Systematically improvable optimized atomic basis sets for \textit{ab initio} calculations

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Abstract
We propose a unique scheme to construct fully optimized atomic basis sets for density-functional calculations. The shapes of the radial functions are optimized by minimizing the spillage of the wavefunctions between the atomic orbital calculations and the converged plane wave results for dimer systems. The quality of the bases can be systematically improved by increasing the size of the bases within the same framework. We show that the spillage can describe the convergency of the total energy very well and the cutoff radii of the atomic orbitals are extremely important for the quality of the atomic orbitals. The scheme is easy to implement and very flexible. We have performed extensive tests of this scheme for a wide variety of systems, including semiconductors, oxides, metals, clusters, etc. The results show that the obtained atomic bases are very satisfactory for both accuracy and transferability.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The last few years have seen the development of first-principles methods in the application of complex material systems containing hundreds and even thousands of atoms [1–4]. This has been made possible because of the so-called linear scaling algorithms [5], which take advantage of the locality of the electronic structures [6]. The widely used plane wave basis is not suitable for the linear scaling algorithms because of its extended nature. Instead, the local bases such as atomic orbitals are the better choices.

The advantages of atomic orbitals are twofold. First, the basis size of atomic orbitals is much smaller than other basis sets, such as plane waves or real space mesh, etc. Second, the atomic orbitals are strictly localized and therefore compatible with the linear scaling algorithms [5] for electronic calculations. However, the atomic basis sets must be constructed very carefully to ensure both good accuracy and transferability. Furthermore, the quality of the basis sets should be systematically improvable in an unbiased way.

Several schemes have been proposed [2, 7, 8] to construct atomic orbitals. For example, the atomic orbitals can be constructed by applying certain confinement potentials to the isolated atoms [9, 10]. To ensure the transferability of the orbitals, one could use larger basis set, by using more than one radial function for each angular moment (multi-\(\zeta\)), or by including higher angular moment orbitals (polar orbitals). Empirically, the multi-\(\zeta\) functions can be generated by the split-valence method [7], whereas the polar orbitals can be generated by applying an electric field in addition to the confinement potential. These methods have been demonstrated to be effective [7]. Nevertheless, different levels of orbitals are treated in different ways, and are not guaranteed to be the optimized ones [4]. Volker et al proposed a way to systematically improve the basis so that they chose the one that improves the energy most from a large pool of pre-selected orbitals [2]. Alternatively, Ozaki optimized the shape of atomic orbitals adopted to different environments as part of the self-consistency cycle [8]. However, in this scheme, every atom must have a different orbital shape even for the same element.

In this work, we propose a unique method that allows us to construct systematically improvable fully optimized atomic basis sets for density-functional calculations. Unlike previous methods, all orbitals (including multi-\(\zeta\) and polar orbitals) can be constructed in the same procedure. The shapes of the radial functions are optimized by minimizing the spillage of the wavefunctions between the converged plane wave calculations and those from atomic orbital calculations for dimer systems, and therefore no pre-assumption of the radial functions is needed. The scheme is easy to implement and is very flexible.
and efficient. We have performed extensive tests of this scheme for a wide variety of systems. The results are very promising, showing very satisfactory results for both accuracy and transferability.

The rest of the paper is organized as follows. In section 2 we give a detailed description of our scheme to construct atomic orbitals. We test the obtained orbitals by calculating the structural and electronic properties of a wide variety of systems in section 3, including III–V and group IV semiconductors, and GaN, ZnO, Al, Pb, MgO, etc. We summarize the work in section 4.

2. Methods

One of the most popular ways to generate the atomic orbitals is to use atomic orbitals of isolated atoms in certain confinement potentials. This procedure usually gives the minimal basis set for the atom. To make the basis more complete, one has to use multi-zeta orbitals and polar orbitals. The multi-zeta orbitals can be obtained via a split-valence method [7], whereas the polar orbitals are generated by applying a constant electric field in addition to the confinement potential [7]. Obviously, the orbitals are constructed in very different procedures. The quality of the orbitals is uncontrolled, even though it is usually good. When larger basis sets are needed for high quality calculations, the procedures to get the orbitals are tedious.

