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Complete function projectors for the projector augmented wave (PAW) method of electronic structure calculations.

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Abstract

The Projector Augmented Wave (PAW) method for electronic structure calculations developed by Blöchl [Phys. Rev. B **50**, 17953 (1994)] has been very successfully used for density function studies. It has the numerical advantages of pseudopotential techniques while retaining the physics of all-electron formalisms. In the present paper, we describe a new method, based on the use of a complete set of functions, for generating the set of atom-centered projector and basis functions that are needed for the PAW method. Preliminary results indicate that this "complete function projector" scheme can be easily used to enhance the efficiency of the PAW algorithm for a wide variety of materials throughout the periodic table.

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I. INTRODUCTION

The Projector Augmented Wave (PAW) method of electronic structure calculations, developed by Blöchl [1] and also used by our group [2], is a very powerful method for electronic structure calculations within the framework of density functional theory. [3] In order to use this method, it is necessary to find three types of atom-centered functions – including "projectors", all-electron basis functions, and smooth pseudo basis functions. A number of schemes for constructing these functions have been discussed in the literature [1,2,4]. Our earlier scheme [2] was found to work well for many, but not all materials throughout the periodic table. At the same time, the PAW method has been clearly established as a powerful electronic structure technique, having been used by Blöchl and co-workers [5] and also by our group to study a wide variety of interesting materials problems. In the present paper, we describe a mathematically well-controlled method for generating the projector and basis functions that promises to work very well throughout the periodic table.

The projector functions, as developed by Blöchl [1], are localized functions which should span the space of pseudo wavefunctions in the vicinity of each atom. In the present work, we describe a method for constructing these projectors from a complete set of orthogonal functions.

The formalism is presented in section II and the details are given in the appendix. In section III, we demonstrate the method by calculating the cohesive energy of CaF_2 and of Mo. The method and results are summarized in section IV.

II. FORMALISM

In the notation of references 1 and 2, the functions which are needed for each atomic type a can be denoted $\{\phi_i^a(\mathbf{r}), \tilde{p}_i^a(\mathbf{r}), \tilde{\phi}_i^a(\mathbf{r})\}$ 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 $\{\phi_i^a(\mathbf{r})\}$ having one-electron energies $\{\varepsilon_i^a\}$. The task is then to choose the corresponding projector functions $\{\tilde{p}_i^a(\mathbf{r})\}$ and PS basis functions $\{\tilde{\phi}_i^a(\mathbf{r})\}$, which satisfy a number of conditions. First, in order to accurately transform between the calculated PS wavefunctions and their corresponding AE functions, the projectors should approximately satisfy a generalized completeness condition within each atomic sphere of radius r_c^a:

$$\sum_i |\tilde{\phi}_i^a(\mathbf{r})><\tilde{p}_i^a(\mathbf{r}')| \approx \delta(\mathbf{r}-\mathbf{r}') \text{ for } r, r' \leq r_c^a. \tag{1}$$

These projector functions are assumed to be localized about each atom:

$$\tilde{p}_i^a(\mathbf{r}) = 0 \quad \text{for } r \geq r_c^a. \tag{2}$$

Each PS basis function becomes equal to its corresponding AE basis function outside each atomic sphere:

$$\tilde{\phi}_i^a(\mathbf{r}) = \phi_i^a(\mathbf{r}) \text{ for } r \geq r_c^a. \tag{3}$$

The projector and PS basis functions must satisfy a generalized orthonormality relation [1]:

$$\int d^3r \ \tilde{\phi}_i^a(\mathbf{r})\, \tilde{p}_j^a(\mathbf{r}) \ = \delta_{ij}. \tag{4}$$

In addition, the PS basis functions $\{\tilde{\phi}_i^a(\mathbf{r})\}$ satisfy an atomic PAW Hamiltonian equation of the form [1,2]:

$$(\varepsilon_i^a - \tilde{H}^a)|\tilde{\phi}_i^a> = \sum_j |\tilde{p}_j^a><\tilde{\phi}_j^a|(\varepsilon_i^a - \tilde{H}^a)|\tilde{\phi}_i^a>, \tag{5}$$

where the pseudo-Hamiltonian function $\tilde{H}^a$ has a kinetic energy operator and an effective potential contribution:

$$\tilde{H}^a(\mathbf{r}) \equiv -\frac{\hbar^2}{2m}\nabla^2 + \tilde{v}_{\text{eff}}^a(r). \tag{6}$$

