Notes for revised form of *atompaw* code.

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These notes are based on published work on the PAW formalism ([1, 2, 3, 4]) as implemented in the *atompaw* and *pwpaw* codes (http://pwpaw.wfu.edu). Please send any questions and report errors to natalie@wfu.edu.

1 PAW basis and projector functions

PAW calculations require a set of basis and projector functions which are denoted (in the notation of previous work[1, 2, 5, 6, 3, 4]) $|\phi_i^a(\mathbf{r})\rangle$, $|\tilde{\phi}_i^a(\mathbf{r})\rangle$, and $|\tilde{p}_i^a(\mathbf{r})\rangle$, for the all-electron basis functions, pseudopotential basis functions, and projector functions, respectively. Here the "a" superscript denotes the atom index (which is suppressed in most of the remainder of this section), and the "i" subscript represents the atomic quantum numbers n_i, l_i, and m_i. Since these function are constructed from equations for a spherical atom, each can be written as a product of a radial function times a spherical harmonic function, such as:

$$|\phi_i^a(\mathbf{r})\rangle \equiv |\phi_{n_i l_i m_i}^a(\mathbf{r})\rangle \equiv \frac{\phi_{n_i l_i}^a(r)}{r} Y_{l_i m_i}(\hat{\mathbf{r}}). \tag{1}$$

This notation is used to also enumerate the radial functions $\phi_{n_i l_i}^a(r)$, $\tilde{\phi}_{n_i l_i}^a(r)$, and $\tilde{p}_{n_i l_i}^a(r)$. The symbol n_i often corresponds to the principal quantum number for the state but also can correspond to enumerate generalized functions needed for the basis.[1] The symbol l_i corresponds to the angular momentum quantum number. Although the PAW method works using any of a variety of basis and projector functions, the efficiency and accuracy of the calculation are affected by this choice. In earlier work[2, 5] we investigated several alternative construction schemes. However, we found a slight modifications of the original schemes developed Vanderbilt[7] for his ultra-soft pseudopotential formalism and by Blöchl[1] for the PAW formalism, to be the most robust. In the following we refer to these different schemes as the "Vanderbilt" or "Blöchl" schemes by which we mean to credit their basic ideas, but imply no responsibility to either of them for how we have implemented them in the *atompaw* code.

The starting point of the construction process is an all-electron self-consistent solution of the Schrödinger equation for the reference atom a. (For the remainder of this section, we will drop the index a.) It is assumed that the total electron density can be partitioned into a core electron density $n_{\text{core}}(r)$, corresponding to Q_{core} electrons and a valence electron density. The core density $n_{\text{core}}(r)$ is assumed to be fixed ("frozen") in the same form in the atom as it is in the solid. Thus, all of the calculational effort can be focused on the valence electrons. For some materials, especially transition metals or ionic compounds, it is prudent to extend the notion of "valence" electrons beyond the chemical definition to include upper core states. It is for the purpose of representing these generalized valence electrons in the atom and in the solid that we construct the basis and projector functions. The symbol $n(r)$ is used to denote the corresponding valence electron density.

The all-electron basis functions $|\phi_i(\mathbf{r})\rangle$ are valence and continuum eigenstates of the Kohn-Sham[8] Hamiltonian.

$$H(\mathbf{r})|\phi_i(\mathbf{r})\rangle = \varepsilon_i|\phi_i(\mathbf{r})\rangle, \tag{2}$$

The Hamiltonian takes the form:

$$H(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(r), \tag{3}$$

where the self-consistent valence density $n(r)$ enters through the effective potential:

$$v_{\text{eff}}(r) \equiv -\frac{Ze^2}{r} + e^2 \int d^3r' \, \frac{n_{\text{core}}(r') + n(r')}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\text{xc}}[n_{\text{core}}(r) + n(r)]. \tag{4}$$

Here Z denotes the nuclear charge. The function μ_{xc} denotes the exchange correlation functional. In the present work, we used the local density approximation (LDA) form of Perdew and Wang[9], but other forms can be easily added to the code. Self-consistency implies that the valence density and the valence basis functions are related according to:

$$n(r) = \sum_{n_i l_i} o_{n_i l_i} \frac{|\phi_{n_i l_i}(r)|^2}{4\pi r^2}, \tag{5}$$

where $o_{n_i l_i}$ denotes the occupancy of the orbital "$n_i l_i$" which can be zero, especially for generalized functions.

The next consideration is to construct a pseudopotential function $V^{PS}(r)$ that will be used to construct the smooth basis functions $\tilde{\phi}_{n_i l_i}(r)$ and whose unscreened version will be appear as a local pseudopotential contribution to the smooth Hamiltonian. Our current recommendation for $V^{PS}(r)$ is to construct $\tilde{v}_{\text{loc}}(r)$ using a norm-conserving pseudopotential[10, 11, 12] approach. The idea is that in this way, the local potential can be constructed to force the good representation of partial wave components with the chosen angular momentum L_v. The partial wave components with smaller angular momentum will be represented with the non-local terms in the usual PAW construction. This is by no means a new idea and was inspired by David Vanderbilt's webpage on soft-pseudopotential generation http://www.physics.rutgers.edu/ dhv/uspp/.

We recommend using the Troullier-Martins[12] form of the norm-conserving pseudopotential (keywords VNCT or VNCTV). The main equations describing the method are as follows. L_v represents the angular momentum chosen for constructing the norm-conserving (screened) pseudopotential. The pseudowavefunction is chosen to have the form:

$$\tilde{\phi}(r) = \begin{cases} r^{L_v+1} f(r) & \text{for } r \leq r_c \\ \phi(r) & \text{for } r > r_c. \end{cases} \tag{6}$$

Here $\phi(r)$ represents a chosen continuum wavefunction of the all-electron Hamiltonian at energy E. The function $f(r)$ is chosen to have the form

$$f(r) = \mathrm{e}^{p(r)}, \tag{7}$$

where $p(r)$ is chosen to be an even 12^{th} order polynomial:

$$p(r) = \sum_{m=0}^{6} C_m r^{2m}. \tag{8}$$

The 7 polynomial coefficients $\{C_m\}$ are chosen to ensure that the wavefunction and its first 4 derivatives are continuous at the matching radius in addition to the norm conservation condition. The last constraint is that screen pseudopotential has zero slope at the origin which, as shown by Troullier and Martins[12] means that $C_1^2 + (2l+5)C_2 = 0$. The matching radius r_c defines an augmentation sphere about each atom. It is assumed that there should be little or no overlap between augmentation spheres in all of the materials studied with the pseudopotential and basis functions. The screened norm-conserving pseudopotential can be determined from polynomial according to

$$V^{PS}(r) = E + \frac{\hbar^2}{2m}\left(\frac{d^2p}{dr^2} + \left(\frac{dp}{dr}\right)^2 + + \frac{2(L_v+1)}{r}\frac{dp}{dr}\right). \tag{9}$$

By construction, this function and its first two derivatives are equal to $v_{\text{eff}}(r)$ for $r \geq r_c$.

