Implementing Free-Space Boundary Conditions in a Plane-Wave AIMD Method

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Abstract: An algorithm that can modify an existing pseudopotential plane-wave (PSPW) ab initio molecular dynamics (AIMD) code (e.g. Car-Parrinello) to use free-space boundary conditions, instead of periodic boundary conditions, is described. Equations for representing pseudopotentials and the electron-electron Greens function kernel with free-space boundary conditions are presented and demonstrated to be extremely accurate. Using the atoms and dimers of aluminum and oxygen as examples, it is shown that a modified free-space PSPW code can give total energies that are in good agreement with a regular periodic PSPW code, but also allows for calculations of charged systems. It is also demonstrated that implementing free-space boundary conditions into an existing parallel periodic PSPW code will not significantly degrade its parallel efficiency. In addition, the free-space PSPW code is used to calculate non-trivial charged complexes. Proton binding energies of a series of Group IIIB hexaqua complexes obtained with our free-space PSPW code are shown to agree quite well with standard Gaussian basis set

methods. These results demonstate that free-space PSPW codes can provide accuracy similar to more traditional Gaussian based first principles methods for non-trivial charged complexes.

I. Introduction

In 1985, a breakthrough paper by Car and Parrinello demonstrated that ab initio molecular dynamics (AIMD) was computationally possible[1]. Since that time AIMD calculations have been applied to a variety of realistic systems, offering an alternative to molecular dynamics simulations with empirical potentials. The majority of these calculations have been based on the local-density approximation (LDA) of density-functional theory (DFT)[1,2], although gradient-corrected approximations (GGA) are gaining popularity[3,4] and the feasibility of higher-level ab initio approximations are being investigated[5,6]. In the LDA and GGA calculations the one-electron orbitals are expanded in terms of periodic plane-wave basis sets. Pseudopotentials are introduced to represent the ion-electron interaction and the effects of the core electrons. To treat most systems the plane-wave basis must be very large. However, the Fast Fourier Transform (FFT) algorithm is used to make the calculations manageable. Describing the one-electron orbitals with a periodic plane-wave basis set implies periodic replications of the simulation cell. For non-periodic systems this construction is artificial. For neutral isolated systems, a large simulation cell can be used to make the interactions between periodic images negligible. For isolated molecular systems that are non-neutral or have strong dipoles, corrections are required to remove the artificial forces generated by the periodic images[7,8]. Furthermore, comparison of energies for systems having different charges, such as might arise in models of acid/base and redox reactions, necessarily involves an unphysical neutralizing charge, as the lattice energy of a charged system is not defined.

In this article, we detail an algorithm that can be used to modify an existing pseudopotential plane-wave (PSPW) code so that free-space boundary conditions are used instead of periodic boundary conditions. This algorithm is thus applicable to the calculation of isolated molecular and cluster systems. Although parts of this algorithm have been presented[8-10], to our knowledge previous presentations have either been incomplete or they have presented an algorithm that does not provide the required accuracy. Secondly, we present equations for accurately representing pseudopotentials and the electron-electron Greens function kernel, even when the simulations are in irregular shaped boxes. We also discuss the issues involved with implementing this algorithm on large MPP machines.

II. Implementing Free-Space Boundary Conditions into PSPW Calculations

The total energy of a system of nuclei and electrons in DFT may be written[11]:

$$(1)\quad E[\rho] = T_S[\rho] + \int V_{ion}(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r} + \tfrac{1}{2}\iint \rho(\mathbf{r})g(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' + E_{xc}[\rho] + E_{ion-ion}[\{\mathbf{R}_I\}]$$

This energy contains five terms, the Kohn-Sham kinetic energy ($T_s[\rho]$), the ion-electron energy, the electron-electron energy, the exchange-correlation energy ($E_{xc}[\rho]$), and the ion-ion energy. The density is given by

$$(2)\quad \rho(\mathbf{r}) = \sum_{i} \sum_{\sigma=\pm\frac{1}{2}} \left|\psi_{i,\sigma}(\mathbf{r})\right|^2$$

In this equation i labels the orbital number, and σ labels the spin. To make the PSPW approximation to these DFT equations, one expands the one-electron orbitals in terms of a discrete plane-wave basis set

$$(3)\quad \psi_{i,\sigma}(\mathbf{r}) = \sum_{\mathbf{G}} C_{i,\mathbf{G}}\ \mathrm{e}^{[i\mathbf{G}\bullet\mathbf{r}]}$$

where the reciprocal lattice vectors, **G,** are defined with respect to a defined lattice vectors, $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, and their corresponding reciprocal lattice vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ as

$$(4)\quad \begin{aligned} &\mathbf{G} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3, \qquad \mathrm{k}_1, \mathrm{k}_2, \mathrm{k}_3 = 0, \pm1, \pm2, \ldots \\ &\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{i,j} \end{aligned}$$

and replaces the ion-electron potential, $V_{ion}(\mathbf{r})$, with non-local pseudopotentials[1].