The effective potential $\tilde{v}_{\text{eff}}^a(r)$ 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,

$$\phi_i^a(\mathbf{r}) \equiv \phi_{n_i l_i m_i}^a(\mathbf{r}) \equiv \frac{\phi_{n_i l_i}^a(r)}{r} Y_{l_i m_i}(\hat{\mathbf{r}}). \tag{7}$$

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 attention on the radial functions $\{\phi^a_{nl}(r)\}$, $\{\tilde{\phi}^a_{nl}(r)\}$, and $\{\tilde{p}^a_{nl}(r)\}$. In general, the index n denotes a principal quantum number corresponding to upper core and valence states and can also be used to enumerate continuum functions needed to augment the basis [1,2].

In the present work, we ensure the completeness property (1) by *setting the projectors to be equal to a set of weighted orthogonal functions*. A convenient set of such functions can be derived, for example, from the eigenstates of the Schrödinger equation for the three-dimensional harmonic oscillator:

$$f_{Nl}(r) \equiv \mathcal{N}_{Nl}\, e^{-r^2/\sigma^2} r^{l+1} F(-N, l+\frac{3}{2}, \frac{r^2}{\sigma^2}). \tag{8}$$

Here, the parameter σ is chosen so that $f_{Nl}(r > r^a_c) \approx 0$ within a specified tolerance and the normalization constant $\mathcal{N}_{Nl}$ is defined such that

$$\mathcal{N}^2_{Nl} \int_0^\infty dr\, e^{-r^2/\sigma^2} r^{2l+2} F^2(-N, l+\frac{3}{2}, \frac{r^2}{\sigma^2}) = 1. \tag{9}$$

In these equations, $F(-N, l+\frac{3}{2}, \frac{r^2}{\sigma^2})$ denotes a confluent hypergeometric function, [6] which is a finite polynomial of order N (N = 0,1, etc.) in the variable of (r^2/σ^2). Fig. (1) shows the shape of some of the orthonormal functions $f_{Nl}(r)$.

Our "complete function projector" formalism thus starts by assuming the radial projector functions to be proportional to the orthonormal functions $f_{Nl}(r)$:

$$\tilde{p}^a_{nl}(r) = \mathcal{A}_{nl} f_{(n-n_0)l}(r), \tag{10}$$

where the amplitude $\mathcal{A}_{nl}$ will be evaluated below and where n_0 corresponds to the first of the chosen AE radial basis functions $\phi^a_{n_0 l}(r)$ for a given l. The following recipe then ensures that the atom-centered radial functions $\{\phi^a_{nl}(r)\}$, $\{\tilde{\phi}^a_{nl}(r)\}$, and $\{\tilde{p}^a_{nl}(r)\}$ satisfy the relations 2, 3, 4, and 5.

For each AE radial basis function $\phi^a_{nl}(r)$, we define the corresponding PS radial basis function $\tilde{\phi}^a_{nl}(r)$ according to:

$$\tilde{\phi}^a_{nl}(r) = \sum_{n'} \mathcal{B}^{n'}_{nl} \chi^{n'}_{nl}(r). \tag{11}$$

The indices n and n' enumerate all the (M_l) basis functions needed for the given orbital quantum number l. Typically, $M_l = 1$ or 2. The functions $\chi^{n'}_{nl}(r)$ are defined to be solutions of inhomogeneous differential equations of the form:

$$\left(\varepsilon^a_{nl} - \left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \tilde{v}^a_{\rm eff}(r)\right]\right) \chi^{n'}_{nl}(r) = \mathcal{C}^{n'}_{nl} f_{(n'-n_0)l}(r), \text{ for each } n', \tag{12}$$

with the boundary conditions that all of the $\chi^{n'}_{nl}(r)$ functions are continuous at $r = 0$ and at the atomic sphere radius $r = r^a_c$ they satisfy:

$$\chi^{n'}_{nl}(r^a_c) = \phi^a_{nl}(r^a_c) \text{ and } \frac{d\chi^{n'}_{nl}(r^a_c)}{dr} = \frac{d\phi^a_{nl}(r^a_c)}{dr}, \text{ for each } n'. \tag{13}$$

The differential equation (12) and boundary conditions (13) *uniquely* determine the functions $\chi_{nl}^{n'}(r)$ and the amplitudes $\mathcal{C}_{nl}^{n'}$. A Numerov algorithm [7] for solving these equations is detailed in the Appendix.