At this point, we can construct a smooth pseudo-Hamiltonian analogous the all-electron Hamiltonian (2) of the form

$$\tilde{H}(r) \equiv -\frac{\hbar^2}{2m}\nabla^2 + V^{PS}(r). \tag{10}$$

We are now in a position to determine the projector and basis functions. The two methods that work well are either the Blöchl scheme (keyword VNCT) or the Vanderbilt scheme (keyword VNCTV). As we have implemented it, the Vanderbilt scheme has more flexibility and it seems possible to derive slightly more rapidly converging projector and basis functions by fiddling with the parameters.

1.1 Vanderbilt scheme

In this scheme, the the shape of the smooth basis functions are directly controlled, $\tilde{\phi}_i(\mathbf{r})$ while the projector functions $\tilde{p}_i(\mathbf{r})$ are derived. Each radial smooth function is chosen to have the form

$$\tilde{\phi}_{n_il_i}(r) = \begin{cases} r^{l_i+1}\sum_{m=0}^{4} C_m r^{2m} & \text{for} \quad r < r_i \\ \phi_{n_il_i}(r) & \text{for} \quad r \geq r_i \end{cases} \tag{11}$$

The matching radii $r_i \leq r_c$ are used to control the shapes. The 5 coefficients $\{C_m\}$ are chosen so that $\tilde{\phi}_{n_il_i}(r) = \phi_{n_il_i}(r)$ at 5 points in the neighborhood of r_i which is roughly equivalent to ensuring that the function at its first 4 derivatives match at r_i. For each smooth basis function, we can form a localized auxiliary function

$$\chi_{n_il_i}(r) = \left(\varepsilon_i + \frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2}\right) - V^{PS}(r)\right)\tilde{\phi}_{n_il_i}(r), \tag{12}$$

which, by design vanishes for $r > r_c$. The projector functions are then formed from a linear combination of these auxiliary functions of the same angular momentum:

$$\tilde{p}_{n_il_i}(r) \equiv \sum_{n_j}\chi_{n_jl_i}(r)\left(\mathbf{B}^{-1}\right)_{n_jn_i}, \tag{13}$$

where the elements of the matrix $\mathbf{B}$ are given by

$$B_{n_in_j} \equiv \int_0^{r_c} dr\tilde{\phi}_{n_il_i}(r)\chi_{n_jl_i}(r). \tag{14}$$

As shown by Vanderbilt[7] this construction ensures that

$$\langle\tilde{\phi}_i|\tilde{p}_j\rangle = \delta_{ij} \tag{15}$$

and that the smooth basis function $\tilde{\phi}_i(\mathbf{r})$ is an eigenfunction of the atomic PAW Hamiltonian.

1.2 Blöchl scheme

In this scheme, the shape of the projector functions $\tilde{p}_i(\mathbf{r})$ are chosen while the smooth basis functions $\tilde{\phi}_i(\mathbf{r})$ are derived. As we have implemented the scheme, the shapes of the functions are generally controlled only with choice of the augmentation radius r_c which is taken to be the same as that used to construct the screened local pseudopotential $V^{PS}(r)$ discussed above. Of course, there addition flexibility in choosing the set of all electron basis functions $\{\phi^0_{n_i l_i}(r)\}$ as discussed above, where we use the superscript "0" to denote the initial basis functions which may change later due to orthogonalization requirements.

In Blöchl's pseudo-function construction scheme, the projector functions are constructed with the help of a shape function $k(r)$ which vanishes outside the augmentation region. In previous work we find the following shape function to work the best:

$$k(r) = \begin{cases} \left[\dfrac{\sin(\pi r/r_c)}{(\pi r/r_c)}\right]^2 & \text{for } r < r_c \\ 0 & \text{for } r \geq r_c \end{cases} . \tag{16}$$

The pseudo-basis functions $|\tilde{\phi}^0_i(\mathbf{r})\rangle$ are found by solving a self-consistent Schrödinger-like equation involving the "smooth" Hamiltonian $\tilde{H}$. The equation takes the form:

$$\left(\tilde{H}(\mathbf{r}) - \varepsilon_i\right) |\tilde{\phi}^0_i(\mathbf{r})\rangle = C_i k(r) |\tilde{\phi}^0_i(\mathbf{r})\rangle. \tag{17}$$

In this equation, ε_i is fixed at the all-electron eigenvalue found in Eq. (2), while C_i is to be determined. In numerically integrating the radial part of this equation for $\tilde{\phi}^0_{n_i l_i}(r)$, the coefficient C_i is adjusted so that $\tilde{\phi}^0_{n_i l_i}(r)$ has the correct number of nodes for each l value (zero nodes for the basis function with the lowest one-electron energy $\varepsilon_{n_i l_i}$, incremented by one node for each additional basis function at higher one-electron energies). In addition, the coefficient C_i is adjusted so that $\tilde{\phi}^0_{n_i l_i}(r)$ satisfies the boundary condition:

$$\tilde{\phi}^0_{n_i l_i}(r) = \phi^0_{n_i l_i}(r) \quad \text{for } r \geq r_c. \tag{18}$$

In practice, this is achieved by iterating Eq. (17) with variations in C_i so that the logarithmic derivatives of $\phi^0_{n_i l_i}(r_c)$ and $\tilde{\phi}^0_{n_i l_i}(r_c)$ are equal, following the approach described in Hartree's text[13].

Once the pseudo-basis functions $|\tilde{\phi}^0_i(\mathbf{r})\rangle$ have been determined by finding the solution of Eq. (17), the corresponding projector functions are formed according to:

$$|\tilde{p}^0_i(\mathbf{r})\rangle \equiv \frac{k(r)|\tilde{\phi}^0_i(\mathbf{r})\rangle}{\langle\tilde{\phi}^0_i|k|\tilde{\phi}^0_i\rangle}. \tag{19}$$

This means that these initial pseudo-basis functions and the corresponding projector functions are normalized according to

$$\langle\tilde{\phi}^0_i|\tilde{p}^0_i\rangle = 1, \tag{20}$$

and related to the smooth Hamiltonian according to the identity:

$$\left(\tilde{H}(\mathbf{r}) - \varepsilon_i\right) |\tilde{\phi}^0_i(\mathbf{r})\rangle = |\tilde{p}^0_i(\mathbf{r})\rangle\langle\tilde{\phi}^0_i|\tilde{H} - \varepsilon_i|\tilde{\phi}^0_i\rangle. \tag{21}$$

The final basis and projector functions $\{|\phi_i(\mathbf{r})\rangle, |\tilde{\phi}_i(\mathbf{r})\rangle, |\tilde{p}_i(\mathbf{r})\rangle\}$ are formed from the initial functions $\{|\phi_i^0(\mathbf{r})\rangle, |\tilde{\phi}_i^0(\mathbf{r})\rangle, |\tilde{p}_i^0(\mathbf{r})\rangle\}$ by a Gram-Schmidt orthogonalization procedure as described in Eqs.(91-96) of Ref. ([1]). Specifically, for each angular momentum quantum number l, we denote the successive radial functions with indices $n_1, n_2, ...$ etc. The first set of basis and projector functions is given by the initial functions:

$$\tilde{p}_{n_1 l}(r) \equiv \tilde{p}^0_{n_1 l}(r), \quad \tilde{\phi}_{n_1 l}(r) \equiv \tilde{\phi}^0_{n_1 l}(r), \quad \text{and} \quad \phi_{n_1 l}(r) \equiv \phi^0_{n_1 l}(r). \tag{22}$$

