Notes for revised form of *atompaw* code.

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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, 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:

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

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, 3] we investigated several alternative construction schemes. However, we found a slight modification of the original scheme developed by Blöchl[1], to be the most robust.

The starting point of the construction process is an all-electron self-consistent solution of the Schrödinger equation for the reference atom or ion. 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 both the valence and core electron density.

The all-electron basis functions $|\phi_i^0(\mathbf{r})\rangle$ are valence and continuum eigenstates of the Kohn-Sham[5] Hamiltonian. Here the superscript "0" is used to distinguish these initial basis functions from the final orthogonalized ones.

$$H(\mathbf{r})|\phi_i^0(\mathbf{r})\rangle = \varepsilon_i |\phi_i^0(\mathbf{r})\rangle, \qquad (2)$$

The Hamiltonian take the form:

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

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

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

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[6], 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:

$$n(r) = \sum_{n_i l_i} o_{n_i l_i} \frac{|\phi^0_{n_i l_i}(r)|^2}{4\pi r^2}, \tag{5}$$

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 second consideration in constructing the basis and projector functions is to choose an appropriate augmentation radius r_c. This radius should be small enough so that for all the materials to be studied with these functions, the enclosing spheres do not overlap. On the other hand, it should be large enough so that core density $n_{\text{core}}(r)$ is well contained within r_c.[1]

In Blöchl's pseudo-function construction scheme, the smoothness of the functions is controlled by a shape function $k(r)$ which vanishes outside the augmentation region. In previous work we find the following shape function to work the best:

$$k(r) = \begin{cases} \left[\frac{\sin(\pi r/r_c)}{(\pi r/r_c)}\right]^2 & \text{for } r < r_c \\ 0 & \text{for } r \geq r_c \end{cases}. \tag{6}$$

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:

$$\left(\tilde{H}(\mathbf{r}) - \varepsilon_i\right) |\tilde{\phi}^0_i(\mathbf{r})\rangle = C_i k(r) |\tilde{\phi}^0_i(\mathbf{r})\rangle. \tag{7}$$

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:

$$\tilde{\phi}^0_{n_i l_i}(r) = \phi^0_{n_i l_i}(r) \quad \text{for } r \geq r_c. \tag{8}$$

In practice, this is achieved by iterating Eq. (7) 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[7]. The smooth Hamiltonian used in Eq. (7) is given by

$$\tilde{H}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + \tilde{v}_{\text{eff}}(r), \tag{9}$$

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[1]In the present version of the code we have redefined the core tail function differently than in Ref.([2]).

where the smooth effective potential is given by

$$\tilde{v}_{\text{eff}}(r) \equiv \tilde{v}_{\text{loc}}(r) + e^2 \int d^3 r' \frac{\tilde{n}_{\text{core}}(r') + \tilde{n}(r') + \hat{n}(r')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{\text{xc}}[\tilde{n}_{\text{core}}(r) + \tilde{n}(r)]. \tag{10}$$

In this expression for the smooth effective potential, the term $\tilde{v}_{\text{loc}}(r)$, denotes a local potential which vanishes outside the augmentation region. In the present work, this contribution is constructed in terms of the shape function:

$$\tilde{v}_{\text{loc}}(r) \equiv \mathcal{V}_0 \, k(r), \tag{11}$$

where $\mathcal{V}_0$ is a chosen amplitude. In our experience, most systems are not sensitive to this choice, however for highly ionic materials, the best choice for $\mathcal{V}_0$ seems to be the value which makes the non-local coefficient C_{i_s} in Eq. (7) vanish for the index i_s corresponding to the valence s-state of each material. An easy way to accomplish this, is to run the *atompaw* program once with $\mathcal{V}_0 = 0$ to determine the value of $C_{i_s}^0$ and then run the *atompaw* program a second time with $\mathcal{V}_0 = -C_{i_s}^0$. In fact, within numerical accuracy, the basis functions and projector functions are invariant to the choice of $\mathcal{V}_0$. From this point of view, we see that the role of $\mathcal{V}_0$ is to adjust the strength of the local potential contributions relative to the strength of the non-local contributions for each atom. Alternative choices for $\tilde{v}_{\text{loc}}(r)$ are given below.

