ORTHOGONAL POLYNOMIAL PROJECTORS FOR THE PROJECTOR AUGMENTED WAVE METHOD OF ELECTRONIC STRUCTURE CALCULATIONS


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The projector augmented wave (PAW) method for electronic structure calculations developed by Blöchl [Phys. Rev. B 50, 17 953 (1994)] has been very successfully used for density functional studies. It has the numerical advantages of pseudopotential techniques while retaining the physics of all-electron formalisms. We describe a method for generating the set of atom-centered projector and basis functions that are needed for the PAW method. This scheme chooses the shapes of the projector functions from a set of orthogonal polynomials multiplied by a localizing weight factor. Numerical benefits of the scheme result from having direct control of the shape of the projector functions and from the use of a simple repulsive local potential term to eliminate “ghost state” problems, which can plague calculations of this kind. Electronic density of states results are presented for the mineral powellite (CaMoO₄).

I. INTRODUCTION

The projector augmented wave (PAW) method of electronic structure calculations, developed by Blöchl and also used by our group, is a very powerful method for electronic structure calculations within the framework of density functional theory. In order to use this method, it is necessary to find three types of atom-centered functions—“projectors,” all-electron basis functions, and smooth pseudo basis functions. Schemes for constructing these functions have been discussed in the literature. Our earlier scheme was found to work well for some materials, but failed for others. We describe a mathematically well-controlled method for generating the projector and basis functions that promises to work very well throughout the Periodic Table.

II. FORMALISM

Following the notation of Refs. 1 and 2, the functions that are needed for each atomic type $a$ are denoted \{\phi^a_i(\mathbf{r}), \tilde{\phi}^a_i(\mathbf{r}), \tilde{\phi}^{u}_i(\mathbf{r})\}, representing the all-electron (AE) basis functions, the projector functions, and the pseudo (PS) basis functions, respectively. The first step in the process is the solution of the all-electron self-consistent Schrödinger equation for the atom and the selection of the appropriate set of upper core and valence AE basis functions \{\phi^a_i(\mathbf{r})\} having one-electron energies \{\epsilon^a_i\}. The task is then to choose the corresponding projector functions \{\tilde{\phi}^a_i(\mathbf{r})\} and PS basis functions \{\tilde{\phi}^{u}_i(\mathbf{r})\}, which must satisfy a number of conditions. First, in order to accurately transform between the calculated PS wave functions and their corresponding AE functions, the projectors should approximately satisfy a generalized completeness condition within each atomic sphere of radius $r^a_c$:

$$\sum_i \langle \tilde{\phi}^a_i(\mathbf{r}) | \tilde{\phi}^a_j(\mathbf{r}') \rangle = \delta(\mathbf{r} - \mathbf{r}') \quad \text{for} \quad r, r' \leq r^a_c. \quad (1)$$

Each projector function must vanish and each PS basis function must become equal to its corresponding AE basis function outside the atomic sphere:

$$\tilde{\phi}^a_i(\mathbf{r}) = 0 \quad \text{and} \quad \tilde{\phi}^{u}_i(\mathbf{r}) = \phi^a_i(\mathbf{r}) \quad \text{for} \quad r \gg r^a_c. \quad (2)$$

The projector and PS basis functions must satisfy a generalized orthonormality relation:

$$\int d^3r \, \tilde{\phi}^a_i(\mathbf{r}) \tilde{\phi}^a_j(\mathbf{r}) = \delta_{ij}. \quad (3)$$

In addition, the PS basis functions \{\tilde{\phi}^{u}_i(\mathbf{r})\} satisfy an atomic PAW Hamiltonian equation of the form:
\[
(e_i^s - \tilde{H}^a)|\tilde{\phi}_i^a\rangle = \sum_j |\tilde{p}_{ij}^a| (\tilde{\phi}_{ij}^a (e_i^s - \tilde{H}^a)|\tilde{\phi}_i^a\rangle, \tag{4}
\]
where the pseudo-Hamiltonian function \(\tilde{H}^a\) has a kinetic energy operator and an effective potential contribution:
\[
\tilde{H}^a(r) = -\frac{\hbar^2}{2m} \nabla^2 + \tilde{v}_{\text{eff}}(r). \tag{5}
\]
The effective potential \(\tilde{v}_{\text{eff}}(r)\) must be determined self-consistently as discussed below.