We use a very different strategy to construct fully optimized atomic orbitals that are highly transferable. The strategy is based on minimizing the spillage of the wavefunctions between the atomic orbital calculations and the plane wave results. The spillage is a measurement of the difference between the Hilbert space spanned by a set of local orbitals and the space spanned by the ‘exact’ wavefunctions of the interested states of given systems [11, 12]. The spillage is defined as [11],

\[
S = \frac{1}{N_n} \sum_{n=1}^{N_n} |\langle \Psi_n | 1 - \hat{P} | \Psi_n \rangle|,
\]

where \(\Psi_n\) is the plane wave calculated eigenstate and \(N_n\) is the number of states of interest. \(\hat{P}\) is a projector which is spanned by all the atomic orbitals, i.e.

\[
\hat{P} = \sum_{\mu \nu} |\phi_\mu\rangle S_{\mu \nu}^{-1} |\phi_\nu\rangle,
\]

where \(\phi_\mu = \phi_\mu(\mathbf{r} - \mathbf{r}_\mu)\) is the \(\mu\)th local orbital. \(S_{\mu \nu}\) is the overlap matrix between orbitals \(\phi_\mu\) and \(\phi_\nu\), i.e.

\[
S_{\mu \nu} = \langle \phi_\mu | \phi_\nu \rangle.
\]

Here \(\mu = \{a, i, \xi, l, m\}\), in which \(a\) is the element type and \(i\) is the index of the atom of each element type. \(\xi\) is the multiplicity of the radial functions for the angular momentum \(l\), and \(m\) is the magnetic quantum number.

The spillage has been applied to analyze the quality of given atomic basis sets [11–14]. There are also some attempts to choose an optimized local basis for a given system by minimizing the spillage value [11–13]. These methods usually start from certain pre-assumed orbital shapes with a few free parameters. The spillage is then used to determine these parameters. In [12], the authors used the spillage to choose the best Slater-type orbitals or the pseudo-atomic orbitals for a given system. However, the transferability of the atomic orbitals is not taken into consideration. Using a similar idea, Kenny et al took one step further to generate multi-\(\xi\) and polar orbitals [13].

Here we propose a new scheme based on the spillage formulism to generate high quality atomic orbitals that are systematically improvable. Our method improves upon that of previous methods in three aspects: (i) the shape of atomic orbitals can be generated automatically without any pre-assumptions. (ii) The atomic basis can be systematically improved within the same framework. (iii) The transferability of the atomic bases is improved by carefully choosing the reference systems.

2.1. The radial functions

In our scheme, each atomic orbital is written as a radial function multiplied by a spherical harmonic function. The radial functions are expanded into spherical Bessel functions. The \(\mu\)th local orbital is \(\phi_\mu(\mathbf{r}) = f_{\mu,l}(\mathbf{r}) Y_{lm}(\hat{\mathbf{r}})\), where

\[
f_{\mu,l}(\mathbf{r}) = \begin{cases} \sum_q c_{\mu q} j_l(qr), & r < r_c \\ 0, & r \geq r_c. \end{cases}
\]

\(j_l(qr)\) is the spherical Bessel function. \(q\) is chosen to satisfy \(j_l(qr_c) = 0\), where \(r_c\) is the cutoff radius of the radial functions. The atomic orbitals are therefore strictly zero beyond \(r_c\). \(Y_{lm}(\hat{\mathbf{r}})\) is the spherical harmonic function, in which \(l\) is the angular momentum and \(m\) is the magnetic quantum number. The coefficients \(c_{\mu q}\) are chosen to minimize the spillage of the reference systems via a simulated annealing method. We start at a high ‘temperature’ \(T_{\text{max}} = 10^{-3}\) with random coefficients \([c_{\mu q}]\). We change each \(c_{\mu q}\) in order by a small amount \(\Delta c_{\mu q}\), which is randomly generated according to the Cauchy distribution, and calculate the change of the spillage value \(\Delta S\). The change will be accepted according to the acceptance rate,

\[
P = \begin{cases} 1, & \Delta S < 0, \\ e^{-\Delta S}, & \text{otherwise.} \end{cases}
\]

In the simulation, one sweep is defined to consist of a series of attempts on all variables. We find 500–1000 sweeps at each temperature are enough to generate good orbitals. The Cauchy distribution is automatically adjusted in the simulation to ensure the acceptance rate is about 0.2–0.4. We then gradually decrease the temperature by multiplying it by a factor of 0.8, until it reaches \(T_{\text{min}} = 10^{-12}\). The optimal orbitals are the orbitals with minimal spillage in the simulation. Since the first-principles total energy calculations can be performed once for all orbitals in the procedure, the method is very efficient.