If there is a second radial basis function for that l, the final function is orthonormalized with respect to the first according to:

$$\begin{aligned}
\tilde{p}_{n_2 l}(r) &= \mathcal{F}_{n_2 l} \quad \left[\tilde{p}^0_{n_2 l}(r) - \tilde{p}_{n_1 l}(r)\langle\tilde{\phi}_{n_1 l}|\tilde{p}^0_{n_2 l}\rangle\right], \qquad (23)\\
\tilde{\phi}_{n_2 l}(r) &= \mathcal{F}_{n_2 l} \quad \left[\tilde{\phi}^0_{n_2 l}(r) - \tilde{\phi}_{n_1 l}(r)\langle\tilde{p}_{n_1 l}|\tilde{\phi}^0_{n_2 l}\rangle\right],\\
\phi_{n_2 l}(r) &= \mathcal{F}_{n_2 l} \quad \left[\phi^0_{n_2 l}(r) - \phi_{n_1 l}(r)\langle\tilde{p}_{n_1 l}|\tilde{\phi}^0_{n_2 l}\rangle\right],
\end{aligned}$$

where,

$$\mathcal{F}_{n_2 l} \equiv \left(1 - \langle\tilde{\phi}^0_{n_2 l}|\tilde{p}_{n_1 l}\rangle\langle\tilde{\phi}_{n_1 l}|\tilde{p}^0_{n_2 l}\rangle\right)^{-1/2}. \tag{24}$$

If there were addition radial basis functions for that l, they would be orthonormalized in a similar way. In our experience, and in that of previous workers[14, 15], one or two radial basis functions are usually sufficient to span the Hilbert space of smooth functions within each atomic sphere.

2 Self-consistency requirements

The self-consistent smooth Hamiltonian is expected take the following form:

$$\tilde{H}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + \tilde{v}_{\text{eff}}(r), \tag{25}$$

where the smooth effective potential is given by

$$\tilde{v}_{\text{eff}}(r) \equiv \tilde{v}_{\text{loc}}(r) + e^2 \int d^3r' \frac{\tilde{n}_{\text{core}}(r') + \tilde{n}(r') + \hat{n}(r')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{\text{xc}}[\tilde{n}_{\text{core}}(r) + \tilde{n}(r)]. \tag{26}$$

Here the pseudo-density $\tilde{n}(r)$ in Eq. (26) is determined from the pseudo-basis functions and their occupancies $o_{n_i l_i}$ according to

$$\tilde{n}(r) = \sum_{n_i l_i} o_{n_i l_i} \frac{|\tilde{\phi}^0_{n_i l_i}(r)|^2}{4\pi r^2}. \tag{27}$$

In Eq. 26, the function $\tilde{n}_{\text{core}}(r)$ is introduced to represent the tail of the core density for $r > r_c$ and a smooth continuous function for $r < r_c$. In particular, we choose

$$4\pi r^2 \tilde{n}_{\text{core}}(r) \equiv \begin{cases} r^2(U_0 + U_2 r^2 + U_4 r^4) & \text{for} \quad r \leq r_c \\ 4\pi r^2 n_{\text{core}}(r) & \text{for} \quad r \geq r_c, \end{cases} \tag{28}$$

where the constants U_0, U_2, and U_4 are chosen so that $4\pi r^2 \tilde{n}_{\text{core}}(r) \equiv d_0$ and its first two derivatives d_1 and d_2 are continuous at r_c. This determines the constants to be

$$U_0 r_c^2 = 3d_0 - \frac{9}{8} d_1 r_c + \frac{1}{8} d_2 r_c^2. \tag{29}$$

$$U_2 r_c = -3d_0 + \frac{7}{4} d_1 r_c - \frac{1}{4} d_2 r_c^2. \tag{30}$$

$$U_4 = d_0 - \frac{5}{8} d_1 r_c + \frac{1}{8} d_2 r_c^2. \tag{31}$$

The additional "compensation" charge density contribution in Eq. 26 denoted by $\hat{n}(r)$, represents the total atomic charge minus the pseudo charge, redistributed to a convenient smooth form. This charge density is spherically symmetric for the atom and can be written:

$$\hat{n}(r) = Q_{00} g_{00}(\mathbf{r}), \tag{32}$$

where the monopole moment Q_{00} is

$$Q_{00} \equiv -Z + \int d^3 r \ \left[n_{\text{core}}(r) + n(r) - \tilde{n}_{\text{core}}(r) - \tilde{n}(r) \right]. \tag{33}$$

The functional form of atom-centered moments of the compensation charge is now chosen to be proportional to the shape function (16):

$$g_{LM}(\mathbf{r}) \equiv \mathcal{N}_L r^L k(r) Y_{LM}(\hat{\mathbf{r}}), \ \ \text{where,} \ \ [\sqrt{4\pi}\mathcal{N}_L]^{-1} \equiv \int_0^{r_c} dr \ r^{2+2L} \ k(r). \tag{34}$$

Here, $Y_{LM}(\hat{\mathbf{r}})$ denotes the spherical harmonic function and $\mathcal{N}_L$ denotes a normalization factor. For the atom, only the monopole term is needed; Eq.(34) applies more generally to the solid.

Finally, the local potential term of Eq. (26) can be determined from a knowledge of the smooth ($\tilde{n}(r)$), compensation ($\hat{n}(r)$, and coretail ($\tilde{n}_{\text{core}}(r)$ densities by unscreening the local pseudopotential (9) according to:

$$\tilde{v}_{\text{loc}}(r) = V^{PS}(r) - e^2 \int d^3 r' \frac{\tilde{n}_{\text{core}}(r') + \tilde{n}(r') + \hat{n}(r')}{|\mathbf{r} - \mathbf{r}'|} - \mu_{\text{xc}}[\tilde{n}_{\text{core}}(r) + \tilde{n}(r)]. \tag{35}$$

In this formulation, the unscreened local pseudopotential $\tilde{v}_{\text{loc}}(r)$ is confined within the augmentation sphere ($r \leq r_c$).

3 PAW Hamiltonian

In terms of these basis functions, the generalized eigenvalue equation for the PAW formalism can be written

$$\mathbf{H^{PAW}}(\mathbf{r}) |\tilde{\Psi}_E(\mathbf{r})\rangle = E\mathbf{O} |\tilde{\Psi}_E(\mathbf{r})\rangle, \tag{36}$$

where

$$\mathbf{H^{PAW}} \equiv \tilde{H}(\mathbf{r}) + \sum_{aij} |\tilde{p}_i^a\rangle \left(\langle \phi_i^a | H^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{H}^a | \tilde{\phi}_j^a \rangle \right) \langle \tilde{p}_j^a | \equiv \tilde{H}(\mathbf{r}) + \sum_{aij} |\tilde{p}_i^a\rangle D_{ij}^a \langle \tilde{p}_j^a |. \tag{37}$$

The overlap term is given by

$$\mathbf{O} \equiv \mathbf{1} + \sum_{aij} |\tilde{p}_i^a\rangle \left(\langle \phi_i^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{\phi}_j^a \rangle \right) \langle \tilde{p}_j^a |. \tag{38}$$

It can be shown that the pre-orthonormalized smooth basis functions functions $\{|\tilde{\phi}_i^0(\mathbf{r})\rangle\} \to |\tilde{\Psi}_E(\mathbf{r})\rangle$ in the Blöchl formulation and the corresponding smooth basis functions in the Vanderbilt formulation are exact solutions of the PAW equations (36).