Since the required functions are constructed from equations for a spherical atom, each of them can be written as a radial function times a spherical harmonic function, such as
\[
\phi_i^a(r) = \phi_{nl}^a(r) = \frac{\phi_{nl}^a(r)}{r} Y_{l,m}(\hat{r}). \tag{6}
\]

Since we can construct the projector and basis functions for a single atom at a time, it will be convenient to suppress the index \(a\) from some of the expressions below. We will also suppress the running orbital index \(i\) throughout the rest of the manuscript and focus our attention on the radial functions \(\{\phi_{nl}^a(r)\}, \{\tilde{\phi}_{nl}^a(r)\}, \text{ and } \{\tilde{p}_{nl}^a(r)\}.\)

In the present work, we approximate the completeness property (1) by setting the projectors to be equal to a set of weighted orthogonal functions. One convenient set of such functions can be derived from the eigenstates of the Schrödinger equation for the three-dimensional harmonic oscillator:
\[
f_{Nl}(r) = N_{Nl} e^{-r^2/2\sigma^2} r^{l+1} F\left(-N,l+\frac{3}{2},\frac{r^2}{2\sigma^2}\right). \tag{7}
\]

Here, the parameter \(\sigma\) is chosen so that \(f_{Nl}(r > r_c) \approx 0\) within a specified tolerance, \(N_{Nl}\) is a normalization constant, and \(F\left(-N,l+3/2,r^2/\sigma^2\right)\) denotes a confluent hypergeometric function, which is a finite polynomial of order \(N (N=0,1,\text{ etc.})\) in the variable of \((r^2/\sigma^2)\). Figure 1 shows the shape of some of the functions \(f_{Nl}(r)\).

Our “orthogonal polynomial projector” formalism thus starts by assuming that each radial projector function is proportional to one of the functions \(f_{Nl}(r)\):
\[
\tilde{p}_{nl}^a(r) = A_{nl} f_{n(n-n_0)}(r), \tag{8}
\]
where the amplitude \(A_{nl}\) will be evaluated below and where \(n_0\) corresponds to the first of the chosen AE radial basis functions \(\phi_{nl}^a(r)\) for a given \(l\). The following recipe then ensures that the atom-centered radial functions \(\{\phi_{nl}^a(r)\}, \{\tilde{\phi}_{nl}^a(r)\}, \text{ and } \{\tilde{p}_{nl}^a(r)\}\) satisfy the relations 2, 3, and 4.

For each AE radial basis function \(\phi_{nl}^a(r)\), we define the corresponding PS radial basis function \(\tilde{\phi}_{nl}^a(r)\) according to
\[
\tilde{\phi}_{nl}^a(r) = \sum_{n'} \mathcal{E}_{nl}^{n'} \chi_{nl}^{n'}(r). \tag{9}
\]

The indices \(n\) and \(n'\) enumerate all the \((M_l)\) basis functions needed for the given orbital quantum number \(l\). Typically, the functions \(\chi_{nl}^{n'}(r)\) are orthogonal to one of the functions \(\phi_{nl}^a(r)\) proportional to one of the functions \(f_{Nl}(r)\).

FIG. 1. Plots of the projector basis functions defined in Eq. (7) for \(\sigma=1\) and \(N=0\) (solid line), 1 (dashed line), and 2 (dotted line). For each \(n\) and \(n'\), the functions \(\chi_{nl}^{n'}(r)\) are defined to be solutions of inhomogeneous differential equations of the form
\[
\left(e_{nl}^{n'} - \frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \tilde{v}_{\text{eff}}(r)\right) \chi_{nl}^{n'}(r) = C_{nl} f_{(n'-n_0)}(r), \tag{10}
\]

with the boundary conditions that all of the \(\chi_{nl}^{n'}(r)\) functions are continuous at \(r=0\). At the atomic sphere radius \(r=r_c\), they satisfy
\[
\frac{d\chi_{nl}^{n'}(r_c)}{dr} = \frac{d\phi_{nl}^a(r_c)}{dr} + \frac{d\phi_{nl}^a(r_c)}{dr}. \tag{11}
\]

The differential equation (10) and boundary conditions (11) uniquely determine the functions \(\chi_{nl}^{n'}(r)\) and the amplitudes \(C_{nl}^{n'}\). A Numerov algorithm for solving these equations is detailed in the Appendix.

Once the solutions \(\chi_{nl}^{n'}(r)\) are determined, the \(M_l\) expansion coefficients \(\mathcal{E}_{nl}^{n'}\) can be calculated from the following linear relations:
\[
\sum_{n'} \mathcal{E}_{nl}^{n'} = 1, \tag{12}
\]
\[
\sum_{n'} \mathcal{E}_{nl}^{n'} \int_0^\infty dr \chi_{nl}^{n'}(r) f_{(n'-n_0)}(r) = 0 \text{ for } n' \neq n.
\]
In order to derive the optimal functional forms, these equations should be solved self-consistently, since $\nu_{\text{eff}}(r)$ depends upon the basis functions through the corresponding valence PS and AE density functions:

$$ n^a(r) = \sum_{n_l} w_{nl} \frac{|\phi_{nl}^a(r)|^2}{4\pi r^2} \quad \text{and} \quad n^e(r) = \sum_{n_l} w_{nl} \frac{|\phi_{nl}^e(r)|^2}{4\pi r^2}, $$

where $w_{nl} \leq 2(2l+1)$ denotes the orbital occupation. The smooth effective potential for the atom is given by:

$$ \nu_{\text{eff}}(r) = e^2 Q_{\text{Za}}^{00} \frac{\text{erf}(r/\sigma)}{r} + \nu_{\text{loc}}(r) + e^2 \int d^3 r' \frac{n^a(r')}{|r-r'|} + \mu_{\text{xc}}[\rho(r)].$$