We use the same energy cutoff in the plane wave calculations for the spherical Bessel functions. For
pseudopotential calculations, 15–30 spherical Bessel functions are usually good enough to obtain reliable atomic orbitals.

In order to make the kinetic energy integral well defined, one needs to make the second derivative of the atomic orbitals continuous. This can be performed by multiplying the radial part of the atomic orbitals by a smooth function \[ g(r) = 1 - \exp\left[-\frac{(r - r_{\text{cut}})^2}{2\sigma^2}\right]. \] (6)

In our test, we find \( \sigma \) has little influence on the final results, we thus fix \( \sigma = 0.1 \).

In our scheme, we do not have to assume the shape of the atomic orbitals, therefore in principle we can get the fully optimized radial functions.

2.2. Reference systems

One first needs to generate the atomic basis sets for some reference systems, then use them in more general cases, assuming the atomic basis sets are transferable. A good reference system is therefore crucial for generating high quality transferable basis sets. Here, we choose dimer systems as reference systems. The spillage of the system is defined to be the average spillage values of the few selected dimers [2]. We choose several dimers at different bonding lengths, covering the whole dissociate curve of the dimer. If only one dimer is used as the reference, it will leave a fingerprint on the atomic orbitals, therefore worsen their transferability. We find four or five dimers are enough to generate reliable local orbitals. Further increasing the number of dimers in the reference system by as many as 20 does not significantly improve the results. As will be shown in this paper, the atomic basis generated from the dimer systems can be used to calculate different bulk systems with high accuracy, showing remarkable transferability. This is very important for studying complex material systems, which may have complex chemical environments in a single system, including defects, surfaces, alloys etc. However, for some special applications, one can choose the reference systems that are very similar to the system under study to obtain more accurate results.

2.3. Systematically generated atomic orbitals

The quality of the numerical orbital basis set can be systematically improved by increasing the number of radial functions (multi-zeta orbitals) of given angular momentum and by including orbitals with higher angular momentum (polar orbitals). There are several ways in the literature to construct multi-zeta orbitals and polar orbitals. However, there was no systematic way to generate multi-zeta orbitals and polar orbitals, in which all orbitals are treated in an unbiased way [4]. In contrast, in our scheme all orbitals can be generated with the same procedures. To do so, we first generate the orbitals with given angular momentum, which we call level 1 orbitals. The higher level orbitals can be generated using the same procedure, by minimizing the spillage of the remaining Hilbert space, which is orthogonal to the space spanned by all previously generated atomic orbitals. Taking the Si DZP (i.e. double \( \zeta \) functions plus one polar orbital) basis as an example, in the first step, we generate the first \( s \) and \( p \) orbitals, which form a minimal basis set for Si. In the second step, we generate the second \( s \) and \( p \) orbitals (multi-zeta orbitals). We first orthogonalize the wavefunctions of the reference states to the atomic orbitals generated in step 1. Here we define the projector operator formed by level 1 orbitals as

\[ \hat{P}^{(1)} = \sum_{\mu} |\hat{\phi}^{(1)}_{\mu}\rangle S^{-1}_{\mu\nu}|\langle \phi^{(1)}_{\nu}|, \] (7)

where \( \hat{\phi}^{(1)}_{\mu} \) is the \( \mu \)th orbital of level 1 orbitals. The remaining wavefunctions

\[ |\Psi^{(2)}_{n}\rangle = (1 - \hat{P}^{(1)})|\Psi^{(1)}_{n}\rangle, \] (8)

are orthogonal to the atomic orbitals generated at step 1, i.e.

\[ \hat{P}^{(1)}|\Psi^{(2)}_{n}\rangle = 0. \] (9)

We then minimize the spillage between the second \( s \), \( p \) orbitals and the space spanned by \( |\Psi^{(1)}_{n}\rangle \). In step 3, we generate the \( d \) orbitals following exactly the same procedures. The order of the orbitals added into the basis can be determined by choosing the orbitals that decrease the spillage most after the orbitals have been added to the basis. In such a way, we can systematically generate orbitals of any multiplicity and angular momentum in a unified scheme. This is important if high accuracy calculations are needed.

