the Hartree energy the simple form

$$\frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) - \frac{1}{2}(\tilde{n}_T^1)(\tilde{n}_T^1) + \frac{1}{2}(n_T^1)(n_T^1). \quad (14)$$

The notation $\overline{(a)(b)}$ means that the corresponding terms must be evaluated on the radial grid within each augmentation region (in these expressions the densities \tilde{n}_T^1 and n_T^1 contain only contributions arising from the ion centered in

the sphere). The final equation is convenient because there are no interaction terms between the radial support grid and the plane-wave part, but it should be kept in mind that for an incomplete set of projectors an approximation was made in order to obtain this decomposition [see Eq. (13)].

Up to now our derivation was generally similar to Ref. 8, but in the remaining lines we reformulate the three terms of Eq. (14) so that they resemble closely the usual expressions used in pseudopotential codes. Inserting the definition of \tilde{n}_T and \tilde{n}_T^1 [see Eq. (10)] into Eq. (14) one obtains for the first term:

$$\begin{aligned} & \frac{1}{2}(\tilde{n} + \hat{n})(\tilde{n} + \hat{n}) + (\tilde{n}_{Zc})(\tilde{n} + \hat{n}) + \frac{1}{2}(\tilde{n}_{Zc})(\tilde{n}_{Zc}) \\ &= \frac{1}{2}(\tilde{n} + \hat{n})(\tilde{n} + \hat{n}) + (\tilde{n}_{Zc})(\tilde{n} + \hat{n}) + \frac{1}{2} \overline{(\tilde{n}_{Zc})(\tilde{n}_{Zc})} \\ &+ U(\mathbf{R}, Z_{\text{ion}}), \end{aligned} \quad (15)$$

and the second term becomes

$$-\frac{1}{2} \overline{(\tilde{n}^1 + \hat{n})(\tilde{n}^1 + \hat{n})} - \overline{(\tilde{n}_{Zc})(\tilde{n}^1 + \hat{n})} - \frac{1}{2} \overline{(\tilde{n}_{Zc})(\tilde{n}_{Zc})}. \quad (16)$$

In Eq. (15), the first term describes the electrostatic interactions between the valence electrons on the regular grid, the second one that between the frozen pseudocore and the valence electrons, and the final one the interaction between the frozen cores. $U(\mathbf{R}, Z_{\text{ion}})$ is the electrostatic energy of point charges Z_{ion} in an uniform electrostatic background,²⁶ and $\frac{1}{2} \overline{(\tilde{n}_{Zc})(\tilde{n}_{Zc})}$ is the self-interaction energy of the pseudized core charge distribution, which cancels against the similar term in Eq. (16). In going from the first line in Eq. (15) to the second, we have made the assumption that the core charges do not overlap, which is not always the case. But because an overlap of the electronic cores also introduces errors in other places (e.g., the kinetic energy), which are usually neglected in the PAW method, it seems reasonable to neglect the corresponding terms here as well.

Finally, the third term in Eq. (14) is rewritten in a similar way to the other two and we obtain

$$\frac{1}{2} \overline{(n^1)(n^1)} + \overline{(n_{Zc})(n^1)} + \frac{1}{2} \overline{(n_{Zc})(n_{Zc})}. \quad (17)$$

The Hartree energy is given by Eqs. (15), (16), and (17), but in the final equations for the total energy we will not include the core self-interaction term $\frac{1}{2} \overline{(n_{Zc})(n_{Zc})}$ because it only defines the zero of energy.

C. Exchange-correlation energy

To decompose the exchange-correlation energy we insert the following charge density into the exchange-correlation functional:

$$n_c + n = (\tilde{n} + \hat{n} + \tilde{n}_c) + (n^1 + n_c) - (\tilde{n}^1 + \hat{n} + \tilde{n}_c). \quad (18)$$

This expression differs from Ref. 8, where

$$n_c + n = (\tilde{n}) + (n^1 + n_c) - (\tilde{n}^1)$$

was used. The reason for our choice is discussed below. We want to stress that the partial electronic core charge \tilde{n}_c is entirely distinct from the pseudized core charge \tilde{n}_{Zc} . The later must reproduce the exact monopole of n_{Zc} , whereas the former is constructed without this requirement. It is straightforward to obtain the final result, which for a local or semilocal exchange-correlation energy and a complete set of projectors is given by

$$E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] + \overline{E_{xc}[n^1 + n_c]} - \overline{E_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]}, \quad (19)$$

where \bar{E} means that the corresponding quantity is evaluated on the radial grid within the augmentation region.

If the set of partial waves is not complete, an error is introduced that is given by (analogous to Sec. VII C of Ref. 8):

$$\begin{aligned} & \overline{E_{xc}[(\tilde{n} + \hat{n} + \tilde{n}_c) + (n^1 + n_c) - (\tilde{n}^1 + \hat{n} + \tilde{n}_c)]} \\ & - \overline{E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c]} - \overline{E_{xc}[n^1 + n_c]} + \overline{E_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]}. \end{aligned}$$

This term vanishes for $\tilde{n} - \tilde{n}^1 = 0$. Expanding this term in orders of $\tilde{n} - \tilde{n}^1$ yields

$$\int_{\Omega_r} (v_{xc}[n^1 + n_c] - v_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c])(\tilde{n} - \tilde{n}^1) d\mathbf{r}.$$

Without nonlinear core corrections, the first term in the integral would be $(v_{xc}[n^1 + n_c] - v_{xc}[\tilde{n}^1])$. For our PAW datasets (see Sec. IV) $\tilde{n}^1 + \hat{n} + \tilde{n}_c$ is very similar to $n^1 + n_c$ over an appreciable region of the augmentation sphere, which reduces errors due to the incompleteness of the partial waves in comparison to Blöchl's approach. The improvement is particularly large for systems in which the core states extend towards the boundary of the augmentation sphere. An example for the improved behavior is given in Sec. V B. In addition, we also found that the introduction of the partial core charge density \tilde{n}_c reduces numerical instabilities due to gradient corrected functionals in the vicinity of the core.

D. Final expression for the total energy

The final expression of the total energy is most conveniently split up into three terms (similar to Ref. 8),

$$E = \tilde{E} + E^1 - \tilde{E}^1, \quad (20)$$

which are given by

$$\begin{aligned} \tilde{E} &= \sum_n f_n \langle \tilde{\Psi}_n | -\frac{1}{2} \Delta | \tilde{\Psi}_n \rangle + E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] + E_H[\tilde{n} + \hat{n}] \\ &+ \int v_H[\tilde{n}_{Zc}][\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})] d\mathbf{r} + U(\mathbf{R}, Z_{\text{ion}}), \end{aligned} \quad (21)$$

$$\begin{aligned} \tilde{E}^1 &= \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2} \Delta | \tilde{\phi}_j \rangle + \overline{E_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]} + \overline{E_H[\tilde{n}^1 + \hat{n}]} \\ &+ \int_{\Omega_r} v_H[\tilde{n}_{Zc}][\tilde{n}^1(\mathbf{r}) + \hat{n}(\mathbf{r})] d\mathbf{r}, \end{aligned} \quad (22)$$

$$E^1 = \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2} \Delta | \phi_j \rangle + \overline{E_{xc}[n^1 + n_c]} + \overline{E_H[n^1]} + \int_{\Omega_r} v_H[n_{Zc}] n^1(\mathbf{r}) d\mathbf{r}. \quad (23)$$

v_H is the electrostatic potential of the charge density n :

$$v_H[n](\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}',$$

and $E_H[n]$ is its electrostatic energy, which is given by

$$E_H[n] = \frac{1}{2} (n)(n) = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

The expression \tilde{E} is evaluated on a regular grid, whereas \tilde{E}^1 , and E^1 are calculated for each sphere individually on a radial support grid (only charge densities deriving from the central ion must be calculated in these terms). A few remarks are required here to elucidate again the differences between Blöchl's and our work. The treatment of the kinetic energy is equivalent, the Hartree energy is treated in a similar way, with the only difference that we neglect core-core overlap in these terms (as it is implicitly done for all other terms in the PAW method). An important (formal) difference concerns the construction of the compensation charge. In Ref. 8, the compensation charge has the same multipoles as $n^1 - \tilde{n}^1 + n_{Zc}$, whereas in our case it is chosen so that it reproduces the multipoles of $n^1 - \tilde{n}^1$. In the former case, the electrostatic interactions between the cores are automatically included in $E_H[\tilde{n} + \hat{n}]$, whereas in our case the interaction between the cores must be evaluated explicitly using an Ewald summation [$U(\mathbf{R}, Z_{\text{ion}})$ in Eq. (21)]. At first sight our expressions also do not include a term similar to \bar{v} in Ref. 8, but a second thought makes clear that $v_H[\tilde{n}_{Zc}]$ accounts for this term because the shape of $v_H[\tilde{n}_{Zc}]$ is entirely free within the augmentation sphere (only outside the core radius $v_H[\tilde{n}_{Zc}] = v_H[n_{Zc}]$ must hold).

Significant differences occur for the exchange-correlation energy. In our case, on the regular grid, the exchange-correlation energy is evaluated for the charge density $\tilde{n} + \hat{n}$ including nonlinear core corrections \tilde{n}_c , whereas Blöchl uses only \tilde{n} to evaluate the exchange-correlation energy. As we have already stressed, this makes only a difference for an incomplete set of projectors, which is in practice always adopted. In that case, we expect our treatment to be superior. Finally, we would like to compare our PAW total energy functional with that of Holzwarth *et al.*,²¹ but because this is a rather specialized topic we do this in the Appendix.

Another interesting point is the comparison with ultrasoft pseudopotentials. It is obvious that \tilde{E} is similar to the total energy functional of Ref. 7 if \hat{n} is associated with the pseudized augmentation charges in the US-PP method. The only differences are evidently the two additional on-site terms E^1 and \tilde{E}^1 , Eqs. (22) and (23). We will come back to this point in Sec. II F.