$$(5)\quad \begin{aligned} &V_{ion}(\mathbf{r}) \rightarrow W_{ion}(\mathbf{r}, \mathbf{r}') = \sum_{I} w^{psp}(\mathbf{r} - \mathbf{R}_I, \mathbf{r}' - \mathbf{R}_I) \\ &w^{psp}(\mathbf{r}, \mathbf{r}') = \sum_{l=0}^{\mathrm{lmax}} \sum_{m=-l}^{l} Y_{l,m}(\hat{\mathbf{r}}) \left[v_l(|\mathbf{r}|)\delta(|\mathbf{r}| - |\mathbf{r}'|) \right] Y_{l,m}^{*}(\hat{\mathbf{r}}') \end{aligned}$$

where I labels the atom number, and indices l and m represent the angular projections. The exact forms of the energy in PSPW DFT calculations and their implementation using Fast Fourier Transforms (FFT) can be found in several places[13-15], and will not be repeated here.

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[1] We note that external potentials that are non-local are not explicitly considered in the Hohnberg-Kohn theorem[12]. However, since the external non-local potential is fixed, the total energy of the system can still be considered as a functional of only the density.

To implement free-space boundary conditions into a PSPW DFT calculation only the Coulombic interaction terms need to be modified. In the LDA and GGA calculations both the Kohn-Sham kinetic energy $T_s[\rho]$ and exchange-correlation energy $E_{xc}[\rho]$ are basically local operators in real-space and hence do not contain interactions between neighboring supercells. This is true because the density decays to zero at the supercell edges in PSPW DFT calculations of isolated clusters and molecules.

Since we are interested in an isolated system the ion-ion Coulomb energy is written simply as:

$$(6)\quad E_{ion-ion} = \tfrac{1}{2}\sum_I \sum_J \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

rather than as an Ewald summation used in typical PSPW DFT calculations. In this equation I and J label the ions, and Z_I and Z_J label the ion valence charges.

The ion-electron Coulomb energy, within the pseudopotential approximation, can be written as

$$E_{ion-electron} = \int_V \left[V_{local}(\mathbf{r})n(\mathbf{r})\right]d\mathbf{r} + \sum_i \iint_V \left[\psi_i(\mathbf{r})W(\mathbf{r},\mathbf{r}')\psi_i(\mathbf{r}')\right]d\mathbf{r}d\mathbf{r}'$$

$$(7)\quad V_{local}(\mathbf{r}) = \sum_I (-Z_I)\frac{\mathrm{erf}\left(\alpha_I\,|\mathbf{r}-\mathbf{R}_I|\right)}{|\mathbf{r}-\mathbf{R}_I|}$$

$\alpha_I =$ small constant

where $V_{local}(\mathbf{r})$ is the local part of the pseudopotential, and $W_{nonlocal}(\mathbf{r},\mathbf{r})$ is the non-local part of the pseudopotential, corrected for the assumed form of the local potential in Eq. 7. Eq. 7 is presented in this form so that the long-range behavior of the ion-electron interaction is completely contained within the local part of the pseudopotential. In this form, the non-local part of the pseudopotential only interacts around the localized region of each atom, making it a local operator. Just as with the kinetic energy and exchange-correlation terms the integration involving the non-local pseudopotential in Eq. 7 does not have to be changed from a typical periodic PSPW DFT calculation.

The rest of the ion-electron Coulomb energy will obey free-space boundary conditions if the integration is simply restricted to one isolated supercell (V−>) rather than an infinite collection of supercells in periodic boundary conditions. This integration must be done carefully to prevent significant numerical errors from being introduced. We have found that sufficiently high accuracy can be obtained by integrating this integral in real space using the extended midpoint trapezoidal rule

$$\begin{aligned}
&\int_{\Omega} V_{local}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \approx \sum_{i}\sum_{j}\sum_{k} V_{local}\left(\mathbf{r}_{i,j,k}\right)\rho\left(\mathbf{r}_{i,j,k}\right)h^{3} \\
&\mathbf{r}_{i,j,k} = \frac{i}{N_1} * \mathbf{a_1} + \frac{j}{N_2} * \mathbf{a_2} + \frac{k}{N_3} * \mathbf{a_3} \\
&i = 0,1,2,\ldots,(N_1 - 1) \\
&j = 0,1,2,\ldots,(N_2 - 1) \\
&k = 0,1,2,\ldots,(N_3 - 1)
\end{aligned} \tag{8}$$