The eigenstates $|\tilde{\Psi}_E(\mathbf{r})\rangle$ of Eq. (36) are related to the eigenstates of the all-electron Hamiltonian, according to:

$$|\Psi_E(\mathbf{r})\rangle = |\tilde{\Psi}_E(\mathbf{r})\rangle + \sum_{ai} \left(|\phi_i^a(\mathbf{r})\rangle - |\tilde{\phi}_i^a(\mathbf{r})\rangle \right) \langle \tilde{p}_i^a | \tilde{\Psi}_E \rangle, \tag{39}$$

within the accuracy of the PAW representation. For the case of a spherically symmetric atom, the site index a is trivial and all matrix elements are diagonal in $l_i m_i$ indices.

In practice, the Hamiltonians H^a and $\tilde{H}^a$ which appear in Eq. (37) are defined in terms of matrix elements evaluated using the orthogonalized basis functions $\{\phi_i^a\}$ and $\{\tilde{\phi}_i^a\}$ [1, 2, 4]. The construction procedure ensures that $\mathbf{H^{PAW}}$ reproduces the same eigenvalue spectrum as the all-electron Hamiltonian within the energy range spanned by the basis functions.

4 Energy and Hamiltonian for solids.

The total energy expression for the solid is taken to be[1]

$$E = \tilde{E} + \sum_a \left(E^a - \tilde{E}^a \right). \tag{40}$$

The smooth contributions are given by

$$\begin{aligned} \tilde{E} = \quad & \tilde{K} + \frac{e^2}{2} \int d^3r \int d^3r' \frac{(\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r}) + \hat{n}(\mathbf{r}))(\tilde{n}(\mathbf{r}') + \tilde{n}_{\text{core}}(\mathbf{r}') + \hat{n}(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} \qquad (41) \\ & + \int d^3r \; \tilde{v}_{\text{loc}}(\mathbf{r}) \tilde{n}(\mathbf{r}) + E_{xc}[\tilde{n}_{\text{core}} + \tilde{n}]. \end{aligned}$$

For the Bloch wavefunction $\Psi_{n\mathbf{k}}(\mathbf{r})$, with an occupancy of $o_{n\mathbf{k}}$, the smooth density is given by

$$\tilde{n}(\mathbf{r}) = \sum_{n\mathbf{k}} o_{n\mathbf{k}} |\Psi_{n\mathbf{k}}(\mathbf{r})|^2, \tag{42}$$

and the kinetic energy is given by

$$\tilde{K} = -\frac{\hbar^2}{2m} \sum_{n\mathbf{k}} o_{n\mathbf{k}} \langle \Psi_{n\mathbf{k}}(\mathbf{r}) | \nabla^2 | \Psi_{n\mathbf{k}}(\mathbf{r}) \rangle. \tag{43}$$

The total energy expression (41) expression reflects the fact that in the solid, we need to superpose the atom-centered compensation charge, coretail, and local potential contributions. The coretail

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[1] We have simplified the core tail function defined in Ref.([2]) in this formulation so that overlapping core contributions are neglected in the atom-centered contributions.

density takes the form

$$\tilde{n}_{\mathrm{core}}(\mathbf{r}) \equiv \sum_a \tilde{n}^a_{\mathrm{core}}(|\mathbf{r} - \mathbf{R}^a|), \tag{44}$$

allowing for the superposition of the smooth part of the core electron density in the treatment of the smooth parts the Coulomb and exchange-correlation interactions.

The compensation charge density takes the form

$$\hat{n}(\mathbf{r}) \equiv \sum_{aLM} Q^a_{LM} g_{LM}(\mathbf{r} - \mathbf{R}^a), \tag{45}$$

where

$$Q^a_{LM} \equiv (-Z^a + Q^a_{\mathrm{core}} - \tilde{Q}^a_{\mathrm{core}})\delta_{L0}\delta_{M0} + \sum_{ij} W^a_{ij} G^{LM}_{l_i m_i l_j m_j} n^{aL}_{n_i l_i n_j l_j}, \tag{46}$$

where W^a_{ij} is defined below and

$$n^{aL}_{n_i l_i n_j l_j} \equiv \int_0^{r^a_c} dr\, r^L \left[\phi^a_{n_i l_i}(r)\phi^a_{n_j l_j}(r) - \tilde{\phi}^a_{n_i l_i}(r)\tilde{\phi}^a_{n_j l_j}(r)\right]. \tag{47}$$

The Gaunt coefficient is defined as follows[2]

$$G^{LM}_{l_i m_i l_j m_j} = \sqrt{4\pi} \int d\Omega Y^*_{l_i m_i}(\hat{\mathbf{r}}) Y^*_{LM}(\hat{\mathbf{r}}) Y_{l_j m_j}(\hat{\mathbf{r}}). \tag{48}$$

The coretail charge in Eq. (46) is given by

$$\tilde{Q}^a_{\mathrm{core}} \equiv \int d^3r \tilde{n}^a_{\mathrm{core}}(r). \tag{49}$$

The total local pseudopotential contributions which appear in Eq. (41) take the form

$$\tilde{v}_{\mathrm{loc}}(\mathbf{r}) \equiv \sum_a \tilde{v}^a_{\mathrm{loc}}(|\mathbf{r} - \mathbf{R}^a|). \tag{50}$$

As it is written, the Coulomb term in Eq. (41) represents a a neutral system. However, it includes several unphysical self-interaction terms which must be substracted:

$$\sum_a \frac{e^2}{2} \int d^3r \int d^3r' \frac{(\tilde{n}^a_{\mathrm{core}}(\mathbf{r}) + \hat{n}^a(\mathbf{r}))(\tilde{n}^a_{\mathrm{core}}(\mathbf{r}') + \hat{n}^a(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|}. \tag{51}$$

Since these terms depend on each atomic site, they are conveniently expressed in the one-center terms given below. The exchange-correlation energy terms E_{xc} are currently evaluated using the local density approximation of Perdew and Wang[9] or the generalized gradient approximation of Perdew, Burke, and Ernzerhof[17, 18], although additional functionals could easily be added.

The one-center terms are given by

$$E^a - \tilde{E}^a = \sum_{ij} W^a_{ij} \left(K^a_{ij} + [v^a_{\mathrm{at}}]_{ij} - [\hat{v}^a]_{ij} + \frac{1}{2}[V^a_{\mathrm{H}}]_{ij} \right) \tag{52}$$

$$+ (E_{\mathrm{xc}}[n^a_{\mathrm{core}} + n^a] - E_{\mathrm{xc}}[\tilde{n}^a_{\mathrm{core}} + \tilde{n}^a]) - \hat{E}^a - \tilde{E}^a_{\mathrm{core}} - Q_{00}\tilde{E}^a_{\mathrm{core-hat}}.$$

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[2] This usage is convenient to the present application but the extra factor of $\sqrt{4\pi}$ is not included in the "standard" definition of the Gaunt coefficient, such as found in Condon and Shortley[16].