Once the solutions $\chi_{nl}^{n'}(r)$ are determined, the M_l expansion coefficients $\mathcal{B}_{nl}^{n'}$ can be calculated from the following linear relations:

$$\begin{array}{c} \sum_{n'} \mathcal{B}_{nl}^{n'} = 1 \\ \sum_{n'} \mathcal{B}_{nl}^{n'} \left[\int_0^\infty dr\ \chi_{nl}^{n'}(r) f_{(n'-n_0)l}(r)\right] = 0 \ \text{ for } \ n' \neq n. \end{array} \tag{14}$$

Finally, amplitude factor $\mathcal{A}_{nl}$ can be calculated in terms of the expansion coefficients $\mathcal{B}_{nl}^{n'}$:

$$\mathcal{A}_{nl} = \frac{1}{\sum_{n'} \mathcal{B}_{nl}^{n'} \left[\int_0^\infty dr\ \chi_{nl}^{n'}(r) f_{(n-n_0)l}(r)\right]}. \tag{15}$$

It can be shown that the projector functions (10) and PS basis functions (11) found in this way satisfy the PAW Hamiltonian equation (5) and also satisfy conditions 2, 3 and 4. The above procedure, solving equations (12,13, 14 and 15), determines the projector and basis function for a fixed value of the effective potential $\tilde{v}_{\rm eff}^a(r)$. In order to derive the optimal functional forms, these equations should be solved self-consistently, since $\tilde{v}_{\rm eff}^a(r)$ depends upon the PS basis functions (11) through the corresponding valence PS density function:

$$\tilde{n}^a(r) = \sum_{nl} w_{nl} \frac{|\tilde{\phi}_{nl}^a(r)|^2}{4\pi r^2}. \tag{16}$$

Here w_{nl} denotes the orbital occupation ($w_{nl} \leq 2(2l+1)$), with the corresponding AE valence density given by:

$$n^a(r) = \sum_{nl} w_{nl} \frac{|\phi_{nl}^a(r)|^2}{4\pi r^2}. \tag{17}$$

In terms of the PS density, the smooth effective potential for the atom is given by [1], [2]:

$$\tilde{v}_{\rm eff}^a(r) = e^2 Q_{00}^a \frac{\mathrm{erf}(r/\sigma)}{r} + e^2 \int d^3r' \frac{\tilde{n}^a(r')}{|\mathbf{r}' - \mathbf{r}|} + \tilde{v}_{\rm loc}^a(r) + \mu_{xc}[\tilde{n}^a(r)], \tag{18}$$

where Q_{00}^a is the effective charge in terms of the atomic number Z^a, the core electron charge $Q_{\rm core}^a$, and a valence density correction term given by:

$$Q_{00}^a = -Z^a + Q_{\rm core}^a + \int_{r \leq r_c^a} d^3r\ [n^a(r) - \tilde{n}^a(r)]. \tag{19}$$

The localized potential term which appears in Eq. (18) is a potential contribution which vanishes for $r > r_c^a$. In the current scheme, the form of $\tilde{v}_{\rm loc}^a(r)$ is arbitrary and can be used to optimize the PAW calculation. We have briefly investigated the form:

$$\tilde{v}_{\rm loc}^a(r) = V_0\, e^{-r^2/\sigma^2}, \tag{20}$$

where V_0 is an adjustable parameter. Preliminary indications are that it is possible to get good results for many materials using $V_0 \equiv 0$. However, since the PAW formulation uses a separable potential it sometimes suffers from the well-documented phenomenon of "ghost" states [8]. For a few systems, we were able to eliminate the ghost state problem by introducing a repulsive localized potential ($V_0 > 0$).

This self-consistent scheme to determine the PS basis functions $\{\tilde{\phi}^a_{nl}(r)\}$ can be thought of as a constrained minimization of the PS energy functional $\tilde{E}$ defined by Blöchl [1]. For each atom, the shape of the projector and basis functions depends on the choice of the matching radius r^a_c, of the Gaussian length parameter σ, and of the form of $\tilde{v}^a_{\rm loc}(r)$. Typically, we choose σ such that $e^{-(r^a_c/\sigma)^2} \leq 10^{-6}$.