At self-consistency, the pseudo-density $\tilde{n}(r)$ in Eq. (9) is determined from the pseudo-basis functions

$$\tilde{n}(r) = \sum_{n_i l_i} o_{n_i l_i} \frac{|\tilde{\phi}_{n_i l_i}^0(r)|^2}{4\pi r^2}. \tag{12}$$

In Eq. 9, 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

$$4\pi r^2 \tilde{n}_{\text{core}}(r) \equiv \begin{cases} r^2(U_0 + U_2 r^2 + U_4 r^4) & \text{for} \quad r \leq r_c \\ 4\pi r^2 n_{\text{core}}(r) & \text{for} \quad r \geq r_c, \end{cases} \tag{13}$$

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

$$U_0 r_c^2 = 3d_0 - \frac{9}{8} d_1 r_c + \frac{1}{8} d_2 r_c^2. \tag{14}$$

$$U_2 r_c = -3d_0 + \frac{7}{4} d_1 r_c - \frac{1}{4} d_2 r_c^2. \tag{15}$$

$$U_4 = d_0 - \frac{5}{8} d_1 r_c + \frac{1}{8} d_2 r_c^2. \tag{16}$$

The additional "compensation" charge density contribution in Eq. 9 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:

$$\hat{n}(r) = Q_{00} g_{00}(\mathbf{r}), \tag{17}$$

where the monopole moment Q_{00} is

$$Q_{00} \equiv -Z + \int d^3 r \, [n_{\text{core}}(r) + n(r) - \tilde{n}_{\text{core}}(r) - \tilde{n}(r)]. \tag{18}$$

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

$$g_{LM}(\mathbf{r}) \equiv \mathcal{N}_L r^L k(r) Y_{LM}(\hat{\mathbf{r}}), \quad \text{where,} \quad [\sqrt{4\pi}\mathcal{N}_L]^{-1} \equiv \int_0^{r_c} dr \; r^{2+2L} \; k(r). \tag{19}$$

Here, $Y_{LM}(\hat{\mathbf{r}})$ denotes the spherical harmonic function and $\mathcal{N}_L$ denotes a normalization factor.

Once the pseudo-basis functions $|\tilde{\phi}_i^0(\mathbf{r})\rangle$ have been determined by self-consistently solving Eq. (7), the corresponding projector functions are formed according to:

$$|\tilde{p}_i^0(\mathbf{r})\rangle \equiv \frac{k(r)|\tilde{\phi}_i^0(\mathbf{r})\rangle}{\langle \tilde{\phi}_i^0 | k | \tilde{\phi}_i^0 \rangle}. \tag{20}$$

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

$$\langle \tilde{\phi}_i^0 | \tilde{p}_i^0 \rangle = 1, \tag{21}$$

and related to the smooth Hamiltonian according to the identity:

$$\left(\tilde{H}(\mathbf{r}) - \varepsilon_i \right) |\tilde{\phi}_i^0(\mathbf{r})\rangle = |\tilde{p}_i^0(\mathbf{r})\rangle \langle \tilde{\phi}_i^0 | \tilde{H} - \varepsilon_i | \tilde{\phi}_i^0 \rangle. \tag{22}$$

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 $n_1, n_2, \ldots$ etc. The first set of basis and projector functions is given by the initial functions:

$$\tilde{p}_{n_1 l}(r) \equiv \tilde{p}_{n_1 l}^0(r), \quad \tilde{\phi}_{n_1 l}(r) \equiv \tilde{\phi}_{n_1 l}^0(r), \quad \text{and} \quad \phi_{n_1 l}(r) \equiv \phi_{n_1 l}^0(r). \tag{23}$$

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

$$\tilde{p}_{n_2 l}(r) = \mathcal{F}_{n_2 l} \left[\tilde{p}_{n_2 l}^0(r) - \tilde{p}_{n_1 l}(r) \langle \tilde{\phi}_{n_1 l} | \tilde{p}_{n_2 l}^0 \rangle \right], \tag{24}$$

$$\tilde{\phi}_{n_2 l}(r) = \mathcal{F}_{n_2 l} \left[\tilde{\phi}_{n_2 l}^0(r) - \tilde{\phi}_{n_1 l}(r) \langle \tilde{p}_{n_1 l} | \tilde{\phi}_{n_2 l}^0 \rangle \right],$$

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

where,

$$\mathcal{F}_{n_2 l} \equiv \left(1 - \langle \tilde{\phi}_{n_2 l}^0 | \tilde{p}_{n_1 l} \rangle \langle \tilde{\phi}_{n_1 l} | \tilde{p}_{n_2 l}^0 \rangle \right)^{-1/2}. \tag{25}$$

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[8, 9], one or two radial basis functions are usually sufficient to span the Hilbert space of smooth functions within each atomic sphere.

