First-principles density-functional calculations using localized spherical-wave basis sets

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We present a detailed study of the use of localized spherical-wave basis sets, first introduced in the context of linear-scaling, in first-principles density-functional calculations. Several parameters that control the completeness of this basis set are fully investigated on systems such as molecules and bulk crystalline silicon. We find that the results are in good agreement with those obtained using the extended plane-wave basis set. Since the spherical-wave basis set is accurate, easy to handle, relatively small, and can be systematically improved, we expect it to be of use in other applications.

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I. INTRODUCTION

Localized basis sets such as Gaussians, truncated pseudo-atomic orbitals, real-space grids, B-spline (or “blip”) functions, and wavelets, have been used in first-principles calculations. Recently there has been a surge of activity to investigate linear-scaling methods (where the computational effort and memory requirement scale linearly with the system size), all of which use localized basis sets in their implementations. One localized basis set that was introduced for linear-scaling methods, the spherical-wave basis set, is interesting because while sharing some of the properties (such as the concept of energy cutoff) with the extended plane-wave basis set, it possesses other advantages such as each basis function being fully localized within a sphere. Even though it has been used to implement a linear-scaling method and tested against bulk crystalline silicon, this basis set has not yet been fully investigated. This work serves to reveal the properties of this localized basis set using a matrix diagonalization approach, which frees us from having to consider other sources of error introduced by other cutoffs (such as the density-matrix spatial cutoff). The completeness and appropriateness of this basis set are investigated in first-principles calculations within density-functional theory through applications to molecules and bulk crystalline silicon. The remainder of this work is organized as follows. Section II introduces the spherical-wave basis set. In section III, a brief description is given of the first-principles calculation within density-functional theory using the spherical-wave basis set. Section IV contains the results of calculations on different test systems, which are compared with those obtained using the same theory level and approximations, but with a plane-wave basis set. Section V contains the summary and conclusions.

II. ORIGIN OF THE BASIS SET

The spherical-wave basis functions used in this work are eigenfunctions of the Helmholtz equation

\[(\nabla^2 + q^2)\chi(\mathbf{r}) = 0,\]  

subject to boundary conditions such that the solutions \(\chi(\mathbf{r})\) are nonvanishing only inside a sphere of radius \(R\) and vanishing whenever \(|\mathbf{r}| \geq R\). The eigenfunctions are

\[\chi(r,\theta,\phi) = \begin{cases} 
  j_l(q_{nl}r)Y_{\ell m}(\theta, \phi), & r < R, \\
  0, & r \geq R,
\end{cases}\]

where \((r, \theta, \phi)\) are spherical polar coordinates with origin at the center of the sphere, \(\ell\) is a non-negative integer and \(m\) is an integer satisfying \(-\ell \leq m \leq \ell\). \(j_l(x)\) is the spherical Bessel function of order \(\ell\), and \(Y_{\ell m}(\theta, \phi)\) is a spherical harmonic. The eigenvalue \(q_{nl}\) is determined from the nth zero of \(j_l(x)\) where

\[j_l(q_{nl}R) = 0.\]  

We note that each eigenfunction in Eq. (2) has an energy \(\hbar^2 q_{nl}^2/(2m_e)\), hence it is possible to use the concept of cutoff energy to restrict the number of \(q_{nl}\) in the expansion of a wavefunction.

The real spherical-wave basis functions used in this work are

\[\chi_{\alpha, n\ell m}(\mathbf{r}) = \begin{cases} 
  j_l(q_{\alpha, n\ell l}|\mathbf{r} - \mathbf{R}_\alpha|)Y_{\ell m}(\Omega_{\mathbf{r} - \mathbf{R}_\alpha}), & |\mathbf{r} - \mathbf{R}_\alpha| < r_\alpha, \\
  0, & |\mathbf{r} - \mathbf{R}_\alpha| \geq r_\alpha,
\end{cases}\]

where \(\alpha\) signifies a basis sphere with radius \(r_\alpha\) and centered at \(\mathbf{R}_\alpha\). \(Y_{\ell m}(\theta, \phi)\) are the real linear combinations of the spherical harmonics. By construction, all basis functions within a basis sphere are orthogonal to one another. In general, more than one basis sphere is needed to expand a wavefunction