E. The compensation charge

The compensation charges \hat{n} must be chosen so that $\tilde{n}^1 + \hat{n}$ has exactly the same moments as the exact AE charge density n^1 within each augmentation sphere centered at the position \mathbf{R} . This requires that

$$\int_{\Omega_r} (n^1 - \tilde{n}^1 - \hat{n}) |\mathbf{r} - \mathbf{R}|^l Y_L^*(\widehat{\mathbf{r} - \mathbf{R}}) d\mathbf{r} = 0. \quad (24)$$

The charge density difference between the AE and PS partial wave for each channel (i, j) within the augmentation region [see Eqs. (5) and (6)] is described by the functions

$$Q_{ij}(\mathbf{r}) = \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) - \tilde{\phi}_i^*(\mathbf{r}) \tilde{\phi}_j(\mathbf{r}), \quad (25)$$

and their moments q_{ij}^L are given by

$$q_{ij}^L = \int_{\Omega_r} Q_{ij}(\mathbf{r}) |\mathbf{r} - \mathbf{R}|^l Y_L^*(\widehat{\mathbf{r} - \mathbf{R}}) d\mathbf{r}, \quad (26)$$

where L is a shorthand for $L = (l, m)$. Only certain combinations of L and $i = k_i l_i m_i$, $j = k_j l_j m_j$ based on the usual sum rules will give nonzero contributions:

$$m = m_i + m_j \quad \text{and} \quad l = |l_i - l_j|, |l_i + l_j| + 2, \dots, l_i + l_j.$$

The moments q_{ij}^L can be obtained easily using Clebsch-Gordan coefficients and a radial integration. A compensation charge that fulfills the requirement [Eq. (24)] can then be defined as a sum of one center terms

$$\hat{n} = \sum_{(i,j),L} \rho_{ij} \hat{Q}_{ij}^L(\mathbf{r}),$$

$$\hat{Q}_{ij}^L(\mathbf{r}) = q_{ij}^L g_l(|\mathbf{r} - \mathbf{R}|) Y_L(\widehat{\mathbf{r} - \mathbf{R}}), \quad (27)$$

where $g_l(r)$ are functions for which the moment l is equal to 1. The actual functional form of $g_l(r)$ that we have adopted is discussed in Sec. IV A.

F. Ultrasoft pseudopotentials

Before deriving the total energy functional for the US-PP method, we want to stress that the PAW method is an exact AE method for a complete set of partial waves. Therefore, the method should yield results that are indistinguishable from any other frozen core AE method. In the US-PP method additional approximations are made.

The equations for ultrasoft pseudopotentials can be obtained readily from the modified PAW total energy functional given in Eqs. (21)–(23) by linearization of Eqs. (22) and (23) around the atomic reference occupancies ρ_{ij}^a . Let us denote the densities obtained with those occupancies as n_a^1 , \tilde{n}_a^1 , and \hat{n}_a . Linearization of the exchange correlation and Hartree term of E^1 [Eq. (23)] around n_a^1 yields

$$E_{xc}(n_a^1 + n_c) + E_H(n_a^1) + \int (v_{xc}[n_a^1 + n_c] + v_H[n_a^1]) [n^1(\mathbf{r}) - n_a^1(\mathbf{r})] d\mathbf{r}. \quad (28)$$

Using Eq. (5) for $n^1(\mathbf{r})$ we obtain for this expression

$$C + \sum_{(i,j)} \rho_{ij} \langle \phi_i | v_{xc}[n_a^1 + n_c] + v_H[n_a^1] | \phi_j \rangle, \quad (29)$$

where C is a constant. The other two terms—kinetic energy and electrostatic core-valence interaction—are already linear in ρ_{ij} ; and if we combine them with Eq. (29) we obtain for E^1 up to first order in the occupancies ρ_{ij} :

$$E^1 \approx C + \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2}\Delta + v_{\text{eff}}^a | \phi_j \rangle, \quad (30)$$

with

$$v_{\text{eff}}^a = v_H[n_a^1 + n_{Zc}] + v_{xc}[n_a^1 + n_c]. \quad (31)$$

The local potential v_{eff}^a is just the AE potential in the reference atom. A similar linearization can be done for \bar{E}^1 , but care must be taken that both \bar{n}^1 and \hat{n} depend on the occupancies ρ_{ij} . The final result therefore contains two terms:

$$\bar{E}^1 \approx \bar{C} + \sum_{(i,j)} \left[\rho_{ij} \langle \bar{\phi}_i | -\frac{1}{2}\Delta + \bar{v}_{\text{eff}}^a | \bar{\phi}_j \rangle + \int \hat{Q}_{ij}^L(\mathbf{r}) \bar{v}_{\text{eff}}^a(\mathbf{r}) d\mathbf{r} \right],$$

with

$$\bar{v}_{\text{eff}}^a = v_H[\bar{n}_a^1 + \hat{n}_a + \bar{n}_{Zc}] + v_{xc}[\bar{n}_a^1 + \hat{n}_a + \bar{n}_c]. \quad (32)$$

\bar{v}_{eff}^a is the local atomic pseudopotential in the reference atom.

Combining the two linearized expressions with \bar{E} gives the following total energy functional:

$$\begin{aligned} E = & \sum_n f_n \langle \bar{\Psi}_n | -\frac{1}{2}\Delta + \sum_{(i,j)} |\bar{p}_i\rangle \langle \bar{p}_j| G_{ij}^{\text{US}} | \bar{\Psi}_n \rangle \\ & + E_{xc}[\bar{n} + \hat{n} + \bar{n}_c] + E_H[\bar{n} + \hat{n}] \\ & + \int v_H[\bar{n}_{Zc}][\bar{n}(\mathbf{r}) + \hat{n}(\mathbf{r})] d\mathbf{r} + U(\mathbf{R}, Z_{\text{ion}}), \end{aligned} \quad (33)$$

with

$$\begin{aligned} G_{ij}^{\text{US}} = & \langle \phi_i | -\frac{1}{2}\Delta + v_{\text{eff}}^a | \phi_j \rangle - \langle \bar{\phi}_i | -\frac{1}{2}\Delta + \bar{v}_{\text{eff}}^a | \bar{\phi}_j \rangle \\ & - \int \hat{Q}_{ij}^L(\mathbf{r}) \bar{v}_{\text{eff}}^a(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (34)$$

It is evident that the first equation is exactly the same as Eq. (1) in Ref. 11, if the compensation charge \hat{n} is associated with the pseudized augmentation charge in the US-PP approach. It is also simple to show that the first two terms of G_{ij}^{US} [Eq. (34)] are equivalent to the pseudopotential strength parameter D_{ij} defined in Eq. (22) of Ref. 11 [this can be shown by combining Eq. (22), Eq. (20), Eq. (16), and Eq. (17) of Ref. 11]. The last term in Eq. (34) corresponds to the usual unscreening [which is incorrectly specified in Eq. (24) of Ref. 11].

We turn now briefly back to the PAW functional. If the sum of the compensation charge and the pseudocharge density $\bar{n}^1 + \hat{n}$ is equivalent to the onsite AE charge density n^1 , i.e., if

$$\hat{n} = n^1 - \bar{n}^1,$$

and if $\bar{n}_{Zc} = n_{Zc}$ and $\bar{n}_c = n_c$, only the on-site kinetic-energy terms contribute to the total energy:

$$E^1 - \bar{E}^1 = \sum_{(i,j)} \rho_{ij} (\langle \phi_i | -\frac{1}{2}\Delta | \phi_j \rangle - \langle \bar{\phi}_i | -\frac{1}{2}\Delta | \bar{\phi}_j \rangle).$$

It is immediately obvious that the US-PP method is strictly equivalent to the PAW method in this limiting case, and therefore both approaches are then exact within the frozen core approximation. But in the US-PP method this would require one to use the functions

$$\hat{Q}_{ij}^L(\mathbf{r}) = Q_{ij}(\mathbf{r}) = \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) - \bar{\phi}_i^*(\mathbf{r}) \bar{\phi}_j(\mathbf{r}) \quad (35)$$

in the calculation of the compensation charge on the plane wave grid [see Eq. (27)] and this is in practice not possible. However this derivation indicates that the accuracy of the US-PP can be improved systematically by increasing the accuracy of the pseudized augmentation function. In other words, if the AE-augmentation functions [Eq. (35)] are used for the augmentation, the US-PP approach is also an exact frozen core AE method.

On the other hand, the derivation presented at the beginning of the section shows that even if the augmentation functions $\hat{Q}_{ij}^L(\mathbf{r})$ reproduce just the correct moments of $Q_{ij}(\mathbf{r})$, the US-PP method is still *exact up to first order* for changes of the charge-density distribution with respect to the atomic reference system. This is probably part of the reason for the reliability of the US-PP method. However, in the US-PP method obviously, the transferability errors related to the pseudization of the augmentation charges can be large for systems with strong charge transfer (polar or ionic binding), changes of the atomic orbital occupations (hybridization and promotion), strong polarizations (induction of dipole or quadrupole moments at certain atomic sites), or large local magnetic moments (our tests in Sec. V will show that the latter is in fact the most problematic case). To obtain very accurate results even for these problematic cases the functions \hat{Q}_{ij}^L should approach the limiting case of Eq. (35). This is usually achieved by direct l -dependent truncation of the AE-augmentation functions $Q_{ij}(\mathbf{r})$ at some radius r_{comp} (see Ref. 11). An alternative used by Kresse and Hafner¹⁴ is to first construct high quality norm-conserving partial waves $\phi_i^{NC}(\mathbf{r})$:

$$\phi_i^{NC}(\mathbf{r}) = \begin{cases} \phi_i(\mathbf{r}) & r > r_{\text{comp}}^l \\ f_i(\mathbf{r}) & r < r_{\text{comp}}^l, \end{cases} \quad (36)$$

and to define the functions \hat{Q}_{ij}^L as the charge density difference of the NC and US partial waves:

$$\hat{Q}_{ij}^L(\mathbf{r}) = \phi_i^{NC*}(\mathbf{r}) \phi_j^{NC}(\mathbf{r}) - \bar{\phi}_i^*(\mathbf{r}) \bar{\phi}_j(\mathbf{r}). \quad (37)$$

All US-PP's of the present work have been constructed in that way.