III. DEMONSTRATION OF THE COMPLETE FUNCTION PROJECTOR METHOD FOR CAF_2 AND FOR MO

CaF_2 was one of the materials we studied in our previous work [2] where we used a simple scheme to construct the PAW basis functions and projectors. One of the beauties of the PAW method [1] is that the final results are not sensitive to the choice of these functions, so that we are free to choose them on the basis of numerical stability and convenience. The "complete function projector method" allows us to have better control over the convergence of the calculation than was previously possible.

For the electronic structure calculation of CaF_2, using a plane wave expansion to represent the pseudo wavefunctions, the convergence of the calculations is largely controlled by the shapes of the most rapidly varying PS basis functions – namely, $\tilde{\phi}^F_{2p}(r)$ for F and $\tilde{\phi}^{Ca}_{3p}(r)$ for Ca. For this material, good results were obtained without the use of the localized potential term, $V_0 \equiv 0$. Figure (2) shows how these functions vary with r_c. Since the smoother the functional form in real space, the more rapidly convergent the function in reciprocal lattice space, it is apparent that we should choose the atomic radii r_c^F for F and r_c^{Ca} for Ca to be as large as possible, with the constraint that $r_c^F + r_c^{Ca} \leq$ the F-Ca bond length. In the present work, we find the best values are obtained by choosing $r_c^F = 1.8$ bohr and $r_c^{Ca} = 2.5$ bohr.

Figure (3) shows the AE and PS basis functions for F within the atomic radius $r_c^F = 1.8$ bohr. Since there is only one basis function for each l, the corresponding projector functions have the shapes of the $f_{00}(r)$ and $f_{01}(r)$ functions shown in Fig. (1) for the $2s$ and $2p$ states respectively.

For Ca one might wonder whether it is better to construct the atomic functions from the self consistent calculation of the neutral atom (Ca) or of the corresponding ion (Ca^{2+}). In the discussion below, we show that the results are insensitive to this choice. Figure (4) shows the AE and PS basis functions for the upper core states of Ca and Ca^{2+} within the atomic radius $r_c^{Ca} = 2.5$ bohr. The shapes of the functions for the neutral and ionic systems are indistinguishable on this scale. The corresponding projector functions have the shapes of the $f_{00}(r)$ and $f_{01}(r)$ functions shown in Fig. (1) for the $3s$ and $3p$ states respectively. Figure (5) shows the AE and PS basis functions for the valence state of Ca and Ca^{2+} where the differences between the neutral and ionic forms are more apparent. The corresponding projector functions have the shapes of the $f_{10}(r)$, $f_{11}(r)$, and $f_{02}(r)$ functions shown in Fig. (1) for the $4s$, $4p$, and $3d$ states respectively.

The functions constructed in this way are smooth enough so that the band structure calculations can be converged by a plane wave cut-off of $|\mathbf{k} + \mathbf{G}| \leq 10$ bohr^{-1}. This is an improvement over our earlier work for which a cut-off of $|\mathbf{k} + \mathbf{G}| \leq 12$ bohr^{-1} was needed. In Figure (6), the cohesive energy for CaF_2 is plotted versus lattice constant as determined using these F, Ca, and Ca^{2+} basis functions and compared with the results reported in our earlier work using the simple polynomial basis functions [2]. These results were obtained using a uniform sampling of 10 non-equivalent $\mathbf{k}$ points with a Gaussian weighting scheme. [9] As shown in Fig. (6) the results are quite insensitive to the details of these functions. Table I compares the equilibrium properties of CaF_2 obtained by fitting the electronic structure results to the Murnaghan equation of state [10]. The quantitative results of the three calculations are very close, the cohesive energies differing by less than 0.01 eV/atom, the

equilibrium lattice constants differing by less than 0.002 Å, and the bulk moduli differing by less than 0.2 GPa.