\[\psi(\mathbf{r}) = \sum_{\alpha, n\ell m} c_{\alpha, n\ell m} \chi_{\alpha, n\ell m}(\mathbf{r}),\]  

where \(c_{\alpha, n\ell m}\) are the associated coefficients. For most systems tested in this work, we have used one basis sphere per atom, where the basis spheres are centered on the atoms. For some systems we have increased the number of basis spheres by placing basis spheres between the atoms. In principle it is possible to use two or more basis spheres of different radii centered on the same atom, but this arrangement has not been studied in this work. We note that even though the basis functions belonging to
different basis spheres are generally nonorthogonal, one of the main advantages of this basis set is that it is possible to analytically evaluate\(^2\) the overlap matrix elements

\[
S_{\alpha,n\ell m;\beta,n'\ell' m'} = \int \! dr \, \chi_{\alpha,n\ell m}(r) \chi_{\beta,n'\ell' m'}(r),
\]

and kinetic energy matrix elements

\[
T_{\alpha,n\ell m;\beta,n'\ell' m'} = -\frac{\hbar^2}{2m_e} \int \! dr \, \chi_{\alpha,n\ell m}(r) \nabla^2 \chi_{\beta,n'\ell' m'}(r).
\]

We also note that the matrix elements for the nonlocal pseudopotentials in the Kleinman-Bylander\(^3\) form can also be evaluated analytically by first expanding the projectors in the spherical-wave basis set.

### III. DENSITY-FUNCTIONAL CALCULATIONS

The Kohn-Sham (KS) equation for an \(M\)-electron system is\(^4\,5\)

\[
\hat{H}\psi_m(r) = \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r) \right] \psi_m(r) = \varepsilon_m \psi_m(r),
\]

where \(\{\psi_m(r)\}\) are the KS eigenfunctions with corresponding eigenvalues \(\{\varepsilon_m\}\). The effective potential \(V_{\text{eff}}(r)\) consists of the classical electrostatic potential, the ionic potential due to the nuclei and the exchange-correlation potential. The effective potential depends on the electron density, \(\rho(r)\), which is formed from the \(M\) lowest eigenstates

\[
\rho(r) = \sum_{m=1}^{M} |\psi_m(r)|^2.
\]

We use the real spherical-wave basis set \(\{\chi_\nu(r)\}\) to expand the \(n\)-th KS eigenstate

\[
\psi_n(r) = \sum_\nu x_{n\nu} \chi_\nu(r),
\]

where \(\nu\) is a collective label for \((\alpha, n\ell m)\) in Eq. \(6\). Substituting Eq. \(6\) into Eq. \(10\), and taking inner products with the \(\{\chi_\mu(r)\}\), we obtain the generalized eigenvalue problem

\[
\sum_\nu ( H_{\mu\nu} - \varepsilon_n S_{\mu\nu} ) x_{n\nu} = 0,
\]

where the overlap matrix is given by

\[
S_{\mu\nu} = \int \! dr \, \chi_\mu(r) \chi_\nu(r),
\]

and the Hamiltonian matrix is given by

\[
H_{\mu\nu} = \int \! dr \, \chi_\mu(r) \hat{H} \chi_\nu(r).
\]

It should be emphasized that when a large system is studied, \(S\) and \(H\) will be sparse. In this case it is more efficient to use an iterative method based on preconditioned conjugate gradient minimization\(^6\) to find the lowest few eigenvalues and corresponding eigenvectors of Eq. \(9\) than to use a direct matrix diagonalization method\(^7\), in which all eigenvalue-eigenvector pairs are found.

The completeness of the basis set depends on several parameters such as the radius of the basis sphere, \(R\); the maximum angular momentum component, \(\ell_{\text{max}}\); and the number of \(q_{n\ell}\) values for each angular momentum component, which we will take here to be the same for all \(\ell\) and is denoted by \(n_q\). The number of basis functions in a basis sphere is \((\ell_{\text{max}} + 1)^2 n_q\). For a fixed number of \(n_q\), we note that the number of basis functions increases very rapidly with respect to \(\ell_{\text{max}}\). However, we will demonstrate that most physical properties can be deduced using only a small \(\ell_{\text{max}}\), which is typically 2. The cutoff energy \(E_c\) for a basis sphere is roughly given by

\[
E_c = \frac{\hbar^2}{2m_e} \left( \frac{n_q \pi}{R} \right)^2.
\]

Periodicity of the system under study is assumed and the \(\Gamma\) point only is used for the Brillouin zone sampling. We have used the local density approximation (LDA) for the exchange and correlation term. Norm-conserving Troullier-Martins\(^8\) pseudopotentials in the Kleinman-Bylander\(^3\) form are used.