To summarize, in the PAW method the compensation charges can be rather extended, because the only requirement is that they restore the correct moment within the cutoff radius r_c^l . The correct shape of the AE wave function is reconstructed only on the radial support grids. In the US-PP method, ‘‘accurate and hard’’ augmentation charges are desirable for reliable pseudopotentials. This usually requires that the AE augmentation functions are pseudized around the maximum of the AE wave functions, often resulting in rather

contracted and localized compensation charges. For instance, whereas for 3d transition-metal compounds half the nearest-neighbor distance and thus the pseudization radius r_c^l of the partial waves (and the extent of the compensation charges in the PAW method) is around 2 a.u., the maximum in the d wave function is located around 1 a.u. demanding very localized and computationally expensive compensation charges.

III. HAMILTON OPERATOR AND FORCES

A. Overlap operator and orthonormality

In the PAW approach, the pseudo-wave-functions $\tilde{\Psi}_n$ must fulfill the following orthogonality condition:

$$\langle \tilde{\Psi}_n | S | \tilde{\Psi}_m \rangle = \delta_{nm}, \quad (38)$$

where the overlap operator is defined by

$$S[\{\mathbf{R}\}] = 1 + \sum_i |\tilde{p}_i\rangle q_{ij} \langle \tilde{p}_j|, \quad (39)$$

and q_{ij} is given by

$$q_{ij} = \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle = \sqrt{4\pi} q_{ij}^0. \quad (40)$$

B. Hamilton operator

To obtain the Hamilton operator for the modified PAW total energy functional the total energy must be varied with respect to the pseudodensity operator $\tilde{\rho} = \sum_n f_n |\tilde{\Psi}_n\rangle \langle \tilde{\Psi}_n|$ and one can formally write^{8,12}

$$\frac{dE}{d\tilde{\rho}} = H. \quad (41)$$

The density operator $\tilde{\rho}$ enters in several ways—directly [like in the kinetic-energy term in Eq. (21)], via the pseudo-charge-density \tilde{n} or via the occupancies of each augmentation channel ρ_{ij} defined in Eq. (7). If we treat these three contributions separately, the variation of the total energy can formally be written as

$$\frac{dE}{d\tilde{\rho}} = \frac{\partial E}{\partial \tilde{\rho}} + \int \frac{\delta E}{\delta \tilde{n}(\mathbf{r})} \underbrace{\frac{\partial \tilde{n}(\mathbf{r})}{\partial \tilde{\rho}}}_{|\mathbf{r}\rangle \langle \mathbf{r}|} d\mathbf{r} + \sum_{(i,j)} \frac{\partial E}{\partial \rho_{ij}} \underbrace{\frac{\partial \rho_{ij}}{\partial \tilde{\rho}}}_{|\tilde{p}_i\rangle \langle \tilde{p}_j|}. \quad (42)$$

We start with the term \tilde{E} [Eq. (21)]. The partial derivative with respect to $\tilde{\rho}$ yields simply the kinetic-energy operator $-1/2\Delta$, and the variation with respect to $\tilde{n}(\mathbf{r})$ is the usual effective one-electron potential $\tilde{v}_{\text{eff}}(\mathbf{r})$:

$$\tilde{v}_{\text{eff}} = v_H[\tilde{n} + \hat{n} + \tilde{n}_{Zc}] + v_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c]. \quad (43)$$

In \tilde{E} , the occupancies ρ_{ij} enter only via the compensation charge \hat{n} , and we obtain with Eq. (27):

$$\hat{D}_{ij} = \frac{\partial \tilde{E}}{\partial \rho_{ij}} = \int \frac{\delta \tilde{E}}{\delta \hat{n}(\mathbf{r})} \frac{\partial \hat{n}(\mathbf{r})}{\partial \rho_{ij}} d\mathbf{r} = \sum_L \int \tilde{v}_{\text{eff}}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}. \quad (44)$$

This term accounts for the fact that the pseudowave function $\tilde{\Psi}_n$ does not have the same moments as the AE wave function Ψ_n , and the term thus corrects the long-range electrostatic behavior of $\tilde{\Psi}_n$.

In the remaining two energy terms E^1 and \tilde{E}^1 only expressions with ρ_{ij} enter—either directly (kinetic energy) or via n^1 , \tilde{n}^1 , or \hat{n} . Using Eq. (5), it is easy to show that the derivative of E^1 [Eq. (23)] with respect to occupancies ρ_{ij} is given by

$$D_{ij}^1 = \frac{\partial E^1}{\partial \rho_{ij}} = \langle \phi_i | -\frac{1}{2}\Delta + v_{\text{eff}}^1 | \phi_j \rangle,$$

with

$$v_{\text{eff}}^1[n^1] = v_H[n^1 + n_{Zc}] + v_{xc}[n^1 + n_c]. \quad (45)$$

The result for \tilde{E}^1 is similar, and one obtains

$$\tilde{D}_{ij}^1 = \frac{\partial \tilde{E}^1}{\partial \rho_{ij}} = \langle \tilde{\phi}_i | -\frac{1}{2}\Delta + \tilde{v}_{\text{eff}}^1 | \tilde{\phi}_j \rangle + \sum_L \int_{\Omega_r} d\mathbf{r} \tilde{v}_{\text{eff}}^1(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}),$$

with

$$\tilde{v}_{\text{eff}}^1[\tilde{n}^1] = v_H[\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc}] + v_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]. \quad (46)$$

The first term in Eq. (46) derives from the variation with respect to ρ_{ij} and \tilde{n}^1 , and the second one from the variation with respect to \hat{n} . The terms D_{ij}^1 and \tilde{D}_{ij}^1 are evaluated on the radial grid within each augmentation region: they are strictly onsite and restore the correct shape of the AE wave function within the spheres.

The final expression for the Hamilton operator is remarkably elegant and simple:

$$H[\rho, \{\mathbf{R}\}] = -\frac{1}{2}\Delta + \tilde{v}_{\text{eff}} + \sum_{(i,j)} |\tilde{p}_i\rangle (\hat{D}_{ij} + D_{ij}^1 - \tilde{D}_{ij}^1) \langle \tilde{p}_j|. \quad (47)$$

Although our expressions are very similar to those obtained by Blöchl in Ref. 8, the comparison is not quite straightforward. Part of the difficulties are due to the fact that we treat the exchange-correlation term slightly different, but Blöchl's equations are also more complex because he introduces very soft compensation charges, which are allowed to overlap. To see the analogy between both expressions one has to rewrite all terms involving $v_R^0(r)$ in Eqs. (37)–(40) of Ref. 8 into a closed expression. The result resembles \hat{D}_{ij} and the second term in \tilde{D}_{ij} , two expressions that are on first sight not present in Blöchl's equations. It seems to us that our arrangement of terms is more symmetric and intuitively easier to understand: The first two terms (kinetic-energy operator and effective one-electron potential) are usually present in the KS eigenvalue equation. The term involving \hat{D}_{ij} ,

$$\sum_{(i,j),L} \langle \tilde{\Psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\Psi}_n \rangle \int \tilde{v}_{\text{eff}}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r},$$

describes the interaction of the compensation charge associated with one electron with the effective one-electron potential (long-range electrostatic effects). The remaining two terms are strictly onsite and account for the fact that the

potential \bar{v}_{eff} and the pseudo-wave-function $\tilde{\Psi}_n$ do not show the rapid variations usually present in the vicinity of the ionic cores. The symmetry and mutual cancellation between \bar{D}_{ij}^1 [Eq. (46)] and the term $-\frac{1}{2}\Delta + \bar{v}_{\text{eff}} + \sum_{(i,j)} \bar{p}_i \hat{D}_{ij} \langle \bar{p}_j |$ in the Hamilton operator is obvious (in fact the cancellation is exact within the augmentation spheres for a complete set of partial waves).

The Hamilton operator for US-PP's can be obtained from Eqs. (44)–(47) replacing the effective potentials in the augmentation region v_{eff}^1 and \bar{v}_{eff}^1 by the respective atomic potentials v_{eff}^a [Eq. (31)] and \bar{v}_{eff}^a [Eq. (32)]. This means that in the US-PP method the terms D_{ij}^1 and \bar{D}_{ij}^1 can be calculated once—for instance during the pseudopotential generation—and are kept constant during the calculation.

C. Double counting corrections

In many band-structure codes, the total energy is evaluated as the sum of the Kohn-Sham eigenvalues minus double counting corrections. It is relatively straightforward to derive the required equations by rearranging the total energy functional. The usual decomposition into three terms is also possible for the double counting corrections and one obtains

$$\begin{aligned} \tilde{E}_{dc} &= -E_H[\tilde{n} + \hat{n}] + E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] \\ &\quad - \int v_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c](\tilde{n} + \hat{n}) d\mathbf{r}, \\ E_{dc}^1 &= -\overline{E_H[n^1]} + \overline{E_{xc}[n^1 + n_c]} - \int_{\Omega_r} v_{xc}[n^1 + n_c] n^1 d\mathbf{r}, \\ \tilde{E}_{dc}^1 &= -\overline{E_H[\tilde{n}^1 + \hat{n}]} + \overline{E_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]} \\ &\quad - \int_{\Omega_r} v_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c](\tilde{n}^1 + \hat{n}) d\mathbf{r}. \end{aligned} \quad (48)$$

The total energy is then given by

$$E = \sum_n f_n \langle \tilde{\Psi}_n | H | \tilde{\Psi}_n \rangle + \tilde{E}_{dc} + E_{dc}^1 - \tilde{E}_{dc}^1 + U(\mathbf{R}, Z_{\text{ion}}). \quad (49)$$

In the US-PP method, \tilde{E}_{dc}^1 and E_{dc}^1 are constants and must be calculated only once during the pseudopotential generation.