Here $Q_{\text{Za}}^{00}$ is the compensation charge in terms of the atomic number $Z_a^2$, the core electron charge $Q_{\text{core}}^{\text{a}}$, and a valence density correction term $Q_{\text{val}}^{\text{a}} = -Z_a^2 + Q_{\text{core}}^{\text{a}} + \int f < r \rho(r) dr [n^a(r) - n^a(r)]$. The self-consistent scheme to determine the PS basis functions $\{\phi_{nl}^a(r)\}$ can be thought of as a constrained minimization of the PS energy functional $E$ defined by Blochl.

The localized potential term that appears in Eq. (16) vanishes for $r > r^a/2$. In the current scheme, the form of $\nu_{\text{loc}}(r)$ is arbitrary and can be used to optimize the PAW calculation. A convenient form is given by

$$ \nu_{\text{loc}}^a(r) = V_0 e^{-r^2/\sigma^2}, $$

where $V_0$ is an adjustable parameter. Preliminary indications are that it is possible to get good results for many materials (for example, C, O, F, Ca, and Si) using $V_0 = 0$. However, since the PAW formulation uses a separable potential it sometimes suffers from the well-documented phenomenon of “ghost” states. 7 We examined two systems (Fe and Mo) that exhibited this ghost state behavior and, for both of them, we were able to eliminate the problem by introducing a repulsive local potential $\nu_{\text{loc}}^a$ with a large enough amplitude ($V_0 > 0$). Gonze and co-workers studied the mathematical origin of these unphysical states and found that they are more likely to occur when there exist eigenstates of the “local” Hamiltonian ($H^{\text{pw}}$ in the notation of Blochl) below the physical eigenstates of the system. In the PAW approach, the potential due to the “compensation” charge density $\hat{n}(r)$ is usually attractive and thus can shift the eigenvalue spectrum of $H^{\text{pw}}$ toward negative values. Therefore, introducing a repulsive localized potential [Eq. (16) with $V_0 > 0$] can shift the eigenvalue spectrum of $H^{\text{pw}}$ to higher energy values. Of course, the contributions of both $\hat{n}$ and of $\nu_{\text{loc}}$ cancel out in the final result of a well-converged and ghostless calculation.

### III. RESULTS FOR EXAMPLE SYSTEMS

We have tested this scheme for a few solid state systems—CaF$_2$, Mo, and the mineral CaMoO$_4$. For CaF$_2$, results were obtained by generating the projector and basis functions corresponding to neutral F atoms with $r^F_{\text{c}} = 1.8$ bohr and either neutral Ca atoms or doubly charged Ca$^{2+}$ ions with $r^C_{\text{a}} = 2.5$ bohr and 0 values for $V_0^{\text{a}}$ and $V_0^{\text{f}}$. Using a plane-wave cutoff of $|k + G| \leq 10$ bohr$^{-1}$, we obtained results for the cohesive energies differing by 0.01 eV/atom, the equilibrium lattice constants differing by 0.002 Å, and the bulk moduli differing by 0.2 GPa compared with each other and with the results of our previous work. 3 For the body-centered cubic metal Mo, results were obtained using $r^M_{\text{c}} = 1.6$ bohr with $V_0 = 100$ or 500 Ry. Using a plane-wave cutoff of $|k + G| \leq 13$ bohr$^{-1}$, we obtained results for the cohesive energies differing by 0.04 eV, the equilibrium lattice constants differing by 0.002 eV, and the bulk moduli differing by 0.8 GPa for the two different choices of $V_0$.