### IV. RESULTS OF THE CALCULATIONS

In this section we present and discuss the results obtained from density-functional calculations using the spherical-wave basis set. We study the convergence of the total energy as a function of the cutoff energy, \(E_c\); the radii of the basis spheres, \(R\); the maximum angular momentum component, \(\ell_{\text{max}}\); and the number of basis spheres, \(N_{\text{bs}}\). Physical properties are deduced from total energy calculations on the systems. For molecules, we calculate the equilibrium bond lengths and force constants. For bulk crystalline silicon, we calculate the equilibrium lattice parameter and bulk modulus. These results are compared with those obtained using a plane-wave code\(^9\), and from experiment\(^10\).

In Fig. 1 we plot the total energy of the chlorine molecule with a bond length of 1.6 Å as a function of cutoff energy \(E_c\) and basis sphere radius \(R\). The figure shows that the total energy decreases rapidly as the cutoff energy and the basis sphere radius are increased, which is to be expected from the additional variational freedom that is introduced. Convergence in the total energy is achieved for cutoff energies above 800 eV.

Fig. 2 shows that the rate of convergence of the total energy with respect to the cutoff energy is the same for both the localized spherical-wave and extended plane-wave basis sets. This confirms that the energy cutoff...
and \( \ell \) spherical-wave calculation with 

We note that the “best” result obtained from the 

the total energy with respect to 

lengths as a function of the basis sphere radius 

molecule for a variety of bond 

lengths of 2.4 Å, \( \ell_{\text{max}} = 2 \).

FIG. 1. Total energy of the chlorine molecule with a bond 

length of 1.6 Å. Two basis spheres of radius \( R \) centered on 

the atoms are used. The cubic simulation cell has sides of 

length 12 Å. \( \ell_{\text{max}} = 2 \).

FIG. 2. Nature of the convergence of the total energy of 

the chlorine molecule with a bond length of 1.6 Å. The data 

for the spherical-wave basis set are taken from Fig. 1. The 

respective converged total energies \( E_0 \) are subtracted from 

the total energy \( E \) in each case.

concept can be equally applied in the spherical-wave basis 

set.

Using an energy cutoff above 900 eV, we calculate the 

total energy of the chlorine molecule for a variety of bond 

lengths as a function of the basis sphere radius \( R \). Fig. 3 

shows that the total energy converges exponentially with 

respect to \( R \). We also note that the total energy converges 

slightly faster with respect to \( R \) for molecules with 

smaller bond lengths. This reflects the fact that for a 

given \( R \), the basis set is more complete for a smaller 

molecule than a larger one because the basis spheres are 

closer to one another in the smaller molecule.

Since the total energy also depends on other parame- 

ters such as \( \ell_{\text{max}} \) and the number of basis spheres \( N_{\text{bs}} \), 

we have performed calculations on the chlorine molecule 

with a bond length of 2.4 Å. The results in Fig. 4 show 

the convergence of the total energy of the system as a 

function of \( \ell_{\text{max}} \) for different basis-sphere radii \( R \) and 

numbers of basis spheres \( N_{\text{bs}} \). For the three-basis-sphere cal- 

culations, two basis spheres are centered on the atoms and a 

third basis sphere is centered between the atoms. For each 

spherical-wave calculation, we have used a value of \( n_q \) 

which is the smallest integer such that the cutoff energy exceeds 

900 eV. The horizontal solid line corresponds to the total en-

ergy obtained from the plane-wave calculation with a cutoff 

energy of 900 eV.

which lies 0.023 eV above the plane-wave total energy 

of \(-815.981\) eV. This difference, which is due to the incom- 

pleteness of the spherical-wave basis set, could be 

reduced further by increasing the basis-sphere radius \( R \) and 

\( \ell_{\text{max}} \). However, we are content with this accuracy 

because the error due to the incompleteness of the spherical-

wave basis set is only about 3 \( \times 10^{-5} \) of the total energy 

obtained from the plane-wave calculation. The number of 

spherical-wave basis functions in this case is only 672, 

which is a small fraction (0.6%) of 112452, the number 

of plane waves.