D. Forces and stress tensor

The forces are usually defined as the total derivative of the energy with respect to the ionic positions

$$\mathbf{F} = - \frac{dE}{d\mathbf{R}}. \quad (50)$$

In the PAW method (as in the US-PP method), complications arise from the fact that the augmentation spheres and compensation charges are allowed to move with the ions, which gives rise to additional terms in comparison with standard plane-wave codes. These terms are sometimes called Pulay forces,²⁷ although this is not quite correct because the plane-wave basis set is clearly independent of the atomic positions. Another difficulty in comparison to norm-

conserving pseudopotentials is caused by the overlap operator, whose position dependence [Eq. (39)] must be taken into account too. The forces can be derived in several ways, but here we want to keep the derivation as simple as possible. To do that we start from a force theorem first proven by Goedecker and Maschke,²⁸ which states that the total derivative of the energy is given by²⁹

$$\begin{aligned} \frac{dE}{d\mathbf{R}} &= \sum_n f_n \left\langle \tilde{\Psi}_n \left| \frac{\partial(H[\rho, \{\mathbf{R}\}] - \epsilon_n S[\{\mathbf{R}\}])}{\partial\mathbf{R}} \right| \tilde{\Psi}_n \right\rangle \\ &\quad + \frac{\partial U(\mathbf{R}, Z_{\text{ion}})}{\partial\mathbf{R}}. \end{aligned} \quad (51)$$

The second line describes the forces between the ionic cores, and we will not comment further on this term. ϵ_n are the Kohn-Sham eigenvalues, and we assumed that we have determined the ground-state wave functions so that the orthogonality constraint Eq. (38) and the KS equations

$$H|\tilde{\Psi}_n\rangle = \epsilon_n S|\tilde{\Psi}_n\rangle$$

are fulfilled. In Eq. (51), changes of the potentials \bar{v}_{eff} , \bar{v}_{eff}^1 , and v_{eff}^1 in the Hamilton operator H due to changes of one of the densities \tilde{n} , n^1 , \tilde{n}^1 , or \hat{n} must *not* be calculated. The proof of this theorem is quite straightforward and based on the fact that the first-order energy change is given by the sum of the change of the Kohn-Sham eigenvalues: any change of the potentials due to changes of \tilde{n} , n^1 , \tilde{n}^1 , or \hat{n} always cancel against the changes of the double counting corrections [see Eq. (48)].

From Eq. (51) the forces are very simple to derive and we obtain three terms \mathbf{F}^1 , \mathbf{F}^2 , and \mathbf{F}^3 . The first contribution \mathbf{F}^1 derives from the change of the local potential \bar{v}_{eff} if the ions are moved; the effective potential depends explicitly on the ionic positions only via \tilde{n}_{Zc} :

$$\mathbf{F}^1 = - \int \left[\frac{\delta \text{Tr}[H\bar{\rho}]}{\delta v_H[\tilde{n}_{Zc}](\mathbf{r})} \frac{\partial v_H[\tilde{n}_{Zc}](\mathbf{r})}{\partial\mathbf{R}} \right] d\mathbf{r}. \quad (52)$$

Two terms must be considered here, the first one derives from the change of \bar{v}_{eff} in Eq. (47), and the second from the change of \bar{v}_{eff} in \hat{D}_{ij} [Eq. (44)]:

$$\begin{aligned} \mathbf{F}^1 &= - \int \left(\tilde{n}(\mathbf{r}) + \sum_{(i,j),L} \hat{Q}_{ij}^L(\mathbf{r}) \rho_{ij} \right) \frac{\partial v_H[\tilde{n}_{Zc}](\mathbf{r})}{\partial\mathbf{R}} d\mathbf{r} \\ &= - \int [\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})] \frac{\partial v_H[\tilde{n}_{Zc}](\mathbf{r})}{\partial\mathbf{R}} d\mathbf{r}. \end{aligned} \quad (53)$$

The second contribution to the forces arises from \hat{D}_{ij} [Eq. (44)] due to changes of the compensation charges \hat{n} if the ions are moved:

$$\mathbf{F}^2 = - \sum_{(i,j),L} \int \bar{v}_{\text{eff}}(\mathbf{r}) \rho_{ij} q_{ij}^L \frac{\partial g_L(|\mathbf{r}-\mathbf{R}|) Y_L(\widehat{\mathbf{r}-\mathbf{R}})}{\partial\mathbf{R}} d\mathbf{r}. \quad (54)$$

\mathbf{F}^1 and \mathbf{F}^2 together describe the forces deriving from electrostatic contributions.

The final term is due to the change of the projectors \bar{p}_i in Eq. (47), and is given by

$$\mathbf{F}^3 = - \sum_{n(i,j)} (\hat{D}_{ij} + D_{ij}^1 - \tilde{D}_{ij}^1 - \epsilon_n q_{ij}) \times f_n \langle \tilde{\Psi}_n | \frac{\partial |\tilde{p}_i\rangle \langle \tilde{p}_j|}{\partial \mathbf{R}} | \tilde{\Psi}_n \rangle. \quad (55)$$

There is one additional term that is in fact not correctly treated by Eq. (51). It derives from the dependency of the exchange-correlation potential on the nonlinear core correction \tilde{n}_c giving rise to one additional contribution that can be written as

$$\mathbf{F}^{\text{nlcc}} = - \int v_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] \frac{\partial \tilde{n}_c(\mathbf{r})}{\partial \mathbf{R}} d\mathbf{r}. \quad (56)$$

This term is most easily obtained directly from the total energy functional [Eq. (21)].

One thing that is remarkable is that the forces for the PAW method are almost identical to those for US-PP's. All differences are actually automatically absorbed in the definition of $(\hat{D}_{ij} + D_{ij}^1 - \tilde{D}_{ij}^1)$ in Eq. (55). For US-PP's the terms $D_{ij}^1 - \tilde{D}_{ij}^1$ are constant and calculated once and forever, whereas they vary during the calculation of the electronic ground state for the PAW method.

Realizing that the onsite terms only contribute in form of a change of the quantities $D_{ij}^1 - \tilde{D}_{ij}^1$ (i.e., these quantities vary during the determination of the ground state, whereas they are constant for US-PP's), it is also easy to evaluate the stress tensor. We will neither give the full derivation nor the final results here, as the expressions are rather cumbersome and difficult to write in a compact form. But for further details we refer to Ref. 12, where the stress tensor has been derived for US-PP. The changes with respect to US-PP's are trivial.

IV. PAW DATASETS

A. General considerations

To define a PAW data set the following quantities are required: (i) the AE and PS partial waves ϕ_i and $\tilde{\phi}_i$, (ii) the projector functions \tilde{p}_i , (iii) the core-charge density n_c , the pseudized core charge density \tilde{n}_{Zc} and the partial electronic core-charge density \tilde{n}_c and (iv) the compensation functions $g_l(r)$. Our particular choices for these functions are discussed in the following subsections.

B. Construction of the partial waves and projectors

The construction of the partial waves $\tilde{\phi}_i$ and projectors \tilde{p}_i proceeds along the same lines as in Ref. 14. First an all-electron calculation is performed for a spherical reference atom. Then, for each angular quantum number $l=0-1$ ($l=0-2$ for heavy alkali, alkali earth, and d elements), two reference energies are chosen and the AE partial waves $\phi_i(\mathbf{r})$ are calculated. One of the reference energies always coincides with the atomic eigenenergy of a valence orbital. Finally smooth PS partial waves

$$\tilde{\phi}_{i=Lk}(\mathbf{r}) = Y_{Lk}(\widehat{\mathbf{r}-\mathbf{R}}) \tilde{\phi}_{lk}(|\mathbf{r}-\mathbf{R}|)$$

are constructed. Loosely following Rappe, Rabe, Kaxiras, and Joannopoulos³⁰ (RRKJ) we expand the PS partial wave inside a cutoff radius r_c^l in terms of a linear combination of spherical Bessel functions

$$\tilde{\phi}_{lk}(r) = \begin{cases} \sum_{i=1}^2 \alpha_{ijl}(q_i r), & r < r_c^l \\ \phi_{lk}(r), & r > r_c^l \end{cases} \quad (57)$$

with the α_i and q_i chosen so that the PS partial wave $\phi_{lk}(r)$ is two times continuously differentiable. A set of two spherical Bessel functions $j_l(q_i r)$ is always sufficient to satisfy this condition (for details see Ref. 14).

The projectors \tilde{p}_i can be obtained using either Vanderbilt's scheme⁷ or Blöchl's Gram-Schmidt inspired scheme.⁸ It is straightforward to show that both methods result in *exactly the same* PAW functional, but Blöchl's scheme seems to be numerically better suited because it automatically avoids too large or too small numbers.

All PAW potentials and US-PP of the present work have been generated with two partial waves for the s and p orbitals. In terms of computer time, these potentials are slightly more expensive than potentials using only one projector, but potentials with two projectors are better transferable, easier to generate and generally speaking "saver" than those with one partial wave. The use of two projectors also parallels the LAPW method where the radial wave functions at some reference energy and the energy derivatives of these wave functions are used for the expansion of the wave functions inside the augmentation spheres. The PAW and the US-PP are however somewhat less prone to linearization errors, because part of the properties of the potential are described by the local pseudopotential. In some cases and for small cutoff radii, it is even possible to use only one projector in US-PP and PAW method. For more details we refer to Ref. 10.

C. The pseudized core charges and the local pseudopotential

The pseudized core charge \tilde{n}_{Zc} enters only via the local ionic pseudopotential $v_H[\tilde{n}_{Zc}]$, and we prefer to construct the pseudopotential $v_H[\tilde{n}_{Zc}]$ directly instead of \tilde{n}_{Zc} . We have also already pointed out that the potential $v_H[\tilde{n}_{Zc}]$ is entirely free within the augmentation sphere, whereas outside the augmentation sphere it must be identical to the all-electron potential $v_H[n_{Zc}]$. To obtain the local ionic pseudopotential $v_H[\tilde{n}_{Zc}]$, a local *atomic* pseudopotential \tilde{v}_{eff}^a is constructed first. The final ionic potential is obtained by unscreening the local atomic pseudopotential. This intermediate step is reminiscent of standard pseudopotential methods and it is convenient because it allows for a check on the scattering properties of the pseudoatom.