provided that the decay of the Gaussian charge potentials are sufficiently smooth, i.e. α_I is chosen small enough. In Eq. 8 N_1, N_2, and N_3 are the sizes of the first, second and third FFT dimensions respectively, and h^3 is the constant volume of subintervals defined by the volume of the supercell (Ω) divided by the number of FFT grid points ($N_1 * N_2 * N_3$). The accuracy of this integration clearly depends on the choice of α_I inV_{local}(**r**). Nevertheless, choosing V_{local}(**r**) is somewhat arbitrary and other atom based potentials can be used, so long as they decay as $Z_I/|\mathbf{r}-\mathbf{R}_I|$ and they are sufficiently smooth for real-space integration.

The remaining Coulomb interaction terms that need to be modified are the electron-electron energy and the Hartree potential, given by

$$
\begin{aligned}
&E_{electron-electron} = \iint \rho(\mathbf{r}) g(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \\
(9)\quad &V_H(\mathbf{r}) = \int g(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}' \\
&g(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}
$$

Again as with the other Coulomb interactions, free-space boundary conditions restricts the integration to one isolated supercell.

$$
(10)\quad
\begin{aligned}
&E_{electron-electron} = \int_\Omega\int_\Omega \rho(\mathbf{r}) g(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \\
&V_H(\mathbf{r}) = \int_\Omega g(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'
\end{aligned}
$$

This effectively defines a modified coulomb interaction

$$
(11)\quad g(\mathbf{r},\mathbf{r}') = \begin{cases} \dfrac{1}{|\mathbf{r}-\mathbf{r}'|} & \text{for } \mathbf{r},\mathbf{r}' \in \Omega \\ 0 & \text{otherwise} \end{cases}
$$

Hockney and Eastwood showed that an interaction of the form of Eq. 11 could still be used in conjunction with the Fast-Fourier Transform convolution theorem[16-18]. In their algorithm, the interaction between neighboring supercells is removed by padding the density with an external region of zero density, or in the specific case of a density defined in cubic supercell of length L, the density is extended to a cubic supercell of length 2L, where the original density is defined as before on the $[0,L]^3$ domain and the remainder of the $[0,2L]^3$ domain is set to zero. The grid is 8 times larger than the conventional grid. The Coulomb potential is calculated by convoluting the density with the Green's function kernel on the extended grid. The density on the extended grid is defined by expanding the conventional grid to the extended grid and putting zeros where the conventional grid is not defined. After the aperiodic convolution, the free-space potential is obtained by restricting the extended grid to the conventional grid.

In his original work Hockney suggested that the cutoff Coulomb kernel could be defined by[16]

$$(12)\quad g\left(\mathbf{r}_{i,j,k}\right)=\begin{cases}\dfrac{\text{constant}}{h} & \text{for } \left|\mathbf{r}_{i,j,k}\right| = 0\\ \dfrac{1}{\left|\mathbf{r}_{i,j,k}\right|} & \text{otherwise}\end{cases}$$

where h^3 is the constant volume of subintervals, defined by the unit cell divided by the number of conventional FFT grid points. Hockney suggested a constant at $|\mathbf{r}|=0$ to be between 1 and 3. Barnett *et al* in their implementation defined the constant to be [9]

$$(13)\quad \frac{1}{h^2}\int_{h^3}\frac{1}{|\mathbf{r}|}d\mathbf{r} \approx \begin{cases}2.380077 & \text{for SC lattice}\\ 0.910123 & \text{for FCC lattice}\\ 1.447944 & \text{for BCC lattice}\end{cases}$$

Regardless of the choice of the constant, the singular nature of g($\mathbf{r}$) in real-space can lead to significant numerical error (see Figure 1). James addressed this problem somewhat by expanding the Coulomb kernel to higher orders in real space[19].

