An efficient procedure for the development of optimized Projector Augmented Wave basis functions

R. J. Snow,1 A. F. Wright,2 and C. Y. Fong1

1Department of Physics, University of California, Davis, California 95616, USA
2Sandia National Laboratories, Albuquerque, New Mexico 87185-1415, USA

(Dated: July 21, 2010)

In the Projector Augmented Wave (PAW) method, a local potential, basis functions, and projector functions form an All-Electron (AE) basis for valence wave functions in the application of Density Functional Theory (DFT). The construction of these potentials, basis functions and projector functions for each element can be complex, and several codes capable of utilizing the PAW method have been otherwise prevented from its use by the lack of PAW basis sets for all atoms. We have developed a procedure that improves the ease and efficiency of construction of PAW basis sets. An evolutionary algorithm is used to optimize PAW basis sets to accurately reproduce scattering properties of the atom and which converge well with respect to the energy cutoff in a planewave basis. We demonstrate the procedure for the case of Ga with the 4s, 4p, and 3d electrons treated as valence. Calculations with this Ga PAW basis set are efficient and reproduce results of linearized augmented plane wave (LAPW) calculations. We also discuss the relationship between total energy convergence with respect to the energy cutoff and the magnitude of the matching radius of the PAW set.

I. INTRODUCTION

The Projector Augmented Wave (PAW) method of Blöchl1 provides an efficient, all-electron (AE) basis for Density Functional Theory2,3 (DFT) calculations within the frozen-core approximation. The method is applicable to all atoms, and the efficient treatment of first-row and transition metal elements compared with norm-conserving pseudopotential methods is improved dramatically.4 The PAW method requires the construction of a local potential, atom-centered radial (pseudo- and AE) basis functions, and projector functions for each atom. For PAW functions highly optimized with regard to computational efficiency, this construction can be complex, including a local potential and multiple sets of basis and projector functions for each angular momentum channel and principal quantum number. To accelerate the construction of these PAW functions, and, further, to optimize with respect to the energy cutoff, we have developed an efficient, partially automated procedure for searching this high-dimensional parameter space.

In section II we introduce the basic elements of the PAW and its associated parameters. Our procedure for obtaining efficient ab initio PAW functions is developed in section III. In section IV results of the construction of the Gallium (Ga) PAW are given including logarithmic derivatives, total energy convergence, optimization results, and lattice constant and bulk modulus calculations. A primary key to obtaining optimal total energy convergence is a large matching radius, and this is shown by the comparison of a series of Ga PAW basis sets with increasing matching radii. A moderate variation of lattice constant with the matching radius parameter is found, and this will be discussed later. PAW basis sets constructed in this way are expected to accurately and efficiently calculate the properties of solids within the DFT framework and the frozen-core approximation.

II. ELEMENTS OF THE PAW CONSTRUCTION

The construction of PAW basis sets5 is similar to the construction of pseudopotentials. First, a reference configuration is chosen and electrons are divided into core and valence electrons. A local potential is created which is smooth within the PAW matching radius $R_{PAW}$ and matches the AE potential at and beyond $R_{PAW}$, as in figure 1. Radial basis functions and dual projector functions used as the basis for electronic wave functions are constructed for each angular momentum channel such that a projection operation of $\tilde{p}$ on a smooth (pseudo) basis function $\tilde{\phi}$ reproduces the AE basis function, $\phi$, as in figure 2. A single basis function per angular momentum channel is often sufficient, but more regularly two functions per channel are required to approach a complete basis set, and in rare cases multiple basis functions in one angular momentum channel but with different principal quantum numbers may also be needed to represent the wave functions of semi-core electrons.

We use the ‘atompaw’ program5 to construct basis sets in an RRKJ (Rappe, Rabe, Kaxiras, and Joannopou-
We discuss further ways that this parameter space can be reduced and efficiently searched.