Another material we used to test the "complete function projector" method was the body-center cubic (bcc) transition metal molybdenum. As for Ca, it is necessary to include the upper core states as well as valence states for Mo, so that the set of AE and PS basis functions include $4s, 4p, 5s, 5p$, and $4d$ states. In order to test the functions needed for studying other Mo-containing materials, we fixed the atomic radius at the relatively small value of $r_c^{Mo} = 1.6$ bohr. We found that the basis functions constructed with $V_0 = 0$ caused the calculation to develop "ghost" states after a several self-consistency iterations. Gonze and co-workers [8] 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 ($\tilde{H}^{PW}$ in the notation of Blöchl [1]) 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 $\tilde{H}^{PW}$ toward negative values. Therefore, we were motivated to study the effects of introducing a repulsive localized potential (Eq. (20) with $V_0 > 0$) in order to shift the eigenvalue spectrum of $\tilde{H}^{PW}$ to higher energy values. Of course, both the contributions of $\hat{n}$ and of $\tilde{v}_{\rm loc}$ cancel out of in the final result of a well-converged and ghostless calculation. The introduction of $V_0 > 0$ changes the shapes of the basis functions slightly. Figure (7) shows the PS basis functions $\tilde{\phi}_{5s}^{Mo}$ constructed with $r_{c_{\sim}}^a = 1.6$ bohr and $V_0 = 0, 100$, and 500 Ryd. The change in shape for the upper core states $\tilde{\phi}_{4s}^{Mo}$ and$\tilde{\phi}_{4p}^{Mo}$ is much smaller than that shown here. Figure (8) shows the calculated cohesive energy for the bcc crystal of Mo as a function of the assumed lattice constant a_0. These results were obtained using a uniform sampling of 26 non-equivalent $\mathbf{k}$ points with a Gaussian weighting scheme [9] and a plane wave cut-off of $|\mathbf{k} + \mathbf{G}| \leq 13$ bohr^{-1}. [11] The cohesive energy has not been corrected for atomic multiplet structure. While the results for $V_0 = 0$ (or for $V_0 = 50$ Ryd.) could not be obtained due to the ghost states, the results for $V_0 = 100$ Ryd. and $V_0 = 500$ Ryd. are very similar and agree well with results of previous workers. [12] Table II compares the equilibrium properties of bcc Mo obtained by fitting our electronic structure results to the Murnaghan equation of state [10].

IV. DISCUSSION AND CONCLUSIONS

In this paper we have presented and demonstrated a new method for constructing projector and basis functions needed in the PAW formalism of electronic structure calculations. In many ways, the construction of these PAW functions is analogous to the construction of the ionic pseudopotential functions in the pseudopotential formalism [13–17]. In both cases, while the resulting electronic structure should be invariant, the computational effort required to obtain converged results is very strongly dependent on the form of these functions.

The "complete function projector" method constructs the PAW projector functions to be proportional to a complete set of localized functions. The corresponding PS basis functions are determined self-consistently from this assumption together with a number of other conditions. Briefly, the construction procedure consists of the following steps. Starting with a reasonable guess of the effective potential $\tilde{v}^a_{\rm eff}(r)$, we obtain solutions of a set of inhomogeneous differential equations (12) with boundary conditions (13). This determines the auxiliary functions $\chi^{n'}_{nl}$ and enables us to evaluate the coefficients of the set of inhomogeneous linear equations (14), the solution of which determines the expansion coefficients $\mathcal{B}^{n'}_{nl}$. From the $\chi^{n'}_{nl}$ functions and the $\mathcal{B}^{n'}_{nl}$ coefficients, we can then calculate the amplitude factors $\mathcal{A}_{nl}$ according to Eq. (15) which multiply the projector functions according to Eq. (10) and we can also calculate the PS basis functions according to Eq. (11). This procedure is iterated until the effective potential $\tilde{v}^a_{\rm eff}(r)$ used to generate the PS basis functions $\{\tilde{\phi}^a_{nl}(r)\}$ is the same as the effective potential determined from these basis functions. The PS basis functions $\{\tilde{\phi}^a_{nl}(r)\}$ determined in this way are those which minimize a pseudo energy functional $\tilde{E}$ [1] under boundary condition (3) and orthonormality (4) constraints.