Here,

$$W^a_{ij} \equiv \sum_{nl} o_{n\mathbf{k}} \langle \Psi_{n\mathbf{k}} | p^a_i \rangle \langle p^a_j | \Psi_{n\mathbf{k}} \rangle. \tag{53}$$

The kinetic energy is given by $K^a_{ij} \equiv K^a_{n_i l_i n_j l_j} \delta_{l_i l_j} \delta_{m_i m_j}$ with

$$K^a_{n_i l_i n_j l_i} \equiv -\frac{\hbar^2}{2m} \int_0^{r^a_c} dr \ \left[\phi^a_{n_i l_i}(r) \left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} \right) \phi^a_{n_j l_i}(r) - \tilde{\phi}^a_{n_i l_i}(r) \left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} \right) \tilde{\phi}^a_{n_j l_i}(r) \right]. \tag{54}$$

The ionic potential term is given by $[v^a_{\text{at}}]_{ij} \equiv [v^a_{\text{at}}]_{n_i l_i n_j l_j} \delta_{l_i l_j} \delta_{m_i m_j}$, where $[v^a_{\text{at}}]_{n_i l_i n_j l_i}$ is modified from its definition in Eq. [3]-26.

$$[v_{\text{at}}]^a_{n_i l_i n_j l_i} \equiv \int_0^{r^a_c} dr \left\{ \phi^a_{n_i l_i}(r) \left(-\frac{Ze^2}{r} + v^a_{\text{core}}(r) \right) \phi^a_{n_j l_i}(r) - \tilde{\phi}^a_{n_i l_i}(r) \left(\tilde{v}^a_{\text{core}}(r) + \tilde{v}^a_{\text{loc}}(r) \right) \tilde{\phi}^a_{n_j l_i}(r) \right\}, \tag{55}$$

where $v^a_{\text{core}}(r)$ and $\tilde{v}^a_{\text{core}}(r)$ denote the Coulomb potentials corresponding to $n^a_{\text{core}}(r)$ and $\tilde{n}^a_{\text{core}}(r)$ respectively. The compensation charge matrix element is given by

$$[\hat{v}^a]_{ij} \equiv \langle \tilde{\phi}^a_i | \hat{v}^a | \tilde{\phi}^a_j \rangle = \sum_{LM} Q^a_{LM} (-1)^M G^{L\,-M}_{l_i m_i l_j m_j} \hat{v}^{aL}_{n_i l_i n_j l_j} \tag{56}$$

where

$$\hat{v}^{aL}_{n_i l_i n_j l_j} \equiv \int_0^{r^a_c} dr \tilde{\phi}^a_{n_i l_i}(r) \hat{v}^a_L(r) \tilde{\phi}^a_{n_j l_j}(r), \tag{57}$$

and, using the definitions in Eq. (34)

$$\hat{v}^a_L(r) \equiv \frac{4\pi e^2}{2L+1} \mathcal{N}_L \int_0^\infty r'^2 dr' \frac{r^L_<}{r^{L+1}_>} \ r'^L \ k(r'). \tag{58}$$

The basis function Hartree term is given by

$$[V^a_H]_{ij} = \sum_{LM} \sum_{kl} (-1)^M G^{L\,-M}_{l_i m_i l_j m_j} G^{LM}_{l_k m_k l_l m_l} W^a_{kl} V^{aL}_{n_i l_i n_j l_j ; n_k l_k n_l l_l}, \tag{59}$$

where

$$\begin{aligned} V^{aL}_{n_i l_i n_j l_j ; n_k l_k n_l l_l} \equiv \frac{4\pi e^2}{2L+1} \int_0^{r^a_c} dr \int_0^{r^a_c} dr' \frac{r^L_<}{r^{L+1}_>} \quad & \Big[\phi^a_{n_i l_i}(r) \phi^a_{n_j l_j}(r) \phi^a_{n_k l_k}(r') \phi^a_{n_l l_l}(r') \\ & - \tilde{\phi}^a_{n_i l_i}(r) \tilde{\phi}^a_{n_j l_j}(r) \tilde{\phi}^a_{n_k l_k}(r') \tilde{\phi}^a_{n_l l_l}(r') \Big]. \end{aligned} \tag{60}$$

In Eq. (52), we have 3 types of "self" interactions which are subtracted from the evaluation. The compensation charge self energy is given by:

$$\hat{E}^a \equiv \sum_{LM} |Q^a_{LM}|^2 \hat{E}^{aL}, \tag{61}$$

where

$$\hat{E}^{aL} \equiv \frac{e^2}{2} \int d^3r d^3r' \frac{g^a_{LM}(\mathbf{r}) g^a_{LM}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{62}$$

The coretail self-energy is given by

$$\tilde{E}^a_{\text{core}} \equiv \frac{e^2}{2} \int d^3r d^3r' \frac{\tilde{n}^a_{\text{core}}(\mathbf{r}) \tilde{n}^a_{\text{core}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{63}$$

The coretail-hat interaction energy is given by

$$Q^a_{00}\tilde{E}^a_{\mathrm{core-hat}} = Q^a_{00} e^2 \int d^3r d^3r' \frac{g^a_{00}(\mathbf{r})\tilde{n}^a_{\mathrm{core}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{64}$$

This treatment of the effects of the coretail density differs from that of our previous work[2]. In this formulation, the one-center terms do not include any core-overlap effects and therefore may not completely cancel the corresponding terms in the smooth Hamiltonian in the augmentation sphere, hopefully a very small error. The core tail density which is included in the smooth Hamiltonian represents the Coulombic and exchange-correlation contributions from the small overlap of the frozen core densities. The interactions of the core tail density from a single atomic site are subtracted out using the self-energy terms.

The PAW Hamiltonian (37) can be determined [1] by taking the variation of the energy (40) with respect to the the smooth wavefunctions $\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})$. This gives the smooth contribution

$$\tilde{H}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + \tilde{v}_{\mathrm{eff}}(\mathbf{r}), \tag{65}$$

where

$$\tilde{v}_{\mathrm{eff}}(\mathbf{r}) = \tilde{v}_{\mathrm{loc}}(\mathbf{r}) + e^2 \int d^3r' \frac{\tilde{n}_{\mathrm{core}}(\mathbf{r}') + \tilde{n}(\mathbf{r}') + \hat{n}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\mathrm{xc}}[\tilde{n}_{\mathrm{core}}(\mathbf{r}) + \tilde{n}(\mathbf{r})]. \tag{66}$$

The atom-centered contributions are given by

$$D^a_{ij} = K^a_{ij} + [v^a_{\mathrm{at}}]_{ij} - [\hat{v}^a]_{ij} + [V^a_{\mathrm{H}}]_{ij} + [v^a_0]_{ij} + [V^a_{XC}]_{ij}. \tag{67}$$

Here the exchange matrix element is given by

$$\begin{aligned}[V^a_{XC}]_{ij} = \int d\Omega\;\; Y^*_{l_im_i}(\hat{\mathbf{r}})Y_{l_jm_j}(\hat{\mathbf{r}}) \int_0^{r^a_c} dr\;\; \Big[&\mu_{\mathrm{xc}}[n_{\mathrm{core}}(\mathbf{r}) + n(\mathbf{r})]\phi_{n_il_i}(r)\phi_{n_jl_j}(r) \\ &-\mu_{\mathrm{xc}}[\tilde{n}_{\mathrm{core}}(\mathbf{r}) + \tilde{n}(\mathbf{r})]\tilde{\phi}_{n_il_i}(r)\tilde{\phi}_{n_jl_j}(r)\Big].\end{aligned} \tag{68}$$