The matching of logarithmic derivatives of the pseudo- and AE wave functions, evaluated with respect to the radius at $R_{PAW}$, as a function of energy, represents an equivalence of the scattering properties of the PAW basis set and the atom. The matching of logarithmic derivatives over a wide range of energies is one indication of a transferable basis set. In this $ab\ initio$ construction of PAW basis sets, the primary aim is to accurately reproduce logarithmic derivatives, and we do not optimize the sets by the matching of results of calculations with any observable.

Traditionally PAW parameters are chosen by hand, logarithmic derivatives are inspected visually, and post-testing of basis sets for optimal total energy convergence, and eventually for completeness by comparing with other AE results, is done individually for each constructed PAW. This may take many iterations to discover well-matching logarithmic derivatives which are also optimal for total energy convergence. Also, much of parameter space invariably remains unexplored due to its prohibitive size. In this paper we propose an approach to reduce the time and labor associated with producing PAW basis sets and to discover otherwise unobtainable optimized PAWs. In our procedure, first logarithmic derivatives are given a visual inspection to define a limited range of possible construction parameters, thereby reducing the available parameter space significantly. Then an evolutionary algorithm is used to further optimize both the matching of logarithmic derivatives and the total energy convergence of a PAW. In some cases, it is necessary to also optimize with respect to the number of self-consistent iterations.

III. METHOD

The method described in this paper for obtaining an optimized PAW basis set consists of, first, the selection of configurational parameters, including the division of electrons into core and valence electrons and the selection of the basic types of local potentials and basis functions. Next, parameter ranges are reduced through a visual inspection of logarithmic derivative matching and basis function smoothness. Then, an evolutionary algorithm further optimizes the PAW within the reduced parameter space. Lastly, a few tests are performed to ensure the basic accuracy and transferability of the PAW. Further testing of the PAW may be necessary depending on the intended calculation.

Initial parameter ranges can be restricted as follows. A local potential matching radius $R_{PAW}$ should be as large as possible without resulting in sphere overlap in crystalline, molecular, or molecular dynamics calculations, in order to optimize the total energy convergence, as will be discussed in section IV.5. This is usually a little less than half the nearest neighbor distance in a particular system, with room to allow for ionic motion or relax-
ation. In our case, a Troullier-Martins style local potential is used, and the energy parameter often ranges from -2 to 5 Rydbergs, while energy parameters for the RRKJ projector functions have ranges from -2 to 8 Rydbergs. After the local potential matching radius \( R_{PAW} \) is determined, all individual matching radii \( R_{L,i} \) are set equal to this. Then a range for the local potential energy is determined by viewing the logarithmic derivative for the \( L = L_{max} + 1 \) channel. With a suitable local potential energy chosen in this range, energies of the projector functions are varied simultaneously to find regions with good logarithmic derivatives, but with a secondary goal of obtaining smooth basis functions as well. If well-matched logarithmic derivatives are unobtainable with only these energy parameters, either the \( R_{PAW} \) or the \( R_{L,i} \) may then also be altered to improve the logarithmic derivatives. Ranges of parameters which yield well-matched logarithmic derivatives are then used within the optimization program. In the case of Ga, \( E_r \) ranged from 3.0 to 7.0 Rydbergs, \( E_p \) ranged from 0.0 to 7.0 Rydbergs, \( E_d \) ranged from 0.0 to 3.5 Rydbergs, and \( E_{loc} \) ranged from 0.0 to 5.0 Rydbergs, leaving an effective parameter space for Ga of about five million sets.

In order to automate the process of optimizing logarithmic derivatives and total energy convergence, we define fitness scores for both of these properties which will be used in an optimization algorithm. For this purpose a numerical comparison of logarithmic derivatives is evaluated for each potential PAW set, according to the summation, \( \sum_{i} \left( y_{i,AE} - y_{i,PAW} \right)^2 / \left( \exp(-ABS(dy/dx)) \right) \), where in this expression \( y_{i,AE} \) and \( y_{i,PAW} \) are the all-electron and pseudo-wave function logarithmic derivatives as functions of energy, respectively. The purpose of the denominator here is merely to attenuate the effect of the difference between the AE and PAW values near a divergence in the logarithmic derivatives, as can be seen for example in figure 3. Scores for each angular momentum channel are summed and typically normalized by an average ideal matching score.