The "complete function projector" method was used to generate PAW projector and basis functions for Ca, Ca^{2+}, and F which where then used to calculate the cohesive energy of CaF_2, yielding results which were consistent with each other and with previous results. In addition, the "complete function projector" method was used to generate PAW projector and basis functions for Mo which where then used to calculate the cohesive energy of bcc Mo crystals. In this case, it was necessary to use a repulsive localized potential (20) in order to avoid the appearance of spurious "ghost" solutions to the eigenvalue problem due to its separable form. [8] In addition to the materials discussed here, preliminary evidence indicates that this scheme is easily applicable to materials throughout the periodic table. So far, we have found projector and basis functions for C, O, F, Ca, Fe, and Mo. In addition these indications of its wide applicability, the "complete function projector" construction allows for detailed control over the shape of the basis functions in order to optimize the calculation of a given system. In the present work, we were able to reduce the plane wave cut-off needed for well-converged calculations for CaF_2 from $|\mathbf{k}+\mathbf{G}| \leq 12$ bohr^{-1} to 10 bohr^{-1} and we were able to eliminate the ghost state problem for Mo. It is possible that the present scheme can be further improved by considering other shapes for the localized local potential contribution $\tilde{v}_{\rm loc}(r)$ or perhaps by choosing a different set of complete functions $f_{Nl}(r)$ to define the shape of the projector functions.

While we have demonstrated the feasibility and usefulness of the "complete function projector" construction, further tests are needed to compare it with previous methods described in the literature. The general relationship between the projector and basis functions are defined through Eqs. (2-5). Within this framework, there is still considerable flexibility

in the forms of these functions, as represented by the present and previous construction schemes. The original scheme described by Blöchl [1] is loosely based on the method of constructing norm-conserving pseudopotentials developed by Hamann, Schlüter, and Chiang [13]. In Blöchl's formulation, the shape of an atomic potential related to $\tilde{v}^a_{\rm eff}(r)$ is assumed and the PS basis functions $\tilde{\phi}^a_{nl}(r)$ and the projector functions $\tilde{p}^a_{nl}(r)$ are determined from the equations (2-5) based on that potential form. The localized potential $\tilde{v}^a_{\rm loc}$ is determined by unscreening the assumed atomic potential. This formulation has been successfully used in a large number of simulations [5]. Our earlier scheme [2] is loosely based on the method of constructing norm-conserving pseudopotentials developed by Kerker [14]. In this formulation, the shape of the smooth PS basis function $\tilde{\phi}^a_{nl}(r)$ is assumed while the projector $\tilde{p}^a_{nl}(r)$ and the effective potential $\tilde{v}^a_{\rm eff}(r)$ are determined from Eqs. (2-5). For simplicity, $\tilde{v}^a_{\rm loc}$ has been assumed to be zero. This scheme has been used in a few simulations [2], but for a given atom, the range of r^a_c for which smooth functions can be constructed is somewhat limited. In both of these earlier methods, the functional forms of the projector functions are thus determined by setting the shapes of auxiliary functions, while in the present scheme the functional form of the projector function is controlled directly. The "complete function projector" scheme seems to be a very promising addition to tools of electronic structure calculations.

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APPENDIX: NUMEROV ALGORITHM FOR SOLVING RADIAL DIFFERENTIAL EQUATIONS

The equation that we must evaluate (12) numerically can be written:

$$\frac{d^2\chi(r)}{dr^2} - G(r)\chi(r) = \mathcal{C}F(r), \tag{A1}$$

where we have suppressed all subscripts and superscripts and defined $F(r) \equiv \frac{2m}{\hbar^2}f(r)$ and $G(r) \equiv \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2}\left(\tilde{v}_{\rm eff}(r) - \varepsilon\right)$. The Numerov method [7] is most easily applied to a uniform discretization of the functions. Letting Δ denote the radial step size, we can write $\chi_k \equiv \chi(r = k\Delta)$, with $r_c \equiv n\Delta$. It is convenient to replace the continuity of the function and its first derivative boundary condition (13) 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 equation (A1) then becomes a set of n linear equations for n unknowns: $\{\chi_k$, for $k = 1, 2...n-1\}$ and $\mathcal{C}$. These equations can be written the following matrix form:

$$\begin{pmatrix} b_1 & c_1 & 0 & \dots & 0 & 0 & -d_1 \\ a_2 & b_2 & c_2 & \dots & 0 & 0 & -d_2 \\ 0 & a_3 & b_3 & \dots & 0 & 0 & -d_3 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & b_{n-2} & c_{n-2} & -d_{n-2} \\ 0 & 0 & 0 & \dots & a_{n-1} & b_{n-1} & -d_{n-1} \\ 0 & 0 & 0 & \dots & 0 & a_n & -d_n \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \\ \chi_3 \\ \vdots \\ \chi_{n-2} \\ \chi_{n-1} \\ \mathcal{C} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \\ -c_{n-1}\phi_n \\ -b_n\phi_n - c_n\phi_{n+1} \end{pmatrix}. \tag{A2}$$

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

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TABLES

TABLE I. Comparison of equilibrium cohesive energies, lattice constants, and bulk moduli calculated for crystalline CaF_2 with the PAW method using various projector and basis functions. The labels "Ca" and "Ca^{+2}" refer to results obtained using the "complete function projector" method obtained from neutral and ionic Ca calculations, respectively. The label "previous work" refers Ref. (2).