The shift term comes from the variation of Q_{LM} which Blöchl showed to have the form

$$[v^a_0]_{ij} = \sum_{LM} \frac{\partial E}{\partial Q_{LM}} G^{LM}_{l_im_il_jm_j} n^{aL}_{n_il_in_jl_j}, \tag{69}$$

where

$$\begin{aligned}\frac{\partial E}{\partial Q_{LM}} &= e^2 \int d^3r \int d^3r' \frac{(\tilde{n}(\mathbf{r}) + \tilde{n}_{\mathrm{core}}(\mathbf{r}) + \hat{n}(\mathbf{r}))g_{LM}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &-\sum_{ij} W^a_{ij}(-1)^M G^{L\,-M}_{l_im_il_jm_j} \hat{v}^{aL}_{n_il_in_jl_j} - 2Q_{LM}\hat{E}^{aL} - \tilde{E}^a_{\mathrm{core-hat}}\delta_{L0}\delta_{M0}.\end{aligned} \tag{70}$$

To evaluate the smooth contributions, it is convenient to use a planewave representation

$$\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{1}{\mathcal{V}}}\; \sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G})\mathrm{e}^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \tag{71}$$

were $\mathbf{G}$ denotes a reciprocal lattice vector and $\mathcal{V}$ denotes the volume of the unit cell. In these terms, the smooth energy is given by

$$\tilde{E} = \sum_{n\mathbf{k}} o_{n\mathbf{k}} \left(\sum_{\mathbf{G}} \frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m} |A_{n\mathbf{k}}(\mathbf{G})|^2 \right) + \frac{2\pi e^2}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{|\bar{\tilde{n}}(\mathbf{G}) + \bar{\tilde{n}}_{\mathrm{core}}(\mathbf{G}) + \bar{\hat{n}}(\mathbf{G})|^2}{G^2}$$
$$+ \frac{1}{\mathcal{V}} \sum_{\mathbf{G}} \bar{\tilde{v}}_{\mathrm{loc}}(\mathbf{G}) \bar{\tilde{n}}^*(\mathbf{G}) + E_{\mathrm{xc}}[\tilde{n}_{\mathrm{core}} + \tilde{n}]. \tag{72}$$

The force on an atom a at the site $\mathbf{R}^a$ is given by

$$\mathbf{F}^a \equiv -\left\{\nabla_{\mathbf{R}^a}[E]\right\} = \frac{4\pi i e^2}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{\mathbf{G}\ \left[\bar{\hat{n}}^a(\mathbf{G}) + \bar{\tilde{n}}^a_{\mathrm{core}}(\mathbf{G})\right] \left[\bar{\tilde{n}}^*(\mathbf{G}) + \bar{\hat{n}}^*(\mathbf{G}) + \bar{\tilde{n}}^*_{\mathrm{core}}(\mathbf{G})\right]}{G^2}$$
$$+ \frac{i}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \mathbf{G}\ \bar{\tilde{v}}^a_{\mathrm{loc}}(\mathbf{G}) \bar{\tilde{n}} * (\mathbf{G}) + \frac{i}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \mathbf{G}\ \bar{\tilde{n}}^a_{\mathrm{core}}(\mathbf{G}) \bar{V}^*_{\mathrm{xc}}(\mathbf{G}) - \sum_{ij} \left\{\nabla_{\mathbf{R}^a}\left[W^a_{ij}\right]\right\} D^a_{ij} + \sum_{ij} \left\{\nabla_{\mathbf{R}^a}\left[U^a_{ij}\right]\right\} O^a_{ij}. \tag{73}$$

The first contribution depends on the Fourier transform of the atom-centered compensation and coretail charges and the second contribution depends on the Fourier transform of the atom centered local potential (Eq. [3]-14). The third term represents the effects of the coretail densities in the exchange-correlation interaction. The last term of the force equation involves a weighted projected occupation coefficient which we define according to

$$U^a_{ij} \equiv \sum_{n\mathbf{k}} o_{n\mathbf{k}} E_{n\mathbf{k}} \langle \tilde{\Psi}_{n\mathbf{k}} | \tilde{p}^a_i \rangle \langle \tilde{p}^a_j | \tilde{\Psi}_{n\mathbf{k}} \rangle. \tag{74}$$

The gradient with respect to the atomic position of both W^a_{ij} and U^a_{ij} depends on the gradient of the matrix elements $\langle \nabla_{\mathbf{R}^a}[\tilde{p}^a_i] | \tilde{\Psi}_{n\mathbf{k}} \rangle$ which can be conveniently evaluated in Fourier space using equation [2]-A20.

5 Energy and Hamiltonian for atoms

For atoms, the general PAW equations discussed above apply, but there are some simplications due to spherical symmetry. The smooth contribution to the energy (41) representing the pseudopotential-like contributions can be written in the form

$$\tilde{E} = \sum_{nl} o_{nl}\ K_{nl} + \frac{e^2}{2} \int d^3r \int d^3r' \frac{\tilde{n}(r)\tilde{n}(r')}{|\mathbf{r}-\mathbf{r}'|} + \int d^3r\ \tilde{n}(r) \left\{\tilde{v}_{\mathrm{loc}}(r) + \tilde{v}_{\mathrm{core}}(r) + \hat{v}(r)\right\} + E_{\mathrm{xc}}[\tilde{n}_{\mathrm{core}} + \tilde{n}], \tag{75}$$

where K_{nl} denotes the radial kinetic energy operator.

$$K_{nl} \equiv -\frac{\hbar^2}{2m} \int\ dr\ \ \tilde{\phi}_{nl}(r) \left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right) \tilde{\phi}_{nl}(r). \tag{76}$$

The smooth density $\tilde{n}(r)$, core tail density $\tilde{n}_{\mathrm{core}}(r)$, and compensation charge density $\hat{n}(r)$ have been defined in equations 27,28,and 32, respectively. Their corresponding Coulomb potentials are given by

$$\tilde{v}_{\mathrm{core}}(r) \equiv e^2 \int d^3r' \frac{\tilde{n}_{\mathrm{core}}(r')}{|\mathbf{r}-\mathbf{r}'|} \quad \hat{v}(r) \equiv e^2 \int d^3r' \frac{\hat{n}(r')}{|\mathbf{r}-\mathbf{r}'|}. \tag{77}$$

The remaining terms of the total energy are all atom-centered terms which can be determined from expressions defined above, but because of the spherical symmetry some of these expressions simplify:

$$W^a_{ij} = \sum_{nl} o_{nl} \langle \tilde{\phi}_{nl} | \tilde{p}_{n_i l} \rangle \langle \tilde{p}_{n_j l} | \tilde{\phi}_{nl} \rangle \delta_{l_i l} \delta_{l_j l}. \tag{78}$$

Only the $L = 0$ moment of the density matrix element is relevant:

$$n^{a0}_{n_i l_i n_j l_j} \equiv \int_0^{r^a_c} dr \left(\phi^a_{n_i l_i}(r) \phi^a_{n_j l_j}(r) - \tilde{\phi}^a_{n_i l_i}(r) \tilde{\phi}^a_{n_j l_j}(r) \right) \delta_{l_i l_j} \tag{79}$$