If logarithmic derivatives are not within a reasonable tolerance (of about 0.3), a penalty factor is given as the fitness score and returned to the optimization routine without further testing. Ghost states\(^{11,12} \) may be detected by the presence of a divergence in the PAW logarithmic derivative where there is none in the AE logarithmic derivative, and this case is given a large penalty factor. If logarithmic derivatives are free of ghost states and the matching of PAW and AE derivatives is within tolerance, crystalline tests at two successive energy cutoffs are performed, and their energy difference, normalized by an ideal difference (about 0.01 Ry), is used as a convergence score. Logarithmic derivative matching is emphasized with stepped weighting, using a factor of 10 for the weight function until within an ideal tolerance (about 0.03) at which point the weight is reduced to 1, equivalent to the weight of the total energy convergence scores. Care must be taken so that the test with large energy cutoff is well-converged, in order to prevent a plateau from forming in the total energy convergence figure as a function of energy cutoff. The Socorro\(^{13} \) DFT program with PAW functionality is used for these tests. The normalized logarithmic derivative and total energy convergence scores are then summed to produce a final fitness score.

The Design Analysis Kit for Optimization and Terascale Applications\(^{14} \) (DAKOTA) offers convenient handling of input parameters, a parallel computation framework, and an interface to several optimization techniques and packages. Comprehensive testing of DAKOTA algorithms for searching PAW parameter space, or perhaps new algorithms, could reduce the time requirements for discovering optimal PAW functions, but we find that the evolutionary algorithm of the coliny package\(^{15} \) is sufficient. In the coliny\(_{ga} \) algorithm, after a random group of initial PAW parameter sets are evaluated, future parameter sets are chosen as combinations of well-scoring sets from the previous iteration. In addition to the crossing of well-scoring parameter sets, random mutations are also applied to original sets and to crossed sets, allowing further exploration into diverse areas in parameter space. In our practice, we typically use the 'two-point' method of crossing with a 'cross-over' rate of 0.9, a mutation rate of 0.25 with the 'offset_cauchy' mutation method, and a population size of 100 and maximum number of iterations anywhere from 3,000 to 25,000, depending upon the number of parameters involved. In the 'two-point' method, optimal parent sets from the current generation are crossed by the division of parent sets into three regions, and the middle section is taken from one parent and the end sections from another parent. In the 'offset_cauchy' method for mutation, a random number is generated according to a cauchy distribution with a mean of 0, and this is added to a selected parameter. Since the optimization with DAKOTA is done with nominal testing, further tests of several of the top scoring PAW basis sets are used to better gauge the total energy convergence and to verify the transferability of the PAW. As a function of total energy cutoff, we look at the lattice constant, bulk modulus, and total energy convergence properties to evaluate PAW basis set optimization.

**IV. RESULTS**

**IV.1. Logarithmic Derivative Matching**

The use of an evolutionary algorithm to optimize the numerical matching of logarithmic derivatives results in most cases with a nearly identical matching of logarithmic derivatives in the associated angular momentum channels, a feat which is possible but painstaking when optimizing by hand. The case of the Ga PAW is shown in figure 3. Additionally, in many cases the matching of logarithmic derivatives can be obtained without the use of matching radii \( R_{L,i} \) as optimization parameters in each angular momentum channel; these can often be set to the local potential matching radius, \( R_{PAW} \). The energy of expansion for a second projector function in each channel
then becomes the primary parameter. This reduces the parameter space significantly and eliminates the problem of kinks in projector functions, saving time both in the preliminary inspection of logarithmic derivatives for the restriction of the parameter ranges and in the DAKOTA optimization.