In fact, the local atomic PP \tilde{v}_{eff}^a *must* describe the scattering properties for angular components that are not included in the set of partial waves. The most convenient choice for the local potential is often a (norm-conserving) pseudopotential constructed for the first angular-momentum quantum number l , which is not included in the set of partial waves ($l=2$ or $l=3$). But unfortunately, this approach is often problematic, for instance for transition metals, because the resulting local f -PP is sometimes so attractive that ghost states in the s or p components are difficult to avoid.³¹ In

that case, a convenient choice for the local potential is a ‘‘truncated’’ AE potential, in which we replace the exact (self-consistent) atomic AE potential v_{eff}^a inside a cutoff radius r_{loc} by

$$\bar{v}_{\text{eff}}^a = A \frac{\sin(q_{\text{loc}} r)}{r} \quad \text{for } r < r_{\text{loc}}, \quad (58)$$

where q_{loc} and A are chosen so that the first derivative of the potential is continuous.

The second quantity to be determined is the pseudized partial electronic core-charge density. We expand \tilde{n}_c within a cutoff radius r_{pc} in a set of two spherical Bessel functions j_0 :

$$\sum_{i=1,2} B_i \frac{\sin(q_i r)}{r}. \quad (59)$$

Outside the partial core radius r_{pc} the partial core-charge density \tilde{n}_c is identical to the all-electron core charge n_c , and q_i and B_i are chosen so that the first two derivatives of the partial core-charge density are continuous (gradient-corrected exchange and correlation functionals require that the charge density is at least two times continuously differentiable).

Finally, the local ionic pseudopotential is obtained by un-screening of \bar{v}_{eff}^a [compare with Eqs. (32) and (43)]:

$$v_H[\tilde{n}_{Zc}] = \bar{v}_{\text{eff}}^a - v_H[\tilde{n}_a^1 + \hat{n}_a] - v_{xc}[\tilde{n}_a^1 + \hat{n}_a + \tilde{n}_c]. \quad (60)$$

For the PAW data sets used in the present work, the radius of the radial support grids r_{rad} is set to the largest core radius r_c^l . The partial core radius is set to $r_{pc} \approx r_{\text{rad}}/1.2$, and the local pseudopotential is adjusted so that the scattering properties of all angular-momentum components up to $l=4$ are described with high accuracy; due to the centrifugal wall higher l quantum numbers are automatically described very well. For s and p elements this was achieved by constructing a norm-conserving PP for the d electrons, whereas for transition metals (and some alkali and alkali earth) elements the local PP was, set to a truncated all electron potential with $r_{\text{loc}} < r_{\text{rad}}/1.2$.

D. Compensation charge, double grid technique

The final quantities we want to discuss are the compensation functions $g_l(r)$. We construct each $g_l(r)$ as a sum of two spherical Bessel functions

$$g_l(r) = \sum_{i=1}^2 \alpha_i^l j_l(q_i^l r). \quad (61)$$

The coefficients q_i^l and α_i^l are chosen so that $g_l(r)$ and its first two derivatives are zero at a radius r_{comp} and so that the moment l is equal to 1:

$$\int_0^{r_{\text{comp}}} g_l(r) r^{l+2} dr = 1. \quad (62)$$

This can be accomplished by choosing q_i^l so that

$$\left. \frac{d}{dr} j_l(q_i^l r) \right|_{r_{\text{comp}}} = 0, \quad (63)$$

and setting α_i^l so that the equation $g_l(r_{\text{comp}}) = 0$ and Eq. (62) are fulfilled. In our present work, the radius r_{comp} is usually a factor 1.2–1.3 smaller than the radius of the radial integration sphere r_{rad} . We have chosen this value because due to the continuity condition the AE and PS charge density agree almost perfectly up to this point. A less contracted compensation charge could therefore spoil the transferability if the core regions are allowed to overlap.

The particular form of the compensation functions [Eq. (61)] was chosen because it results in augmentation charges that are strictly confined to a sphere of the radius r_{comp} in real space, and because the compensation charges can be expressed accurately on a relatively coarse real-space grid. In our current implementation, this real-space grid is not necessarily similar to the plane-wave grid used for fast Fourier transforms of the pseudo-wave-functions $\tilde{\Psi}_n$. It contains usually twice to three times more grid points. To interpolate results from one grid to the other we use a dual grid technique that is very similar to that of Laasonen *et al.*¹¹ and has been implemented before by one of us in the total energy program VASP (Vienna *ab initio* simulation package).^{12–15} Therefore, we will only give a very short description of the technique here. The charge density of the PS wave functions $\tilde{n}(\mathbf{r})$ is evaluated on the conventional plane-wave grid in real space. Then the charge density $\tilde{n}(\mathbf{r})$ is transformed to reciprocal space, transferred to a second grid with a larger plane-wave cutoff, and Fourier transformed back to real space [this three-step procedure corresponds to a Fourier interpolation of $\tilde{n}(\mathbf{r})$ from a coarse to a finer grid]. The compensation charge density is calculated directly in real space and added to \tilde{n} on this fine real-space grid. The Hartree potential, exchange-correlation potential, and the local potential are also calculated on this second grid. The final local potential is also required on the coarser plane-wave grid to evaluate the action of the Hamiltonian on the wave functions (see Sec. III B). This is done again using a Fourier interpolation: in this case the local potential is first transformed on the fine grid to the reciprocal space, then it is brought to the plane-wave grid neglecting components, which do not exist on the plane-wave grid, and finally it is Fourier transformed back to real space.

It is important to stress that the compensation charge \hat{n} is added directly in real space, which avoids the complications arising in the moving boxes technique proposed in Ref. 11. The numerical effort for the work on the real-space grid scales like ‘‘ $O(N)$ ’’ whereas in the conventional Kohn–Sham scheme the remaining operations scale asymptotically like ‘‘ $O(N^3)$.’’ Already for an intermediate system (some few ten atoms) or a large number of k points the additional computational effort for the fine real-space grid is almost negligible. Therefore, we have also not attempted to implement the method proposed in Ref. 8, where the compensation charge is allowed to extend over several atomic sites and short-ranged pair potentials are added to correct for the resulting errors. It should also again be stressed that the compensation charges are very soft in the PAW method because it is not required that they mimic the form of the real charge-

density difference between the AE and PS partial wave [Eq. (35)]. Thus, even without the second support grid errors are usually only around 1 meV for s and p elements (where the moments of the augmentation charges q_{ij}^L are small) and 5 meV for d and f elements. If the second support grid has twice or three times more grid points the resulting errors are usually negligible (less than 0.5 meV/atom for d metals). We found an independent support grid also advantageous for the evaluation of the generalized gradient corrections where too coarse grids often cause numerical problems.

E. Ghost states

We want to discuss briefly the problem of ghost states because authors have reported difficulties in the construction of PAW datasets for some elements.²² In contrast to their findings, we never encountered serious problems when employing the scheme outlined in the previous subsections, but it is true that the construction must be done carefully. Fortunately, we had a well-tested database of US-PP for all s , p , and d elements on which our construction of PAW datasets could be based.

Our findings are that ghost-states tend to exist if an unreasonable attractive local atomic pseudopotential \tilde{v}_{eff}^a is chosen, which is in accordance with the observation of Gonze *et al.* (Ref. 31). Anyway for all s , p , and d elements we were able to obtain a reasonable local atomic pseudopotential that avoids ghost states and describes the scattering properties for high angular components ($l > 2$) very accurately.

Another problem is the construction of accurate pseudopotentials for elements with a large covalent radius and a small ionic radius (e.g., K-Mn, Rb-Ru, Cs-Os). In fact, it seems to be impossible to construct PAW data sets and US-PP's with a small r_c (approaching the ionic radius) for these elements if the $3p$, $4p$, or $5p$ semicore states (and sometimes $3s$, $4s$, or $5s$ states) are kept in the core. But this is in no way unexpected and similar problems are well known in the LAPW method:⁵ Let us consider, for example, Ca, for which the covalent radius is 3.7 a.u. For many calculations, a convenient core radius for this elements is around the ionic radius that equals 2.0 a.u. In the valence-band region at this radius, the logarithmic derivatives of the p states exhibit a (albeit very weak) curvature towards the lower-lying $3p$ core states. A PAW data set or an US-PP constructed for the valence-band region only will thus “see” the lower-lying $3p$ semicore state and the resulting potential poses a p ghost state. Once the $3p$ semicore state is treated as a valence state this problem is entirely removed, and very accurate ghost-state-free pseudopotentials can be obtained even with small core radii.

V. RESULTS

A. Small molecules

To test the accuracy of our current implementation, and to illustrate the differences between US-PP's, the PAW and relaxed core all-electron methods we have performed a series of calculations for small test molecules for which accurate AE results have been published (see Refs. 32 and 33). The results of our calculations and a comparison with the AE calculations are shown in Table I; the parameters for the

TABLE I. Results for the bond length of several molecules (and the bond angle α in H₂O) obtained with the PAW, US-PP, and AE approaches. Values in parentheses were obtained with a plane-wave cutoff of 700 eV and “hard” US-PP's and PAW datasets with a core radius of $r_c^l = 1.1$ a.u. for C, N, O, F, and $r_c^l = 0.7$ a.u. for H. The parameters and cutoffs of the other PP's are summarized in Table II.

	US-PP	PAW	AE
H ₂	1.447	1.447	1.446 ^a
Li ₂	5.127	5.120	5.120 ^a
Be ₂	4.524	4.520	4.521 ^a
Na ₂	5.667	5.663	5.67 ^a
CO	2.141 (2.127)	2.141 (2.128)	2.129 ^a
N ₂	2.077 (2.066)	2.076 (2.068)	2.068 ^a
F ₂	2.640 (2.626)	2.633 (2.621)	2.615 ^a
P ₂	3.570	3.570	3.572 ^a
H ₂ O	1.840 (1.834)	1.839 (1.835)	1.833 ^a
α (H ₂ O)	105.3°(104.8°)	105.3°(104.8°)	105.0°
BF ₃	2.476 (2.470)	2.476 (2.470)	2.464 ^b
SiF ₄	2.953 (2.948)	2.953 (2.948)	2.949 ^b

^aNUMOL, Ref. 32.