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

$$\mathbf{H}^{\mathbf{PAW}}(\mathbf{r})|\tilde{\Psi}_E(\mathbf{r})\rangle = E\mathbf{O}|\tilde{\Psi}_E(\mathbf{r})\rangle, \tag{26}$$

where

$$\mathbf{H^{PAW}} \equiv \tilde{H}(\mathbf{r}) + \sum_{aij} |\tilde{p}_i^a\rangle \left(\langle \phi_i^a | H^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{H}^a | \tilde{\phi}_j^a \rangle \right) \langle \tilde{p}_j^a |, \tag{27}$$

and

$$\mathbf{O} \equiv \mathbf{1} + \sum_{aij} |\tilde{p}_i^a\rangle \left(\langle \phi_i^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{\phi}_j^a \rangle \right) \langle \tilde{p}_j^a |. \tag{28}$$

It can be shown that the pre-orthonormalized functions $\{|\tilde{\phi}_i^0(\mathbf{r})\rangle\} \to |\tilde{\Psi}_E(\mathbf{r})\rangle$ are exact solutions of the PAW equations (26).

The eigenstates $|\tilde{\Psi}_E(\mathbf{r})\rangle$ of Eq. (26) are related to the eigenstates of the all-electron Hamiltonian, according to:

$$|\Psi_E(\mathbf{r})\rangle = |\tilde{\Psi}_E(\mathbf{r})\rangle + \sum_{ai} \left(|\phi_i^a(\mathbf{r})\rangle - |\tilde{\phi}_i^a(\mathbf{r})\rangle \right) \langle \tilde{p}_i^a | \tilde{\Psi}_E \rangle, \tag{29}$$

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. By construction, the valence density $n(r)$ (Eq. 5) and pseudo-density $\tilde{n}(r)$ (Eq. 12) are expressed in terms of the initial $\phi_{n_i l_i}^0(r)$ and $\tilde{\phi}_{n_i l_i}^0(r)$ basis functions which determine the all-electron (2) and and smooth (9) Hamiltonians. In turn, these Hamiltonians are used to generate these functions and the projectors. It can be shown that, after the orthonormalization procedure of Eqs. (23,24, and 25), the initial pseudo-wavefunctions $|\tilde{\phi}_i^0(\mathbf{r})\rangle$ are eigenstates of the atomic PAW Hamiltonian (26), with corresponding eigenvalues ε_i of the all-electron Hamiltonian (2). More generally, the Hamiltonians H^a and $\tilde{H}^a$ which appear in Eq. (27) are defined in terms of matrix elements evaluated using the orthogonalized basis functions $\{\phi_i^a\}$ and $\{\tilde{\phi}_i^a\}$ [1, 2, 10]. 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.

2   Alternative forms for $\tilde{v}_{\text{loc}}(r)$

For some of the materials (such as SiC), we noticed that our scheme of constructing the PAW functions give incorrect lattice constants. One possible reason for this systematic error is our previous choice of for $\tilde{v}_{\text{loc}}(r)$ which is very good for avoiding ghost states[11, 12] but which does a very poor job of describing high angular momentum components in the augmentation sphere. Therefore we, have now introduced an option of constructing $\tilde{v}_{\text{loc}}(r)$ using a norm-conserving pseudopotential[13] 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/.

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:

$$\tilde{\phi}(r) = \begin{cases} r^{L_v+1} f(r) & \text{for } r \leq r_c \\ \phi(r) & \text{for } r > r_c. \end{cases} \tag{30}$$

Here $\phi(r)$ represents a chosen continuum wavefunction of the all-electron Hamiltonian at energy

E. The function $f(r)$ is chosen to by one of the following types:

$$f(r) = e^{p(r)} \quad \text{keyword : EXPF.} \tag{31}$$

$$f(r) = p(r) \quad \text{keyword : POLY.} \tag{32}$$

In both cases, $p(r)$ represents a polynomial of the form

$$p(r) = C_0 + C_1 r^{m_1} + C_2 r^{m_2} + C_3 r^{m_3} + C_4 r^{m_4}, \tag{33}$$

where the $\{C_i\}$'s represent coefficients to be determined to satisfy 5 matching conditions and the $\{m_i\}$'s represents polynomial powers chosen by the user. The exponential form was that presented in the original paper of Kerker[13], while the polynomial form allows additional flexibility.