IV.2. DAKOTA Total Score Optimization

The final score used for a fitness evaluation is a combination of scores from the logarithmic derivative matching and from the total energy convergence, as discussed above in section III. Figure 4 shows the scoring of a typical DAKOTA run of around 5,000 parameter sets for the Ga PAW, using only $E_{L,i}$ with $L=0,1,2$ and $E_{Loc}$ as DAKOTA parameters while keeping all $R_{L,i}$ equal to $R_{PAW}$. If an appropriate normalization for both the logarithmic derivatives and the total energy convergence is used, the fitness score should converge to around 1.0. In this particular optimization, an ideal total energy convergence of 1 mRy was used for normalizing the total energy score, the difference between the 25 Rydberg and 100 Rydberg cutoff calculations. An ideal logarithmic derivative matching of 0.01 was used to normalize the logarithmic derivative score. In this case, the total energy convergence normalization was too ambitious, and the optimal fitness score appears to converge to around 6.15, but the order of magnitude is acceptable. The PAW with the best score, known internally as Ga_Rp2.1et001, GaN with soft N was used in figures 3 and 6 with all matching radii set to 2.1 Bohr, $E_s$ found to be 4.287 Rydbergs, $E_p$ found to be 4.647 Rydbergs, $E_d$ found to be 0.797 Rydbergs, and $E_{loc}$ found to be 2.248 Rydbergs. The standard deviation for the top ten scoring sets are 0.36, 1.79, 0.03, and 0.09 for $E_s$, $E_p$, $E_d$, and $E_{loc}$, respectively.

IV.3. Variability of convergence and completeness of the Ga PAW

Total energy convergence rates and physical properties of PAW sets with the top ten DAKOTA scores in this trial run appear to be nearly identical, as can be seen in figures 5 and 7. This is due partly to a large measure of similarity in parameter values of the optimized PAW sets, but also due to the effectiveness of the PAW method and an insensitivity of calculated properties such as lattice constants to the exact parameters of the construction.

In the evaluation of the lattice parameter for Gallium Nitride (GaN) in the zinc-blende structure, the $R_{PAW}$ parameter for Ga had a noticeable effect on the lattice constant, as can be seen in figure 8 with increasing matching radii leading to smaller lattice constants, but with a total range of only 0.5% in the lattice constant. We have similarly generated a series of N PAW sets with increasing $R_{PAW}$ parameters, but this had negligible effect on the GaN lattice constant.

FIG. 3. (Color online) The AE logarithmic derivatives of the Ga atom and its PAW approximation represent the wave function matching and the scattering properties of the atom. Excellent agreement in all angular momentum channels $L=0,1,2,3$ is shown.

FIG. 4. DAKOTA total score optimization. The best score of each group of 100 parameter sets is plotted on the y-axis. A lower score represents better logarithmic derivative matching and better total energy convergence.

FIG. 5. Total energy convergence rates for the top ten results from a particular run are indistinguishable. Matching radii $R_{L,i}$ and $R_{PAW}$ are all equal to 2.1 Bohr. A soft Nitrogen PAW is used here so that the total energy convergence is determined by the Ga PAW.

FIG. 6. Gallium Total Energy Convergence.
FIG. 6. GaN zinc-blende lattice constants as functions of energy cutoff are indistinguishable. Matching radii $R_{L,i}$ and $R_{PAW}$ are all equal to 2.1 Bohr. A hard Nitrogen PAW is used here so any variation in physical properties should be attributed to Ga PAW differences.

IV.4. Transferability

Transferability in the PAW method is effective due to its AE treatment of wave functions and potentials within the core region, limited only by the completeness of basis functions, and by the inherent limitations of the frozen-core approximation and the DFT. To demonstrate the transferability of the Ga PAW, we have calculated lattice constants and bulk moduli for zinc-blende GaN, zinc-blende GaAs, and zinc-blende GaP. The values calculated in the local density approximation (LDA)\textsuperscript{16}, shown in Table I are within 0.2\% error in the lattice constants in comparison with linearized augmented plane wave (LAPW) values. Bulk moduli are within 1\% error, except for zinc-blende GaP, which differs from LAPW\textsuperscript{17} values by nearly 2\%.