To study the effect of \( N_{\text{bs}} \), \( \ell_{\text{max}} \) and \( R \) on the calcu-

lated physical properties such as the equilibrium bond 

length \( r_e \) and force constant \( f \), we perform a series of 

calculations on the chlorine molecule for a range of bond
FIG. 5. Total energy of the chlorine molecule as a function of the bond length. Two basis spheres of the same radius \( R \) centered on the atoms are used. \( \ell_{\text{max}} = 2 \).

FIG. 6. Total energy of the hydrogen molecule with a bond length of 1.0 Å. Two basis spheres of the same radius \( R \) centered on the atoms are used. \( \ell_{\text{max}} = 2 \). The cubic simulation cell has sides of length 12 Å.

FIG. 7. Total energy of the hydrogen chloride molecule with a bond length of 1.6 Å as a function of the cutoff energy and the basis sphere radius \( R \). Two basis spheres of the same radius \( R \) centered on the atoms are used. The cubic simulation cell has sides of length 12 Å. \( \ell_{\text{max}} = 2 \).

### Table I. Results for the equilibrium bond length \( r_e \) and force constant \( f \). The meanings of \( R \) and \( N_{\text{bs}} \) are explained in the caption of Table II.

| \( N_{\text{bs}} = 2 \) | \( N_{\text{bs}} = 3 \) |
|---|---|
| \( R(\text{Å}) \) | \( r_e(\text{Å}) \), \( \delta r_e(\%) \), \( f(N_{\text{max}}) \), \( \delta f(\%) \) | \( r_e(\text{Å}) \), \( \delta r_e(\%) \), \( f(N_{\text{max}}) \), \( \delta f(\%) \) |
| 2.00 | 1.8941, −3.66, 5.276, 39.2 | 1.9158, −2.56, 4.591, 21.1 |
| 2.50 | 1.9609, −0.26, 3.959, 4.5 | 1.9537, −0.63, 4.017, 6.0 |
| 3.00 | 1.9733, 0.37, 3.754, −0.9 | 1.9636, −0.13, 3.849, 1.6 |
| 3.50 | 1.9769, 0.55, 3.694, −2.5 | 1.9658, −0.02, 3.802, 0.3 |
| 4.00 | 1.9777, 0.59, 3.673, −3.1 | 1.9663, 0.01, 3.789, 0.0 |
| 4.50 | 1.9778, 0.60, 3.670, −3.2 | 1.9663, 0.01, 3.786, −0.1 |

Table II. Values of \( f(N_{\text{max}}) \) for the “mini-basis” calculations with \( \ell_{\text{max}} \) = 1, 2, and 3 are displayed. The results show it is impossible to improve the results simply by enlarging \( R \) when \( \ell_{\text{max}} = 1 \) is used.

Table III. Results of the plane-wave calculations for the bond length of 1.6 Å. The cubic simulation cell has sides of length 12 Å.

Table IV. Values of \( f(N_{\text{max}}) \) for the “mini-basis” calculations with \( \ell_{\text{max}} \) = 2.

In Table II, the values of \( r_e \) and \( f \) converge rapidly with respect to \( R \). However, the results with two basis spheres and \( \ell_{\text{max}} = 1 \) shows that the converged results contain unacceptably large systematic errors. The inclusion of a third sphere reduces the errors significantly because the bonding region between the atoms is described better by the third sphere. The results show it is impossible to improve the results simply by enlarging \( R \) when \( \ell_{\text{max}} = 1 \) is used.

We repeat the calculations for \( r_e \) and \( f \) with \( \ell_{\text{max}} = 2 \), for which the results are presented in Table III. The converged results with \( N_{\text{bs}} = 2 \) and \( \ell_{\text{max}} = 2 \) are better than the converged results with \( N_{\text{bs}} = 3 \) and \( \ell_{\text{max}} = 1 \), which indicates the importance of \( \ell_{\text{max}} \) over \( N_{\text{bs}} \) for the “minimal basis set” calculations. With \( \ell_{\text{max}} = 2 \) and \( N_{\text{bs}} = 2 \), the error of the converged results for \( r_e \) and \( f \) are −0.50% and 13.6% compared to the experimental values, respectively. These accuracies are acceptable within the LDA.