For the EXPF form, the screened norm-conserving pseudopotential can be determined from

$$V^{PS}(r) = E + \frac{\hbar^2}{2m} \left(\frac{d^2 p}{dr^2} + \frac{dp}{dr} \left(\frac{dp}{dr} + \frac{2(L_v + 1)}{r} \right) \right). \tag{34}$$

For the POLY form, the screened norm-conserving pseudopotential can be determined from

$$V^{PS}(r) = E + \frac{\hbar^2}{2m} \frac{1}{p(r)} \left(\frac{d^2 p}{dr^2} + \frac{2(L_v + 1)}{r} \frac{dp}{dr} \right). \tag{35}$$

In both cases the 5 matching conditions which determine the coefficients $\{C_i\}$ require that $\tilde{\phi}(r)$ and its first 3 derivatives are continuous at r_c in addition to the norm-conserving condition:

$$\int_0^{r_c} dr |\tilde{\phi}(r)|^2 = \int_0^{r_c} dr |\phi(r)|^2. \tag{36}$$

Alternatively, we can generate the Troullier-Martins[14] form of the norm-conserving pseudopotential (keyword VNCT as opposed to VNCK for the Kerker form described above). The difference here is that the polynomial is chosen to be an even 12th order polynomial appearing in the exponent as in Eq. (34).

$$p(r) = \sum_{m=0}^{6} C_m r^{2m}. \tag{37}$$

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[14] means that $C_1^2 + (2l + 5)C_2 = 0$. These potentials tend to be deeper than the Kerker form described above when the usual choice of powers ($\{m_i\} = 4, 5, 6, 7$) is made, but the Troullier-Martin potentials are quite smooth.

Once the screen pseudopotential is constructed, the PAW functions can be constructed in the usual way. For example, we must solve for the smooth functions according to the equations

$$\left(\tilde{H}(\mathbf{r}) - \varepsilon_i \right) |\tilde{\phi}_i^0(\mathbf{r})\rangle = C_i k(r) |\tilde{\phi}_i^0(\mathbf{r})\rangle, \tag{38}$$

where $k(r)$ is the chosen shape function. Note: the shape function $k(r)$ which is also used to determine the shapes of the compensation charge density $\hat{n}(r)$ is taken to have the squared sinc function shape:

$$k(r) = \begin{cases} \left(\frac{\sin(\pi r/r_c)}{\pi r/r_c} \right)^2 & \text{for } r \leq r_c \\ 0 & \text{for } r > r_c \end{cases}, \tag{39}$$

since we have found this shape to have much better convergence properties than other forms such the Gaussian form.

The Hamiltonian is

$$\tilde{H}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V^{PS}(r). \tag{40}$$

Once the smooth basis functions $\{|\tilde{\phi}_i^0(\mathbf{r})\rangle\}$ are determined and the smooth density $\tilde{n}(r)$ and compensation charge density $\hat{n}(r)$ are constructed, the local potential term can be determined according to

$$\tilde{v}_{\text{loc}}(r) = V^{PS}(r) - e^2 \int d^3r' \frac{\tilde{n}_{\text{core}}(r') + \tilde{n}(r') + \hat{n}(r')}{|\mathbf{r} - \mathbf{r}'|} - \mu_{\text{xc}}[\tilde{n}_{\text{core}} + \tilde{n}(r)]. \tag{41}$$

The output of this new *atompaw* code is very similar to that of the old code with some additional diagnostic files. However, the [atom].atomicdata file that is read by the *pwpaw* program now lists the radial form of $v_{loc}(r)$ using the keyword "VLOCFUN". This required a very minor change in the pwpaw code (which can also read the old form of [atom].atomicdata).