^bGAUSSIAN94, Ref. 33.

pseudopotential generation and the PAW datasets and the cutoff energies are summarized in Table II. For the first-row elements, additional hard PAW and US pseudopotentials with a core radius of 1.1 a.u., which required a plane-wave energy cutoff of approximately 600–700 eV, were generated.

TABLE II. Parameters of the PAW datasets and the US-PP's used in the present work. In all cases, two partial waves are used for the s and p orbitals (for Ca and the transition-metals two partial waves are used for the d orbitals, too). “Valence” indicates which orbitals are treated as valence orbitals, r_c^l are the cutoff radii for the partial waves, and r_{comp}^l are the cutoff radii for the norm-conserving partial waves used in the construction of the augmentation charges of the US-PP's. If small indices are used, they indicate which cutoff was used for s , p , and d partial waves. E_{cut} are the energy cutoffs employed in the calculations with these pseudopotentials.

	Valence	r_c^l (a.u.)	r_{comp}^l (a.u.)	E_{cut} (eV)
H	1s	1.2	0.8	400
Li	1s2s2p	2.0	2.0	160
Be	2s2p	1.9	1.5	240
B	2s2p	1.5 _s , 1.7 _p	1.2	400
C	2s2p	1.3 _s , 1.5 _p	1.1	400
N	2s2p	1.3 _s , 1.5 _p	1.1	400
F	2s2p	1.3 _s , 1.5 _p	1.1	400
Na	2p3s	2.2	1.5	210
Si	3s3p	1.9	1.5	240
P	3s3p	1.9	1.5	240
Ca(1)	3p4s3d	3.0 _s , 2.3 _{p,d}	1.5	230
Ca(2)	3s3p4s3d	2.3		230
V	3p4s4p3d	2.3	2.1	260
Fe	4s4p3d	2.2	1.9 _{s,p} , 1.5 _d	300
Co	4s4p3d	2.2	1.9	300
Ni	4s4p3d	2.2	1.9	300

For these potentials, the overlap between the core spheres is negligible even for first-row dimers. Again two partial waves per l quantum number were used, but for this small core radius, data sets with only one projector per angular-momentum number yield results that are almost equivalent to those obtained with potentials using two projectors.

In our calculations, the Ceperley and Alder³⁴ exchange-correlation functional as parametrized by Perdew and Zunger (CA-PZ) was adopted.³⁵ A cubic box was used in all cases; for the dimers the box size was six times the bond length of the investigated dimer (but at least 8 Å), the box size for the three other molecules was 10 Å. We have checked for several molecules that neither an increase of the box size nor an increase of the plane-wave cutoff changes the bond length by more than 0.1%.

The results in Table I show first of all that there is virtually no difference between the US-PP calculations and the corresponding PAW calculations, typical discrepancies being around 0.1%. However, the generation of the Na US-PP was somewhat difficult, and we have in fact played a little bit with the cutoff radii r_{comp}^l of the augmentation charges till we were able to reproduce the PAW results. And even worse, for Li we were not able to construct an accurate US-PP with unfrozen $1s$ states,³⁶ and therefore the results for the Li dimer have been obtained with an US-PP for which the $1s$ electron was kept in the frozen core. Table I indicates that this PP is reliable for the dimer, but we expect it to be somewhat problematic for strongly ionic environments. The reason for the difficulties is rather easy to understand: The semicore states are strongly localized and it is rather difficult to obtain an accurate pseudized augmentation function [Eq. (37)] for these states and the (almost orthogonal) valence states, that can be described at the same time with a reasonable real-space support grid. Therefore, a delicate optimization of the cutoff radius of the augmentation functions is required to balance accuracy versus computational efficiency. These problems are of course most severe for Li, for which the $1s$ orbitals are strongly contracted.

We now turn to the comparison between the (relaxed core) AE calculations and the frozen core PAW and US-PP method. The agreement is generally excellent, the errors in the dimer bond length being smaller than 0.1% (with the exception of F_2 for which the error is around 0.2%). Similar agreement between plane-wave pseudopotential calculations and AE calculations can rarely be found in the literature (plane-wave-based calculations that come close in terms of accuracy have been reported by Goedecker *et al.*³³ and Andrews *et al.*³⁷). In order to obtain this excellent accuracy, we had to decrease the core radius for the first-row elements to 1.1 a.u. and increase the cutoff energy at the same time to 700 eV. But even with the “standard” 400-eV first-row pseudopotentials, in which the overlap between the core regions is appreciable, the bond length errors are generally smaller than 0.5%. In addition, these first-row pseudopotentials yield reliable results even at 300 eV, the bond length errors are than 1% for N_2 , CO , and F_2 , which is probably acceptable for many calculations. We want to stress that the large overlap between the core regions is only allowed for our specific construction scheme using spherical Bessel functions and one should not expect a similar behavior for other schemes (see also Ref. 10).

Finally, we want to point out that, our test calculations include two rather “difficult” molecules with a large electronegativity difference (BF_3 and SiF_4). The table clearly shows that the PAW method and US-PP approach are capable of handling such difficult cases with good accuracy, and even when soft potentials for the first-row elements are used (cutoff 400 eV), the errors remain well below 0.5%.

B. Bulk

To test our implementation for bulk systems we have chosen the test systems of Ref. 21. These systems are representative of typical covalent, ionic, and metallic materials and can be considered as a rather stringent test of the current implementation. In our calculations, we have used $11 \times 11 \times 11 k$ points in the full wedge of the Brillouin zone for the metallic systems and $7 \times 7 \times 7 k$ points for insulating systems (cubic-diamond structure and CaF_2). The parameters used for the pseudopotential generation and the cutoff energies are again summarized in Table II.

Our results—together with those of Ref. 21—are shown in Table III. The energies in Table III have been calculated as the energy difference between the (non-spin-polarized) atom for which the PAW dataset and the pseudopotential have been constructed, and should not be compared directly with experimental values. It is evident that the agreement between the results of the current PAW implementation and the results of Ref. 21 [PAW, and full potential linearized augmented plane wave (FLAPW)] is excellent. Differences in the lattice constant, bulk modulus, and cohesive energy are smaller than 0.5%, 5%, and 1%, respectively. The slightly larger discrepancies of the bulk moduli are probably related to the fact that elastic properties are very sensitive to the choice of data points and the equation of state used in the fit of the energy-volume curve. Because of the huge difference in electronegativity the most difficult test case is CaF_2 . Very reliable results for this material can be obtained only if the $3p$ semicore states are unfrozen. As can be seen, it does not matter whether the $3s$ states are treated as valence or core states, but unless the $3s$ states are also treated as valence states a rather large cutoff of 3.0 a.u. must be used for the s partial wave to avoid ghost states. Therefore, the second dataset with an unfrozen $3s$ state is more elegant and symmetric. The general conclusion of the bulk calculations is that our current implementation of the PAW method is able to describe bulk properties very accurately, the level of accuracy is comparable to FLAPW calculations.

We now come to the comparison between US-PP’s and all-electron calculations (PAW and FLAPW). Table III clearly shows that the US-PP’s give results that are almost indistinguishable from AE calculations. Even for the rather difficult CaF_2 no differences can be observed. But it should be stressed that the construction of a suitable US-PP for Ca was again not as straightforward as the construction of the PAW dataset. As we have already pointed out before, this is a general obstacle we observed when constructing US-PP for alkali, alkali earth, and transition metals in which semicore states are treated as valence states.

Another point that we want to discuss here is the introduction of nonlinear core corrections. We have claimed in Sec. II C that these corrections improve the robustness of the

TABLE III. Results for the equilibrium lattice constant a , cohesive energy E_{coh} (with respect to the non-spin-polarized atom used for the PP construction) and bulk modulus B for several materials calculated with the PAW, US-PP, and the LAPW approach.

	a (\AA^3)	E_{coh} (eV)	B (GPa)
Diamond			
US-PP(current)	3.535	-10.12	461
PAW(current)	3.535	-10.11	460
PAW ^a	3.54	-10.16	460
LAPW ^a	3.54	-10.13	470
silicon			
US-PP(current)	5.40	-5.96	95
PAW(current)	5.40	-5.96	95
PAW ^a	5.38	-6.03	98
LAPW ^a	5.41	-5.92	98
bcc V			
US-PP(current)	2.93	-9.41	206
PAW(current)	2.93	-9.39	210
PAW ^a	2.94	-9.39	200
LAPW ^a	2.94	-9.27	200
bcc Li			
PAW(1s val)	3.363	-2.034	15.0
PAW(1s frozen)	3.368	-2.037	15.0
PAW(s only)	3.368	-2.026	15.0
PAW(1s frozen, no pc)	3.349	-2.027	15.0
PAW(s only, no pc)	3.463	-1.711	12.6
AE ^b	3.36		15.0
fcc Ca			
US-PP(current-1)	5.34	-2.18	18.3
PAW(current-1)	5.34	-2.19	18.5
PAW(current-2)	5.34	-2.18	18.5
PAW ^a	5.32	-2.24	19
LAPW ^a	5.33	-2.20	19
CaF ₂			
US-PP(current-1)	5.34	-6.35	101
PAW(current-1)	5.34	-6.35	101
PAW(current-2)	5.34	-6.34	100
PAW ^a	5.34	-6.36	100
LAPW ^a	5.33	-6.30	110

^aHolzwarth *et al.* (Ref. 21).

^bPerdew *et al.* (Ref. 38).

PAW method with respect to the completeness of the partial waves. That this is in fact true is shown for bcc Li. If the 1s electron is treated as a valence electron, our results agree perfectly with the AE results of Perdew *et al.*³⁸ If the 1s electrons are kept frozen and if two s and two p partial waves are included (“1s frozen”) very similar results are obtained with nonlinear core corrections. Without nonlinear core corrections the error is slightly larger (“1s frozen, no pc”). If p partial waves are, however, *not* used the results without nonlinear core corrections (“s only, no pc”) become unreliable, whereas those with nonlinear core correction remain correct (“s only”). This behavior is easy to understand: Without p partial waves, the $2p$ contribution of Li is handled by the local potential. This is no problem *per se*, because the local potential can be chose so that the p -scattering properties are described very precisely. But

without partial core corrections, the large overlap between the $2p$ and $1s$ electrons is not treated correctly in the exchange correction part of the total energy resulting in rather large errors.