Calcium molybdate (also known by its mineral name “powellite”) has been studied since the early 1900s for its very interesting luminescence and structural properties. As part of a study of calcium oxide, the electronic structure of this and related materials, 10 we have calculated the density of states for the upper core, valence band, and conduction bands. The CaMoO$_4$ crystal has a tetragonal structure with two formula units (12 atoms) per primitive unit cell. The crystal parameters for the calculation were taken from the experimental neutron analysis. 11 The projector and basis function parameters were similar to those used for our calculations of CaF$_2$ and body-centered cubic Mo, choosing the local potential parameters for Ca and O to be zero and $V_0^{\text{Mo}} = 200$ Ry. (Cal-
cations performed with $V_{0}^{\text{Mo}}=100$ Ry developed ghost states after a few iterations.) The results were obtained using a uniform sampling of the Brillouin zone with three non-equivalent $k$ points with a Gaussian weighting scheme and the plane-wave cutoff of $|k+G|\leq 10$ bohr$^{-1}$. For comparison, we also performed a calculation using the linear combination of atomic orbital (LAPW) method, using the same $k$-point sampling; muffin-tin radii of 2.0, 1.65, and 1.65 bohr for Ca, Mo, and O, respectively; and using the plane-wave cutoff of $|k+G|\leq 6$ bohr$^{-1}$.

For both calculations, $N(E)$ was approximated by a weighted sum of Gaussian functions of width 0.1 eV, centered at each of the energy bands, calculated at the three sampling $k$ points. The results are shown in Fig. 2, with the zero of energy taken at the top of the valence band. What is remarkable about this figure, is that the two results are virtually indistinguishable on both the 66 eV range showing the upper core states and on the 12-eV range showing the bands near the band gap. The fact that two independent calculations can achieve such detailed agreement is a testimony to the accuracy of both methods. Further analysis with a better $k$-point sampling and the inclusion of relativistic effects will be considered elsewhere.\textsuperscript{10}

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**APPENDIX: NUMEROV ALGORITHM FOR SOLVING RADIAL DIFFERENTIAL EQUATIONS**

Equation (10) which we must evaluate numerically can be written as

$$
\frac{d^2\chi(r)}{dr^2} - G(r)\chi(r) = CF(r),
$$

(A1)

where we have suppressed all subscripts and superscripts and defined $F(r) = (2m/\hbar^2)f(r)$ and $G(r) = l(l+1)/r^2 + (2m/\hbar^2)[\nu_{\text{eff}}(r)-\varepsilon]$. The Numerov method\textsuperscript{6} is most easily applied to a uniform discretization of the functions. Letting $\Delta$ denote the radial step size, we can write $\chi_k = \chi(r = k\Delta)$, with $r_n = n\Delta$. It is convenient to replace the continuity of the function and its first derivative boundary condition (11) by requiring that $\chi(k\Delta) = \phi(k\Delta)$ for two consecutive points: $\chi_n = \phi_n$ and $\chi_{n+1} = \phi_{n+1}$. The discretization of Eq. (A1) then becomes a set of $n$ linear equations for $n$ unknowns: $\{\chi_k\}$ for $k=1,\ldots,n-1$ and $C$. These equations can be written in the following matrix form:

\[
\begin{pmatrix}
 b_1 & c_1 & 0 & \cdots & 0 & 0 & -d_1 \\
 a_2 & b_2 & c_2 & \cdots & 0 & 0 & -d_2 \\
 0 & a_3 & b_3 & \cdots & 0 & 0 & -d_3 \\
 \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
 0 & 0 & 0 & \cdots & b_{n-2} & c_{n-2} & -d_{n-2} \\
 0 & 0 & 0 & \cdots & a_{n-1} & b_{n-1} & -d_{n-1} \\
 0 & 0 & 0 & \cdots & a_n & -d_n
\end{pmatrix}
\begin{pmatrix}
 \chi_1 \\
 \chi_2 \\
 \chi_3 \\
 \vdots \\
 \chi_{n-2} \\
 \chi_{n-1} \\
 C
\end{pmatrix}
= \begin{pmatrix}
 0 \\
 0 \\
 0 \\
 \vdots \\
 0 \\
 -c_{n-1}\phi_n \\
 -b_n\phi_n-c_n\phi_{n+1}
\end{pmatrix}.
\]

(A2)

In these equations, the coefficients are defined according to $a_k = 1 - (\Delta^2/12)G_{k-1}$, $b_k = -2 - (10\Delta^2/12)G_k$, $c_k = 1 - (\Delta^2/12)G_{k+1}$, and $d_k = (\Delta^2/12)(F_{k-1} + 10F_k + F_{k+1})$. For $l=1$, some of the coefficients must be corrected for the behavior of the equation at $r=0$: $b_1 \rightarrow b_1 - 1/X$ and $d_1 \rightarrow d_1 - U/X$, where $X = 6[1 + (2m/\hbar^2)[\nu_{\text{eff}}(0) - \varepsilon]\Delta^2/10]$ and $U = (2m/\hbar^2)(\Delta^4/10)\lim_{\Delta \rightarrow 0}[f(r)/r^2]$.

\footnotesize

9. By choosing a larger value of $r_{c}^{\text{Mo}}$ or by relaxing the error tolerance we could have reduced the plane-wave cutoff significantly.