Finally in Table III we present the values of \( r_e \) and \( f \) using two basis spheres centered on the atoms \( \ell_{\text{max}} = 3 \). As expected, the converged values of \( r_e \) and \( f \) agree very well with the plane-wave results. We note that calculations with \( \ell_{\text{max}} = 3 \) are expensive, since the number of basis functions is almost double that for \( \ell_{\text{max}} = 2 \).

Next we calculate the total energy of hydrogen molecule with a bond length of 1.0 Å as a function of the cutoff energy \( E_c \), and the basis sphere radius \( R \), for which the results are displayed in Fig. 4. The total energy converges rather slowly with respect to the cutoff energy because a bare Coulomb potential due to the hydrogen atom is used. Such behavior is also observed in the plane-wave calculations. However, the convergence of energy differences is achieved when the cutoff energy exceeds 800 eV.

We perform a series of total energy calculations on the hydrogen molecule for a range of bond lengths to determine the values of \( r_e \) and \( f \). The results are tabulated in Table IV and show that we can use a value of \( R \) as small as 3.00 Å to obtain an accuracy of less than 1% in \( r_e \) and \( f \) with only two basis spheres. This should be contrasted with the case of the chlorine molecule where with \( N_{\text{bs}} = 2 \), \( \ell_{\text{max}} = 2 \), and \( R = 3.00 \) Å, the values of \( r_e \) and \( f \) agree only fortuitously with the plane-wave results.
We can explain why, to obtain the same accuracy, the chlorine molecule requires a larger $R$ than the hydrogen molecule. The equilibrium bond length of the hydrogen molecule (which is about 0.74 Å) is smaller than the equilibrium bond length of the chlorine molecule (which is about 1.99 Å). The bonding region between the hydrogen atoms is thus described better by the basis functions because the basis spheres are closer to one another. The hydrogen molecule is also “smaller” (in the sense of the extent of the charge distribution) than the chlorine molecule.

In Fig. 7 we show the total energy of the hydrogen chloride molecule with a bond length of 1.60 Å as a function of the cutoff energy and the radius of the basis sphere. The energy differences converge when the cutoff energy exceeds 800 eV. Calculations are performed to obtain $r_e$ and $f$, and the results are tabulated in Table VI.

We repeat the $r_e$ and $f$ calculations for the hydrogen chloride molecule, where the radius of the basis sphere centered on the chlorine atom is fixed at 4.00 Å but the radius of the basis sphere centered on the hydrogen atom is varied. The results are presented in Table VII, which shows that we can use a smaller basis sphere of a radius of 2.0 Å centered on the hydrogen atom to obtain an accuracy of less than 1%. It is thus possible to use different basis spheres depending on the atomic species, which is important because this can reduce the computation time significantly.

![FIG. 8. Total energy of the silane molecule with the Si-H bond length of 1.83 Å. Five basis spheres of the same radius $R$ centered on the atoms are used. The cubic simulation cell has a side length of 12 Å, $\ell_{\text{max}} = 2$.](image)

![FIG. 9. Electronic densities (in units of electrons/Å$^3$) on the plane containing three atoms of the tetrahedral silane molecule with bond lengths of 1.4798 Å. The locations of the atoms are marked by crosses.](image)

![FIG. 10. Electronic densities (in units of electrons/Å$^3$) on the plane containing atoms of the hydrogen chloride molecule with a bond length of 1.2746 Å. The locations of the atoms are marked by crosses.](image)

atom in the hydrogen chloride molecule calculation (c.f. Table VII).

From the pseudo-charge density of the hydrogen chloride molecule (Fig. 9), we observe that the valence electrons are concentrated towards the chlorine atom, as expected from the relative electronegativities of hydrogen and chlorine. This enables us to use a smaller basis sphere centered on the hydrogen atom to obtain accurate results. However, from the pseudo-charge density of the silane (Fig. 10), we observe substantial charge density around the hydrogen atoms, reflecting the fact that hydrogen is more electronegative than silicon. Hence for the silane molecule calculations, the radius of the basis spheres centered on the hydrogen atoms need to be larger than that for hydrogen chloride. These observations lead to the conclusion that the relative electronegativities of neighboring atoms in a calculation should be taken into account when choosing basis sphere radii.