Finally, we want to mention that we have undertaken systematic calculations with US-PP’s and the PAW method for simple structures (fcc, bcc, sc, hcp, cubic diamond, dimers) for all s , p , and d elements and found that the differences in the equilibrium volumes usually do not exceed 1%. The largest differences are found for materials with a large magnetic moment and we will come back to this point in the next section. In all other cases, results for US-PP’s and the PAW method are practically indistinguishable. This is a clear indication for the reliability of the US-PP approach, and it also points to the close link between both approaches.

C. Fe, Co, and Ni

Recently, the accuracy of US-PP’s was investigated by Moroni *et al.*²⁰ for spin polarized calculations in atoms, dimers, and solids. Although a satisfactory agreement with AE methods was found for most properties, a few discrepancies remained. In view of the increased accuracy of the PAW method in comparison to US-PP’s, we have investigated whether the PAW improves upon these discrepancies.

1. Pseudopotential generation

The pseudopotentials are constructed in essentially the same way as in Ref. 20, but here we have chosen the atomic reference configurations $4s^{1.5}3d^{n-1.5}$ for the construction of the pseudopotentials for Fe, Co, and Ni. This configuration minimizes interconfigurational errors in atoms (see below). The core radius is set to 2.2 a.u. for the US-PP and the PAW method. For the augmentation charges in the US-PP method a cutoff of 1.9 a.u. is chosen (see also Table II), only for the d -augmentation charges of Fe a smaller radius was used. Partial core corrections and local pseudopotential are equivalent to Ref. 20. For the LDA calculation we use the Ceperley and Alder³⁴ exchange correlation as parametrized by Perdew and Zunger (CA-PZ).³⁵ For the calculations based on the generalized gradient approximation (GGA), we also used the CA parametrization for the LDA part and applied the gradient corrections according to Perdew-Wang 1991 (PW91).^{38,39} The spin interpolation of the correlation energy was done either with the standard interpolation formula (atoms) or the Vosko-Wilk-Nusair (VWN) interpolation (bulk).⁴⁰

2. Atoms

As a first test we calculated the interconfigurational energy between two magnetic (M) configurations $\Delta E_{ic} = E_M(4s^1 3d^{n-1}) - E_M(4s^2 3d^{n-2})$ and the energy difference between the magnetic ground state and one specific nonmagnetic (NM) configuration $\Delta E_m = E_M(4s^x 3d^{n-x}) - E_{NM}(4s^1 3d^{n-1})$. All test calculations were performed for spherical atoms placed in a large cubic box. Although it is known that calculations for spherical atoms will not reproduce the correct experimental ground state (see, for instance, Refs. 41 and 42) sphericity was assumed because it allows for a simple comparison with all-electron calculations. To calculate the energy of the magnetic ground state $E_M(4s^x 3d^{n-x})$ the occupancies of the s orbitals x were var-

TABLE IV. Comparison of LSD and GGA PAW, US-PP and scalar relativistic all-electron calculations for Fe, Co, and Ni atoms. In the AE calculation, all orbitals were allowed to relax. For each atom the computed ground state (gs) configuration the magnetic energy $\Delta E_m = E_M(\text{gs}) - E_{NM}(4s^1 3d^{n-1})$, and inter-configurational energy ΔE_{ic} (see text) are listed. All energies are in eV. GGA results are in parentheses. The results US-AE have been obtained with an US-PP in which the augmentation charges are very accurate and hard (see text).

		US-PP	PAW	AE
Fe	gs	$3d^{6.2}4s^{1.8}$	$3d^{6.2}4s^{1.8}$	$3d^{6.2}4s^{1.8}$
	ΔE_m	2.75 (2.95)	2.61 (2.77)	2.60 (2.76)
	ΔE_{ic}	0.47 (0.44)	0.38 (0.39)	0.37 (0.39)
Fe US-AE	gs	$3d^{6.2}4s^{1.8}$		
	ΔE_m	2.61 (2.78)		
	ΔE_{ic}	0.38 (0.42)		
Co	gs	$3d^{7.7}4s^{1.3}$	$3d^{7.7}4s^{1.3}$	$3d^{7.7}4s^{1.3}$
	ΔE_m	1.27 (1.40)	1.23 (1.32)	1.22 (1.31)
	ΔE_{ic}	-0.40 (-0.32)	-0.42 (-0.43)	-0.41 (-0.42)
Ni	gs	$3d^9 4s^1$	$3d^9 4s^1$	$3d^9 4s^1$
	ΔE_m	0.47 (0.54)	0.46 (0.52)	0.45 (0.52)
	ΔE_{ic}	-1.20 (-1.17)	-1.22 (-1.23)	-1.20 (-1.21)

ied till a minimum in the total energy was found. The ground-state configuration has “nonphysical” fractional occupancies, but the essential point is that all three methods give the same occupancies. Our results for the ground-state configuration, the interconfigurational energy and the magnetic energy are presented in Table IV.

First, we want to comment on the small discrepancies between our current results for US-PP’s and those presented in Ref. 20: The values differ by at most 0.02 eV (with the exception of ΔE_m for Fe). The main reason for these discrepancies is that we have chosen a different reference configuration in the present work, and that the cutoff of the d part of the augmentation function was smaller in the present work.

From a first look it is obvious that the agreement between the (frozen core) PAW and the (relaxed core) AE method is excellent, the differences are at most 10 meV. Agreement between the US-PP and the AE method is slightly worse: The US-PP clearly overestimates the magnetization energies, the discrepancies being generally larger for the GGA calculations. The most likely explanation for the latter observation is that the GGA depends more strongly on the exact shape of the wave functions than the LDA. Whereas discrepancies are difficult and expensive to avoid in the US-PP method, the PAW is of course able to reproduce the shape of the AE wave function exactly (including all nodes). To check that the insufficient representation of the augmentation charges is indeed responsible for the observed errors, we have generated an US-PP in which the augmentation charges and the partial core corrections approach the AE quantities (US-AE). We found that we were able to reproduce the PAW and AE results with a radial pseudization radius of 0.5 a.u. for the augmentation charges, and a partial core radius around 0.3 a.u. With this setting the pseudocore and wave functions exhibit the correct shape even in the region of the $2p$ electrons. Although we obtained excellent agreement with the AE methods in that case, the calculations are rather expensive for routine calculation because a very fine real-space grid is required in order to represent the hard augmentation charges.

3. Bulk

The results for the structural properties of bcc ferromagnetic (FM) Fe, hcp NM Fe, hcp FM Co, and fcc FM Ni are shown in Table V. To facilitate comparison with other calculations we have used the spin-interpolation formula of Vosko-Wilk-Nusair⁴⁰ (VWN) here. This is also the interpolation scheme usually applied in context of the PW91 functional, and it increase the magnetization energy of bcc FM Fe by approximately 40–50 meV. When comparing the current results with those of Ref. 20 some caution is required, because the standard interpolation formula was used in Ref. 20. Despite that the general agreement with Ref. 20 is very good, the differences in the lattice constant are generally smaller than 0.5%. The main reason for the presently slightly smaller lattice constants is that in the current calculations, the cutoff radius for the pseudopotential was somewhat smaller.

The discrepancies between the US-PP and the PAW method are—with the exception of bcc FM Fe—also minute. As for atoms the differences for FM Fe are larger for the GGA than for LDA. We have already attributed this to the fact that GGA functionals are more sensitive to the shape of the wave functions than LDA functionals. To double check our results we applied again the US-PP for Fe in which the augmentation charges and the partial core corrections are truncated around 0.5 and 0.3 a.u., respectively. The results for this ultrasoft pseudopotential are shown in the rows “US-AE” in Table V. It is obvious that this pseudopotential yields essentially the same results as the PAW method, and this shows that the errors of our conventional US-PP (in which the augmentation charges are pseudized around 1.5–1.9 a.u.) are again clearly related to the insufficient representation of the shape of the wave function within the core region. We performed several tests to find out how small the truncation radius of the augmentation charges must be in order to obtain an accuracy that is comparable to the PAW. The results of that calculation showed again that the shape of the d wave functions must be reproduced even in the region of the $2p$ electrons, putting an upper limit of around 0.5 a.u.

TABLE V. Comparison of the equilibrium lattice constant (a), bulk modulus (B), and magnetic moment (M_0) for bcc FM Fe, hcp NM Fe, hcp FM Co, and fcc FM Ni calculated with PAW, US-PP, and FLAPW scalar relativistic calculations (the GGA results are in parentheses).

		a (Å)	B (Mbar)	M_0 (μ_B)
bcc Fe (FM)	FLAPW ^a	2.76 (2.83)	2.45 (1.89)	2.04 (2.17)
	PAW	2.75 (2.83)	2.47 (1.74)	2.00 (2.20)
	US-AE	2.75 (2.83)	2.45 (1.75)	2.01 (2.19)
	US-PP	2.76 (2.85)	2.37 (1.51)	2.08 (2.32)
hcp Fe (NM)	FLAPW ^a	2.38 (2.43)	3.44 (2.91)	
	PAW	2.38 (2.43)	3.46 (2.85)	
	US-AE	2.38 (2.43)	3.46 (2.82)	
	US-PP	2.38 (2.43)	3.38 (2.78)	
hcp Co (FM)	PAW	2.43 (2.49)	2.73 (2.13)	1.51 (1.59)
	US-PP	2.43 (2.50)	2.67 (2.07)	1.52 (1.62)
fcc Ni (FM)	FLAPW ^b	(3.52)	(2.00)	(0.60)
	PAW	3.43 (3.52)	2.51 (1.94)	0.58 (0.61)
	US-PP	3.44 (3.53)	2.48 (1.94)	0.56 (0.62)

^aFLAPW, Stixrude *et al.* (Ref. 43).

^bFLAPW, Herper *et al.* (Ref. 44).

on the truncation radius of the augmentation charges. The error decreases very slowly (almost linearly) until the cutoff radius r_{comp} reaches this value.