This allows us to calculate the charge moments

$$Q^a_{00} = -Z^a + \int d^3r \left(n_{\text{core}}(r) - \tilde{n}_{\text{core}}(r) \right) + \sum_{ij} W^a_{ij} n^{a0}_{n_i l_i n_j l_j}. \tag{80}$$

For the atomic case, only the $L = 0$ term appears in the Hartree term and the corresponding matrix element can be determined from

$$[V^a_H]_{ij} = \sum_{kl} W^a_{kl} \; V^{a0}_{n_i l_i n_j l_j ; n_k l_k n_l l_l}. \tag{81}$$

The compensation charge term is given by

$$< \tilde{\phi}^a_i | \hat{v}^a | \tilde{\phi}^a_j > = Q^a_{00} \hat{v}^{a0}_{n_i l_i n_j l_j}. \tag{82}$$

The matrix elements involving the compensation charge potential depend upon:

$$\hat{v}^{a0}_{n_i l_i n_j l_j} \equiv \int_0^{r^a_c} dr \; \tilde{\phi}^a_{n_i l_i}(r) \hat{v}^a_0(r) \tilde{\phi}^a_{n_j l_j}(r), \tag{83}$$

where $\hat{v}^a_0(r)$ represents the potential due to a unit compensation charge density.

The Coulomb shift term takes the form

$$[v^a_0]_{ij} = \frac{\partial E}{\partial Q^a_{00}} \; n^{a0}_{n_i l_i n_j l_j}, \tag{84}$$

where for the atomic case,

$$\frac{\partial E}{\partial Q^a_{00}} = \int dr \; 4\pi r^2 \tilde{n}(r) \hat{v}^a_0 - \sum_{ij} W^a_{ij} \hat{v}^{a0}_{n_i l_i n_j l_j}. \tag{85}$$

The radial densities can be easily determined from

$$4\pi r^2 \tilde{n}(r) = \sum_{nl} o_{nl} |\tilde{\phi}_{nl}(r)|^2. \tag{86}$$

$$4\pi r^2 \tilde{n}^a(r) = \sum_{ij} W^a_{ij} \tilde{\phi}^a_{n_i l_i}(r) \tilde{\phi}^a_{n_j l_j}(r). \tag{87}$$

$$4\pi r^2 n^a(r) = \sum_{ij} W^a_{ij} \phi^a_{n_i l_i}(r) \phi^a_{n_j l_j}(r). \tag{88}$$

6 Formulation in the *abinit* code

We have been working with the *abinit* project (http://www.abinit.org), especially with Dr. Marc Torrent to interface our projector and basis functions for use in the paw mode of that code. In the *abinit* code[19, 20, 21], the formulation of the PAW equations[22] more closely follows the equations of Kresse and Joubert[6]. For convenience, we compare the notations as follows

Table 1: Correspondence between *pwpaw* (Refs. ([2, 3, 4])) and *abinit* (Ref.([6, 22])).

pwpaw	*abinit*
W^a_{ij}	ρ^a_{ij}
$-Z^a\delta(\mathbf{r}-\mathbf{R}^a) + n^a_{\text{core}}(\lvert\mathbf{r}-\mathbf{R}^a\rvert)$	$n^a_{Z_c}(\lvert\mathbf{r}-\mathbf{R}^a\rvert)$
$\tilde{n}_{\text{core}}(\lvert\mathbf{r}-\mathbf{R}^a\rvert) + (-Z + Q_{\text{core}} - \tilde{Q}_{\text{core}}) g_{00}(\lvert\mathbf{r}-\mathbf{R}^a\rvert)$	$\tilde{n}^a_{Z_c}(\lvert\mathbf{r}-\mathbf{R}^a\rvert)$
$\sum_{ij:LM} W^a_{ij} G^{LM}_{l_i m_i l_j m_j} n^{aL}_{n_i l_i n_j l_j} g_{LM}(\mathbf{r}-\mathbf{R}^a)$	$\hat{\hat{n}}^a(\mathbf{r}-\mathbf{R}^a)$
$G^{LM}_{l_i m_i l_j m_j} n^{aL}_{n_i l_i n_j l_j}/\sqrt{4\pi}$	q^{aL}_{ij}
$\sqrt{4\pi} g_{LM}(\mathbf{r}-\mathbf{R}^a)$	$g_L(\lvert\mathbf{r}-\mathbf{R}^a\rvert) Y_{LM}(\widehat{\mathbf{r}-\mathbf{R}^a})$
$G^{LM}_{l_i m_i l_j m_j} n^{aL}_{n_i l_i n_j l_j} g_{LM}(\mathbf{r}-\mathbf{R}^a)$	$\hat{Q}^{aL}_{ij}(\mathbf{r}-\mathbf{R}^a)$

Here, we have used a "double hat" notation to distinguish the compensation charge function in the *abinit* convention. In fact, the Coulomb potential corresponding to smooth ionic density term $\tilde{n}^a_{Z_c}(\mathbf{r})$ is not explicitly calculated, but is combined with the local potential term (35) according to Eq.(60) in Ref. [6]. That is, in the construction of the pseudopotential parameters discussed in Sec. (2), unscreening of the local atomic pseudopotential (35) is replaced by

$$\tilde{v}^a_{Z_c}(r) \equiv V^{aPS}(r) - e^2 \int d^3r' \frac{\tilde{n}^a(r') + \hat{\hat{n}}^a(r')}{|\mathbf{r}-\mathbf{r}'|} - \mu_{\text{xc}}[\tilde{n}^a_{\text{core}}(r) + \hat{\hat{n}}^a(r) + \tilde{n}^a(r)], \tag{89}$$

where in this equation $\tilde{n}^a(r)$ represents smooth density in the atomic calculation for atom a. This ionic pseudopotential term is referenced as $v_H[\tilde{n}_{Z_c}]$ in Ref. [6], but since it essentially includes both Hartree and additional local potential corrections, we prefer to use the more generic notation of $\tilde{v}^a_{Z_c}(r)$. By construction, since the pseudopotential $V^{aPS}(r)$ represents a neutral system, the asymptotic form of the ionic potential $\tilde{v}^a_{Z_c}(r)$ is

$$\tilde{v}^a_{Z_c}(r) \underset{r\to\infty}{=} -e^2 \, \frac{Z^a - Q^a_{\text{core}}}{r}. \tag{90}$$

This follows because, by construction,

$$Z^a - Q^a_{\text{core}} = \int d^3r \left(\tilde{n}(r) + \hat{\tilde{n}}^a(r)\right). \tag{91}$$

Correspondingly, we can define the superposed ionic potential and the superposed compensation charge densities as

$$\tilde{v}_{Z_c}(\mathbf{r}) \equiv \sum_a \tilde{v}^a_{Z_c}(|\mathbf{r} - \mathbf{R}^a|) \;\; \text{and} \;\; \hat{\tilde{n}}(\mathbf{r}) \equiv \sum_a \hat{\tilde{n}}^a(\mathbf{r} - \mathbf{R}^a) \equiv \sum_{aij}\sum_{LM} \rho^a_{ij} \hat{Q}^{aL}_{ij}(\mathbf{r} - \mathbf{R}^a). \tag{92}$$