2.4. Optimize the shape

To give an idea of how the obtained radial functions look using the above scheme, we show the radial functions of the first three \( s \), \( p \), \( d \) atomic orbitals in figures 1(a)–(c), respectively, for the carbon atom. The orbitals are obtained by using five carbon dimers of different bond lengths as references. The bond lengths are 1.00, 1.25, 1.50, 2.00, 2.50 Å. The energy cutoff of plane wave basis calculations is set to 100 Ryd. The radius cutoff \( r_c \) is chosen to be 6 au. As we can see, the radial functions of these atomic orbitals have many oscillations. These oscillations are unphysical and may lower the transferability of the atomic basis set. To get rid of the alloying oscillations of the orbitals, we add a procedure to smooth the shape of the radial functions after the spillage minimization, as follows. We define the ‘kinetic energy’ of an atomic orbital as

\[ T_\mu(c_{\mu q}) = \sum_q c_{\mu q}^2 q^2 / 2 + \kappa, \] (10)

where \( q \) satisfy \( j_1(q r_c) = 0 \). \( c_{\mu q} \) are the coefficients of the spherical Bessel functions that normalize the atomic orbitals, i.e. \( \langle \phi_{\mu} | \phi_{\mu} \rangle = 1 \). \( \kappa \) is a penalty function such that

\[ \kappa = \begin{cases} 0, & S/S_0 - 1 < \Delta \\ \infty, & S/S_0 - 1 > \Delta, \end{cases} \] (11)

where \( S_0 \) is the minimal spillage value for the given orbital set and \( S \) is the current spillage value for the given coefficients \( c_{\mu q} \). We found \( \Delta = 0.002–0.005 \) can be sufficient to smooth out the
atomic orbitals. The ‘kinetic energies’ of the atomic orbitals are also minimized via a simulated annealing method similar to the one described in section 2.1. We start the optimization from the orbitals of minimal spillage. The starting temperature is chosen to be $10^{-3}$ of the ‘kinetic energy’ of the initial orbitals, which is gradually lowered to $10^{-2}$ of the maximum temperature. We find 100–200 sweeps at each temperature are enough to smooth the orbitals. After the shape optimization, the final spillage values will be slightly larger than the minimal ones, and will have little influence on the accuracy of these basis sets.

The shape optimized orbitals are plotted in figures 1(d)–(f), for the s, p, d orbitals, respectively, compared to those of unoptimized orbitals. As we see, the alloying oscillations in the original orbitals have been removed, and the shapes of the optimized orbitals are much smoother than the origin ones, which implies a better transferability. We calculate the total energies of the reference dimers using the optimized orbitals and find that they offer the same accuracy for the selected dimers as the origin ones.

3. Results and discussion

In this section, we do intensive tests on the accuracy and transferability of the atomic orbital basis sets generated using the scheme given in section 2 for a wide variety of materials, including covalent, ionic, metallic systems. The lattice constants, bulk modulus, and band structures calculated from the atomic bases are compared to those calculated from plane wave bases. Especially, GaN, ZnO, and Al are known to have several stable structures that are energetically very close to each other, which provide very good tests of the quality of the atomic basis sets.

All the calculations are performed by using density-functional theory [15, 16] (DFT) with the local density approximation (LDA) in the Perdew–Zunger form [17]. Norm conserving pseudopotentials [18] are used in a fully separate form [19]. The periodic boundary condition is used for the solids’ systems, and the integration over the Brillouin zone is replaced by the sum of Monkhorst–Pack $k$–points [20].