To further illustrate the differences between the ‘‘standard’’ US-PP and the PAW method, we show the structural energy differences between FM bcc Fe, NM bcc Fe, NM fcc Fe, and NM hcp Fe in Table VI. It is obvious that the agreement between the PAW method, the US-AE pseudopotential method, and the FLAPW calculations is again almost perfect. For nonmagnetic structures, the ‘‘standard’’ US-PP agrees also well with the other two calculations, but the disagreement is large for the magnetic bcc phase. In the LDA, the differences are a tolerable 50 meV, but in the GGA the US-PP overestimates the magnetic energy by 120 meV. A look at Table IV shows that this is almost exactly half of the error observed in the atom, it seems therefore likely that the overestimation of the magnetic energy is directly proportional to the magnetic moment on the Fe atom and amounts to approximately 60 meV/ μ_B .

As a final check we have evaluated the transition pressure from the FM bcc to NM hcp phase and we obtained a transition pressure of 11 GPa with the PAW method, which is in excellent agreement with other theoretical studies.^{43,45} In the present work, the transition pressure is seriously overestimated with the ‘‘standard’’ US-PP. It should be stressed again that we have used the Vosko-Wilk-Nusair formula for

the spin interpolation of the correlation energy, whereas in Ref. 20 the standard interpolation was applied resulting in a reasonable but still somewhat too high transition pressure with US-PP’s.

VI. DISCUSSION

In this work, we have presented a slightly modified PAW functional, which is rather easy to implement in programs supporting US-PP’s. The key modifications are, first, that the Hartree energy is split in a way that closely resembles the tradition of pseudopotential plane-wave codes, and second, that partial core corrections are included when the exchange-correlation energy is evaluated on the plane-wave grid. We have shown that our treatment of the exchange-correlation energy is superior for an incomplete set of partial waves (which is in practice always adopted). Because our existing plane-wave program could handle two distinct FFT grids (double grid technique) we have also avoided the introduction of very soft compensation charges extending over several augmentation spheres. This makes the implementation of the PAW method very easy and convenient, without compromising the efficiency of the method seriously. In Sec. III, we have derived the Hamilton operator and the forces for this modified PAW functional and in our discussion we have tried to highlight the significance of individual terms in the energy, the Hamilton operator and in the forces. The implementation of the stress tensor was also briefly discussed.

One important point of the present work is that we derived the US-PP method proposed by Vanderbilt⁷ by linearizing two terms in the PAW method. This derivation clearly reveals the close connection between the PAW and the US-PP method. It also indicates that the US-PP method will give results that are almost indistinguishable from that of the PAW method for materials in which the charge-density distribution closely resembles that of the reference system within the core region. However, for materials with a strong electronegativity difference and systems with large magnetic

TABLE VI. Energy differences between different phases of Fe. The NM hcp phase was chosen as the energy zero (results for GGA are in parentheses).

	FLAPW ^a	PAW	US-AE	US-PP
bcc Fe NM		412 (373)	413 (372)	413 (369)
bcc Fe FM	133 (−73)	139 (−73)	139 (−73)	81 (−191)
fcc Fe NM	77 (78)	71 (61)	70 (62)	70 (62)
hcp Fe NM		0	0	0

^aFLAPW, Stixrude *et al.* (Ref. 43).

moments, the US-PP method is more problematic and care must be taken to construct pseudized augmentation functions that restore the AE charge distribution with sufficiently high accuracy.

The second part of the present work was concerned with a comparison of the US-PP method, the PAW method and all electron approaches for small molecules and simple bulk systems. With a maximum bond length error of 0.3%, this section shows clearly that the PAW method gives results that are in general as accurate as relaxed core all-electron calculations, indicating that all approximations of the PAW method are well under control. These approximations are, first, the use of a finite set of partial waves, and second, the frozen-core approximation. The presented calculations show that two partial waves per occupied orbital are sufficient to obtain excellent results in the PAW method (see also Ref. 10). At first sight, the frozen-core approximation seems to be a more severe restriction. However, we believe that this is in fact not the case. Whenever necessary it is anyway possible to unfreeze semicore states in the PAW method. For several cases—for instance, most alkali and alkali-earth metals and transition metals at the left side of the Periodic Table (e.g., Sc–Mn)—it is in fact well known that the treatment of semicore states as valence states is very desirable. Fortunately, the unfreezing of lower-lying core states is straightforward and very simple in the PAW method, because only one partial wave (and projector) for the semicore state must be added. It is important to stress that the unfreezing of core states also does not worsen or compromise the efficiency of the method seriously. As an example let us consider CaF_2 . Since for this system, the energy cutoff and the size of the plane-wave basis set are determined by the “hard” F dataset, the unfreezing of the semicore states of Ca increases only the number of occupied and calculated bands, whereas the size of the basis set remains unchanged. The same holds for most compounds and molecules that contain Ca because the required energy cutoff for Ca remains a rather modest 230 eV, even if the Ca 3s states are treated as valence states. It is worthwhile mentioning that accurate FLAPW calculations also require that semicore states are treated in the same way as other valence states,⁵ so that we expect that the PAW method is in that respect as efficient as the FLAPW method.⁴⁶

We have also presented a thorough comparison of the US-PP method and the PAW method. Our derivation of the US-PP method shows that in the limit of very accurate augmentation charges the US-PP method should—and in fact does—reproduce the results of the PAW method. Differences between both methods are solely related to the pseudization of the augmentation charges in the US-PP approach. For magnetic Fe, we have demonstrated that such discrepancies can be removed by choosing very accurate pseudized augmentation function. Unfortunately, in the US-PP method, compromises in the presentation of the augmentation charges are inevitable because the augmentation charges must be represented on a regular grid. Within the US-PP approach, hard and accurate pseudized augmentation charges are therefore expensive in terms of computer time and in terms of computer memory. The PAW avoids these compromises by introducing radial support grids. From that point of view, one could say that the PAW method is just an elegant and effi-

cient technique to treat rapidly varying functions on radial support grids. However, the PAW method offers an additional consistent and elegant framework for pseudopotential related methods.

Finally, it is important to emphasize that—despite the previously discussed difficulties—the US-PP method yields very reliable results for all *p* elements and most nonmagnetic transition metals. This is the case, because the construction of US-PP for these elements is relatively straightforward, since reasonably soft and accurate augmentation charges are easy to obtain. We found however also several instances where the PAW method has distinctive advantages over US-PP. In particular, for transition metals with a large magnetic moment (e.g., Fe) very accurate results are difficult to obtain with the US-PP approach with reasonably soft augmentation charges. Another case where the PAW method seems to be superior to the US-PP method are the alkali and alkali-earth metals, and transition metals to the left of the periodic table. We have already stressed that for accurate calculations in these materials the semicore states should be treated as valence states. In principle, this can be achieved within the US-PP approach, and our results for CaF_2 and many other results obtained with our code VASP for transition-metal oxides, silicides, and sulfides (e.g., CoSi ,⁴⁷ TiO_2 ,⁴⁸ YSi_2 ,⁴⁹ and transition-metal sulfides⁵⁰) show that reasonable results can usually be obtained if the US-PP’s have been constructed with care. But generally speaking, the construction of PAW datasets is significantly easier for these cases than the generation of US-PP’s.

VII. CONCLUSION

The PAW method is capable of handling even the most difficult cases (strong magnetic moments, large electronegativity differences) with exceptional precision. The typical bond length errors are smaller than 0.5% even if rather soft PAW data sets requiring less than 400 eV are used. This demonstrates both the efficiency and the reliability of the PAW method. The closely related US-PP method offers in general a similar precision, it is however less reliable for magnetic systems.

ACKNOWLEDGMENTS

We thank J. Hafner, M. Gillan, G. De Wijs, and D. Alfe for helpful discussions and comments. The support of EPSRC through Grants Nos. GR/L08946 and GR/L38592 is gratefully acknowledged. Part of the work has been undertaken within the Groupement de Recherche Européen “Dynamique Moléculaire Quantique appliqué à la catalyse et à l’adsorption” supported by the French Center National de la Recherche Scientifique (CNRS) and the Institut Français du Pétrole. One of us (G.K.) acknowledges financial support through the joint research project “Gas-Surface Interaction,” Grant No. S8106-PHY.

APPENDIX: COMPARISON WITH OTHER PAW IMPLEMENTATIONS

In this appendix we compare our total energy functional with that of Holzwarth *et al.*²¹ In many respects, both func-

tionals are in fact equivalent, but our arrangement is clearly more symmetric. Part of the differences stem from the fact that Holzwarth *et al.* have introduced a pseudized frozen-core charge $\tilde{n}_{\text{core}} = \tilde{n}_{Zc}$, which does not have the same multipole moments as n_{Zc} . Therefore in their case, part of the long-range electrostatic core-core interaction has to be accounted for by the compensation charge \hat{n} . In addition, in Ref. 21 the overlap of the core-charge densities n_{core} into neighboring spheres is evaluated by means of the on-site terms [for instance terms involving v_{core} in Eqs. (10) and (11) of Ref. 21]. Within the frozen-core approximation this is in principle the most accurate approach, but it makes the on-site terms explicitly structure dependent, which is inconvenient for the calculation of forces. A simpler approach is to add

$$\int d\mathbf{r} \int d\mathbf{r}' \frac{\hat{n}(\mathbf{r})n_{\text{core}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

to Eq. (9) of Ref. 21, as it is done in our case [fourth term in Eq. (21)]. This is also the method Blöchl has used to approximate the overlap between different spheres. The underlying idea is that the soft pseudocharge $\tilde{n} + \hat{n} + \tilde{n}_{Zc}$ is equivalent to the exact all-electron charge $n + n_{Zc}$ even within a certain region *within* the augmentation sphere (continuity of the derivatives at the sphere boundary, see Sec. IV A), thus, the resulting errors are small. In view of the limited accuracy of the frozen-core approach, it also seems to us that the complications arising from structure-dependent on-site terms are not worth the additional effort, and as our tests show, the more approximate treatment seems to be sufficiently accurate anyway.

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