In these terms, the total energy can be written in terms of smooth and a summation of atom-centered contributions as defined in Eq. (40). In this case the smooth energy term analogous to Eq. (41) takes the form:

$$\begin{aligned}\tilde{E} = \;\; & \tilde{K} + \frac{e^2}{2}\int d^3r \int d^3r' \frac{(\tilde{n}(\mathbf{r}) + \hat{\tilde{n}}(\mathbf{r}))(\tilde{n}(\mathbf{r}') + \hat{\tilde{n}}(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} + U_{\text{ion}-\text{ion}} \\ & + \int d^3r \; \tilde{v}_{Z_c}(\mathbf{r}) \left(\tilde{n}(\mathbf{r}) + \hat{\tilde{n}}(\mathbf{r})\right) + E_{xc}[\tilde{n}_{\text{core}} + \hat{\tilde{n}} + \tilde{n}].\end{aligned} \tag{93}$$

Here, the ionic interaction term is defined by

$$U_{\text{ion}-\text{ion}} = \frac{1}{2}\int d^3r \; \tilde{v}_{Z_c}(\mathbf{r})\tilde{n}_{Z_c}(\mathbf{r}) - \sum_a \frac{1}{2}\int d^3r \; \tilde{v}^a_{Z_c}(\mathbf{r})\tilde{n}^a_{Z_c}(\mathbf{r}), \tag{94}$$

which can be evaluated using Ewald summation techniques. While the ionic self-interaction term is easily treated in the Ewald term (94), additional self-interaction terms

$$\sum_a \left\{ \int d^3r \; \tilde{v}^a_{Z_c}(\mathbf{r})\hat{\tilde{n}}^a(\mathbf{r}) + \frac{e^2}{2}\int d^3r \int d^3r' \; \frac{\hat{\tilde{n}}^a(\mathbf{r})\hat{\tilde{n}}^a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\}, \tag{95}$$

must also be subtracted from Eq. (93) and included in the atomic center contributions. Apart from a different arrangement of the terms, the main difference between this form of the smooth total energy and that of the *pwpapw* approach is, following the work of Kresse [6] the compensation charge $\hat{\tilde{n}}$ is included in the exchange-correlation expression. In principle, since the compensation charge is localized within the augmentation sphere, is should be canceled out of the final energy by atom-center terms. The *abinit* version of the one-center contributions corresponding to Eq. (52) is given by

$$E^a - \tilde{E}^a = \sum_{ij} \rho^a_{ij} D^{a0}_{ij} + \frac{1}{2}\sum_{ijkl} \rho^a_{ij}\rho^a_{kl} e^a_{ijkl} + E_{xc}[n^a + n^a_{\text{core}}] - E_{xc}[\tilde{n}^a + \tilde{n}^a_{\text{core}} + \hat{\tilde{n}}^a]. \tag{96}$$

Here D^{a0}_{ij} denotes the matrix elements which are diagonal in the angular momentum indices:

$$D^{a0}_{ij} = (K^a_{n_i l_i n_j} + X^a_{n_i l_i n_j} - S^a_{n_i l_i n_j})\delta_{l_i l_j}\delta_{m_i m_j}, \tag{97}$$

where the kinetic energy $K^a_{n_i l_i n_j}$ is the same as defined in Eq. (54) and the potential energy term is given by

$$X^a_{n_i l_i n_j} \equiv \int_0^{r_c^a} dr \left\{ \phi^a_{n_i l_i}(r) v_H[n^a_{Z_c}](r) \phi^a_{n_j l_i}(r) - \tilde{\phi}^a_{n_i l_i}(r) \tilde{v}^a_{Z_c}(r) \tilde{\phi}^a_{n_j l_i}(r) \right\}, \tag{98}$$

which is similar to Eq. (55). Here we have adopted the notation of Ref. [6] for $v_H[n]$ to denote the Hartree (Coulomb) potential corresponding to a charge density n. The self-energy contribution to D^{a0}_{ij} corresponding to the first term of (95) is given by

$$S^a_{n_i l_i n_j} \equiv \int d^3r \; \tilde{v}^a_{Z_c}(r) \hat{Q}^{a0}_{ij}(r). \tag{99}$$

The four-component contribution comes from the Hartree contributions from the basis function expansion, from the compensation charges, and from the last term of Eq. (95) correspond to the compensation charge self-energy contribution:

$$e^a_{ijkl} \equiv \sum_{LM} \Big\{ (-1)^M G^{L\,-M}_{l_i m_i l_j m_j} G^{LM}_{l_k m_k l_l m_l} V^{aL}_{n_i l_i n_j l_j; n_k l_k n_l l_l} \tag{100}$$

$$-2 G^{LM}_{l_i m_i l_j m_j} n^{aL}_{n_i l_i n_j l_j} (-1)^M G^{L\,-M}_{l_k m_k l_l m_l} v^{aL}_{n_k l_k n_l l_l} - 8\pi q^{aL}_{ij} q^{aL}_{kl} \hat{E}^{aL} \Big\}.$$

In this expression. $\hat{E}^{aL}$ is defined in equation (62).

We can now again take the variation of the energy functional with respect to the smooth wavefunction $\Psi_{n\mathbf{k}}(\mathbf{r})$ to find the corresponding PAW Hamiltonian in this formulation. The smooth term takes the form (65) with the effective potential given by

$$\tilde{v}_{\text{eff}}(\mathbf{r}) = \tilde{v}_{Z_c}(\mathbf{r}) + e^2 \int d^3r' \frac{\tilde{n}(\mathbf{r}') + \hat{\tilde{n}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{\text{xc}}[\tilde{n}_{\text{core}}(\mathbf{r}) + \hat{\tilde{n}}(\mathbf{r}) + \tilde{n}(\mathbf{r})]. \tag{101}$$

The corresponding atom-centered contributions can be written

$$D^a_{ij} = D^{a0}_{ij} + \sum_{kl} \rho^a_{kl} e^a_{ijkl} + D^{axc}_{ij} + \hat{D}^a_{ij}. \tag{102}$$

Here D^{axc}_{ij} is very similar to $[V^a_{XC}]_{ij}$ as defined in Eq. (69) except for the appearance of $\hat{\tilde{n}}^a$ in the argument of the smooth exchange-correlation potential and for an additional contribution due to the dependence of $\hat{\tilde{n}}^a$ on the smooth wavefunction. The last term takes the form:

$$\hat{D}^a_{ij} \equiv \int d^3r \; \tilde{v}_{\text{eff}}(\mathbf{r}) \hat{Q}^{aL}_{ij}(\mathbf{r} - \mathbf{R}^a), \tag{103}$$

where $\tilde{v}_{\text{eff}}(\mathbf{r})$ is the smooth effective potential for the system defined in Eq. (101). It corresponds to Eq. (44) in Ref. [6].

The current version of the *atompaw* code now outputs the information needed by the *pwpaw* and *socorro*[23] codes as well as by the *abinit* code. For *pwpaw* and *socorro* the local potential needed is neutral originally defined by Blöchl[1] and is calculated here by Eq. (35) and is listed in the [atom].atomicdata file with the keyword "VLOCFUN". For *abinit*, the local potential is ionic and is calculated here by Eq. (89) and is listed in the [atom].atomicdata files with the keyword "VLOCION". It is our experience that by using the consistently unscreened local potentials, it is possible to get identical results with the different codes.

7 Acknowledgements

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