3.1. Cutoff radii of orbitals

The range of radial function $r_c$ is one of the most important parameters of the atomic orbitals. Usually larger $r_c$ leads to more accurate results, but at the same time demands more computational time and memory. One needs to choose proper $r_c$ that balance the two factors. For a three-dimensional (3D) solid, the number of neighboring atoms increases very fast as $r_c^3$, so one has to use modest $r_c$, whereas for two-dimensional (2D) and one-dimensional (1D) systems, $r_c$ can be larger. It is also important to balance the errors of different elements in the system [21]. As one shall see below, it is straightforward to use the spillage value as a criterion to choose a proper $r_c$ for each element. Using the silicon diamond structure as an example. An energy cutoff of 50 Ryd and $6 \times 6 \times 6 k$–meshes are used, which are enough to converge the total energies. In
The value of the DZP basis can be as small as 8 eV for Si dimers, if one chose $r_c$ significantly improve the quality of the basis. For example, not lower the spillage too much. However, increasing $r_c$ changes with $r_c$. The spillage values for the two $r_c$ are about $9 \times 10^{-3}$ and $2 \times 10^{-3}$, respectively. Tests on other elements show similar results, which clearly demonstrate that the spillage is an excellent criterion for the quality of the atomic basis set.

In order to further show how $r_c$ affects the spillage, we show in figures 3(a) and (b) the spillage of different basis size changes with $r_c$ for Si and C diamond structures. As we see, if $r_c$ is too small, further increasing the size of the basis does not significantly improve the quality of the basis. For example, for Si dimers, if one chose $r_c = 7$ au, the DZP basis has spillage about $3.5 \times 10^{-3}$; further increasing the basis size does not lower the spillage too much. However, increasing $r_c$ will dramatically decrease the spillage. For $r_c = 12$ au, the spillage value of the DZP basis can be as small as $8 \times 10^{-4}$. Figure 3(b) shows similar results for diamond. As shown in the figure, carbon DZP orbitals with $r_c = 6$ au are as good as DZP orbitals of silicon with $r_c = 8$ au. Therefore one should choose proper basis size for a given $r_c$.

### 3.2. III–V and group IV semiconductors

Semiconductors are a class of important materials. Here we test our atomic bases for III–V and group IV semiconductors. The energy cutoff is chosen to be 50 Ryd and the $k$ points are chosen as $6 \times 6 \times 6$, unless otherwise noted. The results are summarized in table 1. The $r_c$ of Ga, In, Al, As, P, Sb, Ge elements are chosen to be 9 au whereas $r_c$ of silicon and carbon is chosen to be 8 au and 6 au, respectively. We use plane wave basis results as the benchmark (also listed in table 1). We can see that the results from the single-zeta (SZ) basis (the minimal basis) have large deviations for both lattice constants and bulk modulus. SZ basis predicts much larger lattice constants than those calculated from the plane wave basis for more than 0.1–0.2 au and underestimates the bulk modulus by more than 10%. However, a modest size DZP basis always offers good results. The largest difference occurs in Ge, where the deviations of lattice constant and bulk modulus between the DZP and the plane wave basis are 0.07 au and 4 GPa, respectively. We can see systematic improvement over the DZP orbitals when the triple-zeta plus double polarized (TZDP, we also use the notation 3s3p2d) orbitals are used. The obtained results are almost identical to those calculated from plane wave bases. The atomic orbitals generated from a dimer reference system can also achieve such good results for solid systems, showing remarkable transferability.

The band structures of silicon (diamond structure) are shown in figure 4. The lattice constant is fixed at 10.20 au, and the energy cutoff is 50 Ryd. We show the band structures calculated from DZP, TZDP, and 5ZQP (5s5p4d) bases in figures 4(a)–(c), respectively, and compare them with the plane wave results. The black solid lines represent the plane wave results, whereas the blue dotted lines are the results of atomic orbitals. The Fermi level is fixed at 0 eV. From figure 4(a) we can see that the DZP basis already gives very good band structures for the valence bands and the low energy conduction bands, except around the L point. The TZDP basis improves the band structures around the L point, as illustrated in figure 4(b), though there is still a small difference. If we further increase the basis size to 5ZQP, we can see that the energy bands calculated from atomic orbitals are almost identical to those from the plane wave basis.

We also calculate the electronic states of a silicon cluster containing 29 silicon atoms and 38 hydrogen atoms. We calculate the lowest 100 states and plot the density of states.
3.3. GaN, ZnO, Al, MgO, Pb

Now we test our atomic bases for several important materials, including GaN, ZnO, Al, MgO, and Pb. GaN, ZnO, and Al have several stable structures. Zn has 3d electrons as valence electrons, whereas Al is metallic. They thus offer good examples for comprehensive tests on the quality and transferability of the atomic bases.