We have chosen bulk crystalline silicon to test the performance of the basis set on an extended system. Fig. 11 shows the total energy per atom for a 64-atom cell of sil-
FIG. 11. Total energy of a 64-atom cell of bulk crystalline silicon with a lattice parameter of 5.43 Å and ℓ_{max} = 2. 64 basis spheres of the same radius R centered on the atoms are used.

icon with a lattice parameter of 5.43 Å as a function of the cutoff energy and R. The total energy converges at a cutoff energy of about 250 eV. The rapid convergence of the total energy with respect to R is evident from the figure.

To determine the equilibrium lattice parameter, a, and the bulk modulus, B, we perform a series of calculations on the bulk silicon system for a range of lattice parameters from 5.31 Å to 5.51 Å. The results of the calculations with ℓ_{max} = 1 and 2 are tabulated in Tables IX and X, respectively. It is found that even with ℓ_{max} = 1, the results with R = 3.20 Å agree quite well with the plane-wave and experiment results. The calculations with ℓ_{max} = 2 improve the results slightly. The reason why ℓ_{max} = 1 calculations give rather good results is because silicon atoms mix the s and p states to form four sp^3 orbitals which are obviously well-described by a basis set with ℓ_{max} = 1.

Finally we present Table XI which shows the numbers of basis functions for the spherical-wave and plane-wave basis set calculations. Since in general the number of spherical-wave basis functions is very small for molecules compared to that of plane-wave basis functions, we conclude that spherical-wave basis sets can be used to study molecules and possibly clusters with high efficiency.

V. CONCLUSIONS

Through detailed calculations on molecules and bulk crystalline silicon, we find that the total energy and physical properties can be accurately deduced from density-functional calculations using localized spherical-wave basis sets. We find that for most purposes, the choice of ℓ_{max} = 2 and atom-centered basis spheres is sufficient to obtain an accuracy which is excellent compared to those obtained using the extended plane-wave basis set.

The dependence of the total energy on the cutoff energy of the localized basis set is found to be rather similar to that of the extended plane-wave basis set. We also find that the results converge exponentially with respect to the basis sphere radius R. The angular incompleteness can be improved either by increasing ℓ_{max}, or by introducing additional basis spheres at strategic locations (such as at the middle of a bond).

We find that the radii of the basis spheres depend on the bond lengths. A large bond length usually means large basis spheres are to be used. We find that it is possible to use different radii for the basis spheres depending on the relative electronegativities of the atomic species. Usually we need to use basis spheres with larger radii for atoms that are more electronegative than other atoms in a calculation.

For the bulk silicon case, the accuracy of the results obtained using ℓ_{max} = 1 is marginally acceptable, which is a consequence of the sp^3 hybridization.

Finally, we note that one of the main advantages of this basis set is that the accuracy of the results can be systematically improved. It would be interesting to explore the possibility of using two or more basis spheres of different radii centered on an atom so that a lower cutoff energy for the larger basis spheres might be used.

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TABLE II. Results for the equilibrium bond length $r_e$ and force constant $f$ of the chlorine molecule with $\ell_{\text{max}} = 1$. When $N_{\text{bs}} = 2$, two basis spheres of the same radius $R$ centered on the atoms are used. When $N_{\text{bs}} = 3$, three basis spheres of the same radius $R$ are used, the third basis sphere being centered between the atoms. The experimental values for $r_e$ and $f$ are 1.9878 Å and 3.23 N/cm, respectively. The plane-wave calculations give values of 1.9661 Å and 3.79 N/cm, respectively, where we have used the same pseudopotentials, Brillouin zone sampling, and cutoff energy.

| $R$ (Å) | $r_e$ (Å) | $\delta r_e$ (%) | $f(\frac{N_{\text{bs}}}{\ell_{\text{max}}})$ | $\delta f$ (%) |
|---------|-----------|-----------------|-----------------|----------------|
| 2.00    | 1.8833    | −4.21           | 5.212           | 37.5           |
| 2.50    | 1.9481    | −0.92           | 4.128           | 8.9            |
| 3.00    | 1.9636    | −0.13           | 3.860           | 1.8            |
| 3.50    | 1.9668    | 0.04            | 3.792           | 0.1            |
| 4.00    | 1.9674    | 0.07            | 3.777           | −0.3           |
| 4.50    | 1.9675    | 0.07            | 3.773           | −0.4           |