3 PAW representation of the energy and effective Hamiltonian for atoms

Using the terms above, the total energy of the atom is then given by[2]

$$E_{atom} = \tilde{E} + \left(E^a - \tilde{E}^a \right). \tag{42}$$

The first term represents the pseudopotential-like contributions which take the form

$$\tilde{E} = \sum_{nl} o_{nl} \, K_{nl} + \frac{e^2}{2} \int d^3r \int d^3r' \frac{\tilde{n}(r)\tilde{n}(r')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r \, \tilde{n}(r) \left\{ \tilde{v}_{\text{loc}}(r) + \tilde{v}_{\text{core}}(r) + \hat{v}(r) \right\} + E_{\text{xc}}[\tilde{n}_{\text{core}} + \tilde{n}], \tag{43}$$

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

$$K_{nl} \equiv -\frac{\hbar^2}{2m} \int \, dr \, \, \tilde{\phi}_{nl}(r) \left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right) \tilde{\phi}_{nl}(r). \tag{44}$$

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[2]As noted above, we have redefined the core tail function defined in Ref.([2]) in this formulation.

The remaining terms of Eq. 42 are all atom-centered terms which can be determined from

$$E^a - \tilde{E}^a = \sum_{ij} W_{ij}^a \left(K_{ij}^a + [v_{\text{at}}^a]_{ij} - [\hat{v}^a]_{ij} + \tfrac{1}{2}[V_{\text{H}}^a]_{ij} \right) \tag{45}$$

$$+ \left(E_{\text{xc}}[n_{\text{core}}^a + n^a] - E_{\text{xc}}[\tilde{n}_{\text{core}}^a + \tilde{n}^a] \right).$$

In this expression, $K_{ij}^a \equiv K_{n_i l_i n_j l_i}^a \delta_{l_i l_j} \delta_{m_i m_j}$ and $[\hat{v}^a]_{ij} \equiv \langle \tilde{\phi}_i^a | \hat{v}^a | \tilde{\phi}_j^a \rangle$. The matrix elements $K_{n_i l_i n_j l_i}^a$, $\langle \tilde{\phi}_i^a | \hat{v}^a | \tilde{\phi}_j^a \rangle$, and $[V_{\text{H}}^a]_{ij}$ are defined in Eqs. A10, A23, and A26 of Ref. [2] respectively. In addition, $[v_{\text{at}}^a]_{ij} \equiv [v_{\text{at}}^a]_{n_i l_i n_j l_i} \delta_{l_i l_j} \delta_{m_i m_j}$, where $[v_{\text{at}}^a]_{n_i l_i n_j l_i}$ is modified from its definition in Eq. [15]-26.

$$[v_{\text{at}}]_{n_i l_i n_j l_i}^a \equiv \int_0^{r_c^a} dr \left\{ \phi_{n_i l_i}^a(r) \left(-\frac{Ze^2}{r} + v_{\text{core}}^a(r) \right) \phi_{n_j l_i}^a(r) - \tilde{\phi}_{n_i l_i}^a(r) \left(\tilde{v}_{\text{core}}^a(r) + \tilde{v}_{\text{loc}}^a(r) \right) \tilde{\phi}_{n_j l_i}^a(r) \right\}. \tag{46}$$

The exchange-correlation energy terms E_{xc} are currently evaluated using the local density approximation of Perdew and Wang[6], although additional functionals could easily be added. In this form the compensation charge self energy $\hat{E}^a$ cancels out of the analysis although it is necessary in the solid calculations. For completeness, it is given by the tabulated atomic moment terms (Eq. [15]-27) according to

$$\hat{E}^a \equiv \sum_{LM} |Q_{LM}^a|^2 \hat{E}^{aL}. \tag{47}$$

By evaluating the functional variation of the cohesive energy with respect to $|\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\rangle$, Blöchl derived the Kohn-Sham equations[5] for the PAW formalism which take the form of a generalized eigenvalue problem:

$$\left\{ \mathbf{H}^{\mathbf{PAW}}(\mathbf{r}) - E_{n\mathbf{k}} \mathbf{O} \right\} |\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\rangle = 0, \tag{48}$$

where

$$\mathbf{H}^{\mathbf{PAW}} \equiv \tilde{H}(\mathbf{r}) + \sum_{aij} |\tilde{p}_i^a\rangle D_{ij}^a \langle \tilde{p}_j^a| \quad \text{and} \quad \mathbf{O} \equiv \mathbf{1} + \sum_{aij} |\tilde{p}_i^a\rangle O_{ij}^a \langle \tilde{p}_j^a|. \tag{49}$$

The local term contribution to the PAW Hamiltonian is given by

$$\tilde{H}(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 + \tilde{v}_{\text{eff}}(\mathbf{r}). \tag{50}$$

with the smooth local potential given above.