GaN has two stable crystal structures, namely, the zinc blende structure (B3) and the wurtzite structure (B4). The energy difference between the two structures is very small. The B3 structure has only one structure parameter, i.e. the lattice constant, whereas the B4 structure can be described by three parameters: the lattice constants \(a\), \(c\), and the internal parameter \(u\), which describes the relative position of the two hexagonal close-packed sublattices. The purpose of the test is to see if the atomic basis set can predict correctly the energy difference between the two structures. We use energy cutoff 120 Ryd and the \(6 \times 6 \times 6\) \(k\)-meshes for B3 and \(6 \times 6 \times 4\) for B4. The calculated total energies as functions of volume per atom are shown in figure 6, compared to those calculated from the plane wave basis. Both plane wave and atomic orbital calculations correctly predict that the wurtzite structure is more stable than the zinc blende structure. The total energies are systematically improved from DZP to TZDP. More properties, including structure parameters \((a, c,\) and \(u\)), bulk modulus, and the total energy difference between the two structures, are shown in table 2. We see that the DZP basis already gives very good structure parameters and bulk modulus compared with those calculated from the plane wave basis for both B3 and B4 structures. The TZDP basis further improves all properties. It gives much better bulk modulus than the DZP basis, which reduces the errors from about 10 GPa to less than 1 GPa.
Figure 4. Comparison of the band structures of Si calculated by different atomic bases (blue dotted lines) and the plane wave basis (solid black lines).

Let us see how the current scheme works for systems containing 3d electrons. Zinc is a transition-metal element, which contains 3d electrons. We calculate four structures of ZnO, including rock salt structure (B1), cesium chloride structure (B2), zinc blende structure (B3) and wurtzite structure (B4). The energy cutoff is chosen as 120 Ryd, and we use $6 \times 6 \times 6$ k-meshes for B1, B2, and B3 structures and $6 \times 6 \times 4$ k-meshes for the B4 structure. We define 2s2p1d for O and 2s1p2d for Zn as the DZP basis, whereas we use 3s3p2d for O and 3s2p3d for Zn, as the TZDP basis. The $r_{\text{cut}}$ is 8 au for O and 8 au for Zn. We plot total energies versus volume per atom for these four ZnO structures in figure 7(b) using the DZP basis, compared with the plane wave results shown in figure 7(a). Both bases give the correct energy order for the four structures compared to experiments [22]. As we see, the energy diagrams calculated from the DZP basis shift up for about 0.185 eV/atom relative to the plane wave results. The calculations shows that the structures with decreasing energy order are B2, B1, B3, and B4, and the ground state structure of ZnO is the wurtzite structure.

Table 3 further shows the calculated structure parameters, bulk modulus, and energy differences of ZnO using DZP and TZDP bases in comparison with the plane wave results. Both DZP and TZDP bases give accurate lattice constants. The largest difference is less than 0.02 Å compared to the plane wave results. However, the TZDP basis gives a more accurate bulk modulus for all structures. The energy difference between B3 and B4 structures is also calculated accurately using both bases. The energy of structure B4 is 9 meV/atom lower than that of the structure B3, as calculated by the plane wave basis. DZP and TZDP give exactly the same results. We also show the lattice constant and bulk modulus calculated by the Gaussian basis [22]. We see that the errors due to pseudopotentials and other approximations are bigger than the errors caused by the atomic bases.

Aluminum is a metal system. It is not obvious that the atom-centered atomic basis can describe it well. We test four structures of aluminum, including the simple cubic
Figure 6. Comparison of the total energies of GaN zinc blende structure (B3) and the wurtzite structure (B4) as functions of volume per atom using different atomic bases to those using the plane wave basis.