TABLE III. Results for the equilibrium bond length $r_e$ and force constant $f$ of the chlorine molecule with $\ell_{\text{max}} = 3$.

| $R$ (Å) | $r_e$ (Å) | $\delta r_e$ (%) | $f(\frac{N_{\text{bs}}}{\ell_{\text{max}}})$ | $\delta f$ (%) |
|---------|-----------|-----------------|-----------------|----------------|
| 2.00    | 0.7476    | −3.05           | 5.998           | 15.4           |
| 2.50    | 0.7643    | −0.88           | 5.420           | 4.3            |
| 3.00    | 0.7695    | −0.21           | 5.237           | 0.8            |
| 3.50    | 0.7709    | −0.03           | 5.193           | −0.1           |
| 4.00    | 0.7710    | −0.01           | 5.178           | −0.4           |

TABLE IV. Results for the equilibrium bond length $r_e$ and force constant $f$ of the hydrogen molecule with $\ell_{\text{max}} = 2$. The meanings of $R$ and $N_{\text{bs}}$ are explained in the caption of Table II. Cut-off energies above 1000 eV are used. The experimental values for $r_e$ and $f$ are 0.7414 Å and 5.75 N/cm, respectively. The equivalent plane-wave calculations give values of 0.7711 Å and 5.197 N/cm, respectively.

| $R$ (Å) | $r_e$ (Å) | $\delta r_e$ (%) | $f(\frac{N_{\text{bs}}}{\ell_{\text{max}}})$ | $\delta f$ (%) |
|---------|-----------|-----------------|-----------------|----------------|
| 2.00    | 0.7476    | −3.05           | 5.998           | 15.4           |
| 2.50    | 0.7643    | −0.88           | 5.420           | 4.3            |
| 3.00    | 0.7695    | −0.21           | 5.237           | 0.8            |
| 3.50    | 0.7709    | −0.03           | 5.193           | −0.1           |
| 4.00    | 0.7710    | −0.01           | 5.178           | −0.4           |
TABLE V. Results for the equilibrium bond length $r_e$ and force constant $f$ of the hydrogen chloride molecule with $\ell_{\text{max}} = 2$. The meanings of $R$ and $N_{\text{bs}}$ are explained in the caption of Table II. For the hydrogen chloride molecule, the experimental values for $r_e$ and $f$ are 1.2746 Å and 5.16 N/cm, respectively. The equivalent plane-wave calculations give values of 1.2948 Å and 5.458 N/cm.

| $R$(Å) | $r_e$(Å) | $\delta r_e$(%) | $f$ (N/cm) | $\delta f$(%) |
|--------|----------|----------------|-------------|---------------|
| 2.00   | 1.2928   | -0.15          | 5.508       | 0.9           |
| 2.50   | 1.2937   | -0.08          | 5.488       | 0.5           |
| 3.00   | 1.2943   | -0.04          | 5.472       | 0.3           |
| 3.50   | 1.2939   | -0.07          | 5.468       | 0.2           |
| 4.00   | 1.2942   | -0.05          | 5.466       | 0.1           |

TABLE VI. Results for $r_e$ and $f$ of the hydrogen chloride molecule. Two basis spheres are used. The radius of the basis sphere centered on the chlorine atom is fixed at 4.00 Å but the radius $R$ of the basis sphere centered on the hydrogen atom is varied.

| $R$(Å) | $r_e$(Å) | $\delta r_e$(%) | $f$ (N/cm) | $\delta f$(%) |
|--------|----------|----------------|-------------|---------------|
| 2.00   | 1.4402   | -3.41          | 14.640      | 28.6          |
| 2.50   | 1.4811   | -0.66          | 12.010      | 5.5           |
| 3.00   | 1.4893   | -0.11          | 11.523      | 1.3           |
| 3.50   | 1.4906   | -0.03          | 11.415      | 0.3           |
| 4.00   | 1.4912   | 0.00           | 11.382      | 0.0           |
| 4.50   | 1.4914   | 0.03           | 11.379      | 0.0           |