	Ca	Ca^{2+}	previous work
E_{coh} (eV/atom)	6.36	6.35	6.36
a_0 Å	5.34	5.34	5.34
B (GPa)	101	100	101

TABLE II. Comparison of equilibrium cohesive energies, lattice constants, and bulk moduli calculated for crystalline bcc Mo with the PAW method using Gaussian shaped localized potentials with amplitudes V_0.

	$V_0 = 100$ Ryd.	$V_0 = 500$ Ryd.
E_{coh} (eV/atom)	11.56	11.52
a_0 Å	3.13	3.13
B (GPa)	270	271

FIGURES

FIG. 1. Plots of the projector basis functions defined in Eq. (8) for $\sigma = 1$ and $N = 0$ (solid line), 1 (dashed line), and 2 (dotted line).

FIG. 2. Comparison of PS basis functions constructed with various values of r_c with $V_0 \equiv 0$. Top panel shows F functions $\tilde{\phi}^F_{2p}$ for $r_c = 1.2$, 1.8, 2.0, and 2.5 bohr with the AE function ϕ^F_{2p} included with a thick line for comparison. Bottom panel shows Ca functions $\tilde{\phi}^{Ca}_{3p}$ for $r_c = 1.8$, 2.0, 2.5, and 2.8 bohr with the AE function ϕ^{Ca}_{3p} included with a thick line for comparison.

FIG. 3. Basis functions for F constructed with $r_c = 1.8$ bohr and $V_0 \equiv 0$, including AE basis functions (ϕ_{2s} and ϕ_{2p}; thick lines) and PS basis functions ($\tilde{\phi}_{2s}$ and $\tilde{\phi}_{2p}$; thin lines).

FIG. 4. Basis functions for Ca constructed with $r_c = 2.5$ bohr with $V_0 \equiv 0$, including AE basis functions (ϕ_{3s} and ϕ_{3p}; thick lines) and PS basis functions ($\tilde{\phi}_{3s}$ and $\tilde{\phi}_{3p}$; thin lines). Similar functions constructed from the ion Ca^{2+} are plotted with dashed lines, but are barely distinguishable on this scale.

FIG. 5. Basis functions for Ca constructed with $r_c = 2.5$ bohr with $V_0 \equiv 0$, including AE basis functions (ϕ_{4s}, ϕ_{4p}, and ϕ_{3d}; thick lines) and PS basis functions ($\tilde{\phi}_{4s}$, $\tilde{\phi}_{4p}$, and $\tilde{\phi}_{3d}$; thin lines). Similar functions constructed from the ion Ca^{2+} are plotted with dashed lines.

FIG. 6. Plot of the negative of the cohesive energy of CaF_2 (eV/atom) as a function of cubic lattice constant a_0 (Å) obtained from PAW calculations using projectors functions constructed as described in the present work, compared with previous results reported in Ref. (2). The two curves labeled "Ca" and "Ca^{2+}" refer to the construction of Ca projectors using neutral and ionic Ca calculations, respectively.

FIG. 7. Comparison of PS basis functions for Mo constructed with various values of the local potential amplitude. Plot shows $\tilde{\phi}^{Mo}_{5s}$ constructed using $r_c = 1.6$ bohr and $V_0 = 0, 100$, and 500 Ryd., with the AE function ϕ^{Mo}_{5s} included with a thick line for comparison.

FIG. 8. Plot of the negative of the cohesive energy of bcc Mo (eV/atom) as a function of cubic lattice constant a_0 (Å) obtained from PAW calculations using projectors functions constructed as described in the present work with Gaussian shaped localized potentials with amplitudes $V_0 = 100$ Ryd. and $V_0 = 500$ Ryd.