Table 3. Basis comparison for ZnO rock salt (B1), cesium chloride (B2), zinc blende (B3), and wurtzite (B4) structures. $a$, $c$ (in Å) are the lattice constants, and $c$ (in Å) is the internal parameter. $B$ (in GPa) is the bulk modulus, whereas $\Delta E$ (in eV/atom) is the total energy difference between different structures. The energy difference is set to zero for the B4 structure. The results from Gaussian orbitals and the experimental values are taken from [22].

| Compound | Properties | PW | DZP | TZDP | Gaussian | Experiment |
|----------|------------|----|-----|------|----------|------------|
| ZnO(B1)  | $a$        | 4.286 | 4.296 | 4.296 | 4.218 | 4.271–4.283 |
|          | $B$        | 196  | 198  | 195  | 203  | 177–228    |
|          | $\Delta E$ | 0.068 | 0.066 | 0.058 |      |            |
| ZnO(B2)  | $a$        | 2.653 | 2.659 | 2.658 | 2.614 |           |
|          | $B$        | 194  | 190  | 191  | 201  |           |
|          | $\Delta E$ | 0.639 | 0.647 | 0.620 |      |            |
| ZnO(B3)  | $a$        | 4.583 | 4.596 | 4.595 | 4.509 | 4.62      |
|          | $B$        | 152  | 150  | 151  | 154  |           |
|          | $\Delta E$ | 0.009 | 0.009 | 0.009 |      |            |
| ZnO(B4)  | $a$        | 3.256 | 3.266 | 3.264 | 3.205 | 3.248–3.250 |
|          | $c$        | 5.246 | 5.256 | 5.255 | 5.151 | 5.207–5.210 |
|          | $u$        | 0.381 | 0.381 | 0.381 | 0.381 | 0.382     |
|          | $B$        | 152  | 150  | 151  | 155  | 136–183   |
|          | $\Delta E$ | 0    | 0    | 0    | 0    |            |

(sc) structure, the face-centered cubic (fcc) structure, the body-centered cubic (bcc) structure, and the hexagonal-closed packed (hcp) structure. The energy cutoff is fixed at 70 Ryd, and the $k$ points are chosen as $6 \times 6 \times 6$. Gaussian smearing is used in all calculations. We use DZP (2s2p1d) orbitals for aluminum with $r_c = 9$ au. Figures 8(a) and (b) compare the energy diagrams of the four aluminum structures calculated using the plane wave basis and DZP basis. As we see, the atomic basis provides excellent agreement with the plane wave result for all structures. The fcc structure is the lowest-energy structure of aluminum predicted by both bases. We summarize calculated properties, including lattice constant, bulk modulus, and energy difference between different structures of aluminum in table 4. Surprisingly, we find that the DZP basis can provide extremely good results compared to plane wave calculations [13]. For example, in our calculation, the largest difference of calculated lattice constant is 0.011 Å in bcc structure, whereas the largest difference of bulk modulus is 1 GPa. The DZP basis can also give excellent energy differences between different structures of aluminum.
These results are much better than previous calculations, also using the DZP basis [13]. For example, in [13], the lattice constants’ errors for fcc, hcp, a/c, bcc, and sc are 0.044 Å, 0.054/0.040 Å, 0.037 Å, and 0.013 Å, respectively. The bulk modulus errors for fcc, hcp, bcc, and sc are 4.9 GPa, 8.5 GPa, 5.2 GPa, and 2.9 GPa, respectively, which are much larger than those obtained using our bases.

We also tested the quality of our atomic bases for some other materials, such as MgO, Pb, etc. The results are summarized in Table 5. The energy cutoff was 70 Ryd for MgO and 50 Ryd for Pb. The $k$ points are $6 \times 6 \times 6$. We used 2s2p1d for Mg, O, Pb, $r_e = 8$ au for Mg and O, and $r_e = 9$ au for Pb. When we compared the results with previous calculations using the DZP basis [10], we found that our basis gave much better bulk modulus for Pb than previous calculations.

### 4. Summary

We propose a unique scheme to construct fully optimized atomic basis sets for density-functional calculations. The shape of the radial functions are optimized by minimizing the spillage of the wavefunctions between the atomic orbital calculations and the converged plane wave calculations for dimer systems. Our method improves upon that of previous methods in three aspects: (i) the shape of atomic orbitals can be generated automatically without any pre-assumptions; (ii) the atomic basis can be systematically improved within the same framework; (iii) the transferability of atomic orbital bases is improved by carefully choosing the reference systems. The scheme is easy to implement and very flexible. We have performed extensive tests of this scheme for a wide variety of systems, including semiconductors, ionic, covalent, and metallic materials. The results show that the obtained atomic basis sets are very satisfactory for both accuracy and transferability.

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