The non-local contribution to the PAW Hamiltonian is given by

$$D_{ij}^a = K_{ij}^a + [v_{\text{at}}^a]_{ij} - [\hat{v}^a]_{ij} + [V_{\text{H}}^a]_{ij} + [v_0^a]_{ij} + [V_{\text{xc}}^a]_{ij} \tag{51}$$

and

$$O_{ij}^a \equiv \langle \phi_i^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{\phi}_j^a \rangle = O_{n_i l_i n_j l_j}^a \delta_{l_i l_j} \delta_{m_i m_j}. \tag{52}$$

The matrix elements $[v_0^a]_{ij}$ and $[V_{\text{xc}}^a]_{ij}$ are slightly modified (as indicated in the footnote above) from their definitions in Ref. [2] in Eqs. A27 and A29 respectively.

For the atom, some of these expressions simplify:

$$W_{ij}^a = \sum_{nl} o_{nl} \langle \tilde{\phi}_{nl} | \tilde{p}_{n_i l} \rangle \langle \tilde{p}_{n_j l} | \tilde{\phi}_{nl} \rangle \delta_{l_i l} \delta_{l_j l}. \tag{53}$$

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

$$n^{a0}_{n_i l_i n_j l_j} \equiv \int_0^{r^a_c} dr \left(\phi^a_{n_i l_i}(r) \phi^a_{n_j l_j}(r) - \tilde{\phi}^a_{n_i l_i}(r) \tilde{\phi}^a_{n_j l_j}(r) \right) \delta_{l_i l_j} \tag{54}$$

This allows us to calculate the charge moments

$$Q^a_{00} = -Z^a + \int d^3 r \left(n_{\text{core}}(r) - \tilde{n}_{\text{core}}(r) \right) + \sum_{ij} W^a_{ij} n^{a0}_{n_i l_i n_j l_j}. \tag{55}$$

The Hartree term is given by

$$V^{aL}_{n_i l_i n_j l_j; n_k l_k n_l l_l} \equiv \frac{4\pi e^2}{2L+1} \int_0^{r^a_c} dr \int_0^{r^a_c} dr' \frac{r_<^L}{r_>^{L+1}} \left[\phi^a_{n_i l_i}(r) \phi^a_{n_j l_j}(r) \phi^a_{n_k l_k}(r') \phi^a_{n_l l_l}(r') \right.$$

$$\left. - \tilde{\phi}^a_{n_i l_i}(r) \tilde{\phi}^a_{n_j l_j}(r) \tilde{\phi}^a_{n_k l_k}(r') \tilde{\phi}^a_{n_l l_l}(r') \right]. \tag{56}$$

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

$$[V^a_H]_{ij} = \sum_{kl} W^a_{kl} V^{a0}_{n_i l_i n_j l_j; n_k l_k n_l l_l}. \tag{57}$$

The compensation charge term is given by

$$<\tilde{\phi}^a_i |\hat{v}^a| \tilde{\phi}^a_j> = Q^a_{00} \hat{v}^{a0}_{n_i l_i n_j l_j}. \tag{58}$$

The matrix elements involving the compensation charge potential depend upon:

$$\hat{v}^{a0}_{n_i l_i n_j l_j} \equiv \int_0^{r^a_c} dr \, \tilde{\phi}^a_{n_i l_i}(r) \hat{v}^a_0(r) \tilde{\phi}^a_{n_j l_j}(r), \tag{59}$$

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

The Coulomb shift term takes the form

$$[v^a_0]_{ij} = \frac{\partial E}{\partial Q^a_{00}} n^{a0}_{n_i l_i n_j l_j}, \tag{60}$$

where for the atomic case,

$$\frac{\partial E}{\partial Q^a_{00}} = \int dr \, 4\pi r^2 \tilde{n}(r) \hat{v}^a_0 - \sum_{ij} W^a_{ij} \hat{v}^{a0}_{n_i l_i n_j l_j}. \tag{61}$$