TABLE VII. Results for $r_e$ and $f$ of the silane molecule. Five basis spheres of the same radius $R$ centered on the atoms are used. The cubic simulation cell has sides of length 12 Å. $\ell_{\text{max}} = 2$. The experimental value of $r_e$ is 1.4798 Å, while the equivalent plane-wave calculations give the values of 1.4910 Å and 11.38 N/cm for $r_e$ and $f$, respectively.

| $R$(Å) | $r_e$(Å) | $\delta r_e$(%) | $f$ (N/cm) | $\delta f$(%) |
|--------|----------|----------------|-------------|---------------|
| 2.00   | 1.4851   | -0.40          | 11.847      | 4.1           |
| 2.50   | 1.4856   | -0.36          | 11.948      | 5.0           |
| 3.00   | 1.4902   | -0.05          | 11.438      | 0.5           |
| 3.50   | 1.4906   | -0.03          | 11.419      | 0.3           |
| 4.00   | 1.4912   | 0.01           | 11.382      | 0.0           |

TABLE VIII. Results for $r_e$ and $f$ of the silane molecule. Five basis spheres centered on the atoms are used. The radius of the basis sphere centered on the silicon atom is fixed at 4.00 Å but the radius $R$ of basis spheres centered on the hydrogen atoms is varied.
TABLE IX. Results for the equilibrium lattice parameter $a$ and bulk modulus $B$ of the 64-atom bulk crystalline silicon, with $\ell_{\text{max}} = 1$. 64 basis spheres of the same radius $R$ centered on the atoms are used. The experimental values for $a$ and $B$ are 5.43 Å and 100.0 GPa, respectively. The plane-wave calculations, with a cutoff energy of 250 eV, give the results of 5.395 Å and 92.3 GPa, respectively.

$$
\begin{array}{c|cccc}
R(\text{Å}) & a(\text{Å}) & \delta a(\%) & B(\text{GPa}) & \delta B(\%) \\
\hline
2.60 & 5.353 & -0.78 & 139.1 & 50.7 \\
2.80 & 5.413 & 0.33 & 104.5 & 13.2 \\
3.00 & 5.445 & 0.93 & 97.0 & 5.1 \\
3.20 & 5.453 & 1.08 & 89.8 & -2.7 \\
\end{array}
$$

TABLE X. Results for the equilibrium lattice parameter $a$ and bulk modulus $B$ of the 64-atom bulk crystalline silicon, with $\ell_{\text{max}} = 2$. 64 basis spheres of the same radius $R$ centered on the atoms are used.

$$
\begin{array}{c|cccc}
R(\text{Å}) & a(\text{Å}) & \delta a(\%) & B(\text{GPa}) & \delta B(\%) \\
\hline
2.60 & 5.310 & -1.58 & 238.0 & 157.9 \\
2.80 & 5.353 & -0.78 & 129.8 & 40.6 \\
3.00 & 5.377 & -0.33 & 111.4 & 20.7 \\
3.20 & 5.385 & -0.19 & 96.2 & 4.2 \\
\end{array}
$$

TABLE XI. Numbers of the basis functions required so that the agreement between the results for $r_e$ and $f$ (for molecules); and $a$ and $B$ (for bulk silicon) from the spherical-wave and plane-wave basis set calculations is less than 1%. The numbers of the spherical-wave and plane-wave basis functions are denoted by $N_{\text{sw}}$ and $N_{\text{pw}}$, respectively. For the spherical-wave basis set calculations, the choice of atom-centered and $\ell_{\text{max}} = 2$ is used. $E_c$ is the cutoff energy.

$$
\begin{array}{l|ccc}
\text{System} & E_c(\text{eV}) & N_{\text{sw}} & N_{\text{pw}} \\
\hline
\text{Chlorine molecule} & 800 & 234 & 88663 \\
\text{Hydrogen molecule} & 1000 & 270 & 124097 \\
\text{HCl molecule} & 800 & 288 & 88663 \\
\text{Silane molecule} & 800 & 720 & 88663 \\
\text{Bulk silicon} & 250 & 4608 & 10827 \\
\end{array}
$$