IV.5. $R_{PAW}$ as key to total energy convergence

While the $E_{L,i}$ parameters do affect total energy convergence, the dominant bottleneck parameter is the local potential matching radius, $R_{PAW}$. For a series of PAW basis sets with increasing $R_{PAW}$, figure 9 shows a clear correspondence between the magnitude of the matching radius and the total energy convergence. With a large matching radius, pseudo-basis functions and the local potential can be made smooth and therefore may be expanded in a small number of plane waves. A small amount of overlap of matching radii of atoms in a solid calculation can have negligible effects, but in general the spheres should not overlap, limiting the size of the matching radius and the total energy convergence.

V. CONCLUSION

The procedure described in this paper automates the process of generating optimized PAW basis sets using an
TABLE I. PAW calculations of zinc-blende lattice constants and bulk moduli of GaN, GaAs, and GaP were performed in the LDA with energy cutoffs of 100 Ry (although convergence is expected as in figures 6 and 7). Each of these used a single Ga PAW, Ga\textsubscript{Rp}2.1et0015095.

| Crystal          | PAW ID        | a [Bohr] | B [MBar] | LAPW a [Bohr] | LAPW B [Bohr] | a % error | B % error |
|------------------|---------------|----------|----------|---------------|---------------|-----------|-----------|
| zinc-blende GaN  | N.febsec5953  | 8.439    | 2.03     | 8.447         | 2.05          | -0.09     | -0.9      |
| zinc-blende GaAs | Arsenic\_1058| 10.619   | 0.76     | 10.620        | 0.77          | -0.02     | -0.7      |
| zinc-blende GaP  | P.cen22169    | 10.226   | 0.91     | 10.242        | 0.89          | -0.16     | 1.89      |

\(a\) LAPW data from ‘atompaw’ website\textsuperscript{17}.

An evolutionary algorithm to efficiently search a large parameter space. In the example of the Ga PAW, the resulting PAW matches all-electron scattering properties and is as efficient as the construction method and the particular element permits. Efficiency and efficacy of the PAW was confirmed in a handful of crystalline environments. This method will be of assistance in ongoing efforts to produce efficient PAW sets for various DFT codes.

VI. ACKNOWLEDGEMENTS

We acknowledge many discussions with Natalie Holzwarth and Marc Torrent, as well as for helpful guidance given on the atompaw website\textsuperscript{8}. We would like to thank Alan Tackett, Greg Walker, and Rachael Hansel for an introduction to the DAKOTA program. Brian Adams helped in a critical way with details of the DAKOTA program. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

1. P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
2. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
3. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
4. G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
5. N. A. W. Holzwarth, A. R. Tackett, and G. E. Matthews, Computer Physics Communications 135, 329 (2001), ISSN 0010-4655.
6. M. Y. Chou, Phys. Rev. B 45, 11465 (1992).
7. A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B 41, 1227 (1990).
8. M. Torrent and N. Holzwarth, A user’s guide for atompaw code (2007), http://www.abinit.org/downloads/PAW/AtomPAW2Abinit-Manual-html/atompawUG.pdf.
9. V. Heine, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc, 1970), vol. 24.
10. A. Kiejna, G. Kresse, J. Rogal, A. De Sarlar, K. Reuter, and M. Scheffler, Phys. Rev. B 73, 035404 (2006).
11. X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B 44, 8503 (1991).
12. X. Gonze, P. Käckell, and M. Scheffler, Phys. Rev. B 41, 12264 (1990).
13. Socorro is developed at Sandia National Laboratories and available from http://dft.sandia.gov/Socorro/.
14. M. Eldred, S. Brown, B. Adams, D. Dunlavy, D. Gay, L. Swiler, A. Giunta, W. Hart, J.-P. Watson, J. Eddy, et al., Dakota, a multilevel parallel object-oriented framework for design optimization, parameter estimation, uncertainty quantification, and sensitivity analysis: Version 4.0 users manual (2006), sandia Technical Report SAND2006-6337, Version 4.2, Updated November 2008.
15. W. Hart, The coliny optimization library (2004), http://software.sandia.gov/Acro/Coliny.
16. J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
17. N. Holzwarth et al., atompaw, http://www.wfu.edu/~natalie/papers/pwpaw/man.html.