The radial densities can be easily determined from

$$4\pi r^2 \tilde{n}(r) = \sum_{nl} o_{nl} |\tilde{\phi}_{nl}(r)|^2. \tag{62}$$

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$$4\pi r^2 \tilde{n}^a(r) = \sum_{ij} W_{ij}^a \tilde{\phi}_{n_i l_i}(r) \tilde{\phi}_{n_j l_j}(r). \tag{63}$$

$$4\pi r^2 n^a(r) = \sum_{ij} W_{ij}^a \phi_{n_i l_i}(r) \phi_{n_j l_j}(r). \tag{64}$$

4   Energy and Hamiltonian for solids.

We can use the notation

$$\tilde{n}_{\text{core}}(\mathbf{r}) = \sum_a \tilde{n}_{\text{core}}^a(\mathbf{r}), \tag{65}$$

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. In these terms the total energy expression for the solid is taken to be

$$E = \tilde{E} + \sum_a \left(E^a - \tilde{E}^a \right), \tag{66}$$

where

$$\tilde{E} = \tilde{K} + \frac{e^2}{2} \int d^3 r \int d^3 r' \frac{(\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r}) + \hat{n}(\mathbf{r}))(\tilde{n}(\mathbf{r}') + \tilde{n}_{\text{core}}(\mathbf{r}') + \hat{n}(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\tilde{n}_{\text{core}} + \tilde{n}]. \tag{67}$$

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

$$\tilde{K} = -\frac{\hbar^2}{2m} \sum_{n\mathbf{k}} o_{n\mathbf{k}} \langle \Psi_{n\mathbf{k}}(\mathbf{r}) | \nabla^2 | \Psi_{n\mathbf{k}}(\mathbf{r}) \rangle. \tag{68}$$

The one-center terms are given by

$$E^a - \tilde{E}^a = \sum_{ij} W_{ij}^a \left(K_{ij}^a + [v_{\text{at}}^a]_{ij} - [\hat{v}^a]_{ij} + \tfrac{1}{2}[V_{\text{H}}^a]_{ij} \right) \tag{69}$$

$$+ (E_{\text{xc}}[n_{\text{core}}^a + n^a] - E_{\text{xc}}[\tilde{n}_{\text{core}}^a + \tilde{n}^a]) - \hat{E}^a - \tilde{E}_{\text{core}}^a - \tilde{E}_{\text{core-hat}}^a.$$

In this expression we have 3 types of "self" interactions which are subracted from the evaluation. The compensation charge self energy is given by:

$$\hat{E}^a \equiv \sum_{LM} |Q_{LM}^a|^2 \hat{E}^{aL}, \tag{70}$$

where

$$\hat{E}^{aL} \equiv \frac{e^2}{2} \int d^3 r d^3 r' \frac{g_{LM}^a(\mathbf{r}) g_{LM}^a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{71}$$

The coretail self-energy is given by

$$\tilde{E}_{\text{core}}^a \equiv \frac{e^2}{2} \int d^3 r d^3 r' \frac{\tilde{n}_{\text{core}}^a(\mathbf{r}) \tilde{n}_{\text{core}}^a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{72}$$

The coretail-hat interaction energy is given by

$$\tilde{E}_{\text{core-hat}}^a = Q_{00}^a e^2 \int d^3 r d^3 r' \frac{g_{00}^a(\mathbf{r}) \tilde{n}_{\text{core}}^a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{73}$$

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.

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

$$\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{1}{\mathcal{V}}} \sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G}) \mathrm{e}^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \tag{74}$$

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

$$\tilde{E} = \sum_{n\mathbf{k}} o_{n\mathbf{k}} \left(\sum_{\mathbf{G}} \frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m} |A_{n\mathbf{k}}(\mathbf{G})|^2 \right) + \frac{2\pi e^2}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{|\bar{\tilde{n}}(\mathbf{G}) + \bar{\tilde{n}}_{\mathrm{core}}(\mathbf{G}) + \hat{\bar{n}}(\mathbf{G})|^2}{G^2}$$

$$+ \frac{1}{\mathcal{V}} \sum_{\mathbf{G}} \bar{\tilde{v}}_{\mathrm{loc}}(\mathbf{G}) \bar{\tilde{n}}^*(\mathbf{G}) + E_{\mathrm{xc}}[\tilde{n}_{\mathrm{core}} + \tilde{n}]. \tag{75}$$

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

$$\mathbf{F}^a \equiv -\left\{ \nabla_{\mathbf{R}^a} [E] \right\} = \frac{4\pi i e^2}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{\mathbf{G} \left[\hat{\bar{n}}^a(\mathbf{G}) + \bar{\tilde{n}}^a_{\mathrm{core}}(\mathbf{G}) \right] \left[\bar{\tilde{n}}^*(\mathbf{G}) + \hat{\bar{n}}^*(\mathbf{G}) + \bar{\tilde{n}}_{\mathrm{core}}(\mathbf{G}) \right]}{G^2}$$

$$+ \frac{i}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \mathbf{G} \, \bar{\tilde{v}}^a_{\mathrm{loc}}(\mathbf{G}) \bar{\tilde{n}}*(\mathbf{G}) + \frac{i}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \mathbf{G} \, \bar{V}_{\mathrm{xc}}(\mathbf{G}) \left[\bar{\tilde{n}}^a_{\mathrm{core}}(\mathbf{G}) \right]^* - \sum_{ij} \left\{ \nabla_{\mathbf{R}^a} \left[W^a_{ij} \right] \right\} D^a_{ij} + \sum_{ij} \left\{ \nabla_{\mathbf{R}^a} \left[U^a_{ij} \right] \right\} O^a_{ij}. \tag{76}$$

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. [15]-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

$$U^a_{ij} \equiv \sum_{n\mathbf{k}} o_{n\mathbf{k}} E_{n\mathbf{k}} \langle \tilde{\Psi}_{n\mathbf{k}} | \tilde{p}^a_i \rangle \langle \tilde{p}^a_j | \tilde{\Psi}_{n\mathbf{k}} \rangle. \tag{77}$$

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.

References

[1] P. E. Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50:17953–17979, 1994.

[2] N. A. W. Holzwarth, G. E. Matthews, R. B. Dunning, A. R. Tackett, and Y. Zeng. Comparison of the projector augmented wave, pseudopotential, and linearized augmented plane wave formalisms for density functional calculations of solids. *Phys. Rev. B*, 55:2005–2017, 1997.

[3] N. A. W. Holzwarth, G. E. Matthews, A. R. Tackett, and R. B. Dunning. Orthogonal polynomial projectors for the projector-augmented-wave (paw) method of electronic-structure calculations. *Phys. Rev. B*, 57:11827–11830, 1998.

[4] G. Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, 59:1758–1775, 1999.

[5] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140:A1133–A1138, 1965.

[6] John P. Perdew and Yue Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, 45:13244–13249, 1992.

[7] Douglas R. Hartree. *The Calculation of Atomic Structures*, pages 85–86. John Wiley & Sons, Inc., 1957.

[8] Peter E. Blöchl. Generalized separable potentials for electronic-structure calculations. *Phys. Rev. B*, 41:5414–5416, 1990.

[9] M. Y. Chou. Reformulation of gneralized separable pseudopotentials. *Phys. Rev. B*, 45:11465–11468, 1992.

[10] A. R. Tackett, N. A. W. Holzwarth, and G. E. Matthews. A Projector Augmented Wave (PAW) code for electronic structure calculations, Part II: *pwpaw* for periodic solids in a plane wave basis. *Computer Physics Communications*, 135:348–376, 2001. Available from the website http://pwpaw.wfu.edu.

[11] Xavier Gonze, Peter Käckell, and Matthias Scheffler. Ghost states for separable, norm-conserving, *ab initio* pseudopotentials. *Phys. Rev. B*, 41:12264–12267, 1990.

[12] Xavier Gonze, Roland Stumpf, and Matthias Scheffler. Analysis of separable potentials. *Phys. Rev. B*, 44:8503–8513, 1991.

[13] G. P. Kerker. Non-singular atomic pseudopotentials for solid state applications. *J. Phys. C: Solid St. Phys.*, 13:L189–L194, 1980.

[14] Norman Troullier and J. L. Martins. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B*, 43:1993–2006, 1991.

[15] N. A. W. Holzwarth, A. R. Tackett, and G. E. Matthews. A Projector Augmented Wave (PAW) code for electronic structure calculations, Part I: *atompaw* for generating atom-centered functions. *Computer Physics Communications*, 135:329–347, 2001. Available from the website http://pwpaw.wfu.edu.