The convolution theorem suggests that defining g($\mathbf{r}$) in reciprocal space will lead to a much higher accuracy. A straightforward definition in reciprocal space is

$$(14)\quad g(\mathbf{r}) = \sum_{\mathbf{G}} g_{uniform}(\mathbf{G})\mathrm{e}^{i\mathbf{G}\bullet\mathbf{r}}$$

$$g_{uniform}(\mathbf{G}) = \frac{1}{h^3}\int_{\Omega'} \frac{e^{\left(-i\frac{\mathbf{G}\bullet\mathbf{r}}{2}\right)}}{|\mathbf{r}|}d\mathbf{r}$$

where Ω’ is the volume of the extended unit cell and h^3 is the volume of the unit cell divided by the number of conventional FFT grid points. The reciprocal space definition gains accuracy because the singularity at **r**=**r**’ in Eq. 9 is analytically integrated out. Even when Eq. 14 is used to define the kernel, a slight inexactness in the calculated electron-electron Coulomb energy will always present due to the discontinuity introduced in the definition of the extended density where the extended density is forced to be zero in the extended region outside of Ω. However, this discontinuity is small, since the densities we are interested in decay to zero within Ω, thus making the finite Fourier expansion of the extended densities extremely close to zero in extended region outside of Ω.

Equation 14 could be calculated numerically, however we have found that alternative definitions can be used with little loss of numerical accuracy. In our earlier work in which the charged isomers of C_{20} were calculated, we suggested that the cutoff Coulomb kernel could be defined as 10

$$g(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} g_a(\mathbf{G})\,\mathrm{e}^{(\mathrm{i}\,\mathbf{G}\bullet\mathbf{r})} & \text{for } |\mathbf{r}| \leq R_{\max} - \delta \\ \dfrac{1}{|\mathbf{r}|} & \text{otherwise} \end{cases}$$

$$g_a(\mathbf{G}) = \begin{cases} \dfrac{2\pi(R_{\max})^2}{h^3} & \text{for } |\mathbf{G}| = 0 \\ \dfrac{4\pi}{h^3\,|\mathbf{G}|^2}\left[1 - \cos(|\mathbf{G}|^2\ R_{\max})\right] & \text{otherwise} \end{cases}$$

$$(15)\quad R_{\max} = \begin{array}{l} L,\ \text{(simple cubic)} \\ \dfrac{\sqrt{2}}{2}L,\ \text{(face - centered cubic)} \\ \dfrac{\sqrt{3}}{2}L\ \ \text{(body - centered cubic)} \end{array}$$

$$\delta\ =\ \text{small constant}$$

Figure 1 demonstrates that the error in calculating the electron-electron Coulomb energy can be made very small when Eq. 15 is used to define the kernel. A similar kernel has been more recently suggested by Jarvis *et al*[8]

$$g(\mathbf{r}) = \sum_{\mathbf{G}} g(\mathbf{G})\,\mathrm{e}^{(\mathrm{i}\,\mathbf{G}\bullet\mathbf{r})}$$

$$g_a(\mathbf{G}) = \begin{cases} \dfrac{2\pi(R_{\max})^2}{h^3} & \text{for } |\mathbf{G}| = 0 \\ \dfrac{4\pi}{h^3\,|\mathbf{G}|^2}\left[1 - \cos(|\mathbf{G}|^2\ R_{\max})\right] & \text{otherwise} \end{cases}$$

(16)

$$R_{\max} = \sqrt{3}L\ \text{(simple cubic)}$$

The kernel in Eq. 15 is more correct near the box edges than Eq. 16. However, it is also evident that other forms could also be used. The Fourier-represented kernels improve the integration accuracy by removing the singularity at |**r**-**r’**| in a trapezoidal integration. A disadvantage of the kernels defined by Eqs. 15-16 is that only regular shaped cells can be used. To extend this method to irregular shaped cells, a short and long range decomposition similar to what we used with pseudopotentials can be used

$$g(\mathbf{r}) = g_{short-range}(\mathbf{r}) + g_{long-range}(\mathbf{r})$$

$$g_{short-range}(\mathbf{r}) = \sum_{\mathbf{G}} g_{short-range}(\mathbf{G}) e^{(i\mathbf{G}\bullet\mathbf{r})}$$

$$(17)\quad g_{short-range}(\mathbf{G}) = \begin{cases} \dfrac{4\pi}{h^3\,|\mathbf{G}|^2}\left[1-\exp\left(\dfrac{-|\mathbf{G}|^2}{4\varepsilon^2}\right)\right] & \text{for } |\mathbf{G}| \neq 0 \\ \dfrac{\pi}{h^3\varepsilon^2} & \text{for } |\mathbf{G}| = 0 \end{cases}$$

$$g_{long-range}(\mathbf{r}) = \begin{cases} \dfrac{\operatorname{erf}(\varepsilon|\mathbf{r}|)}{|\mathbf{r}|} & \text{for } |\mathbf{r}| \neq 0 \\ \dfrac{2\varepsilon}{\sqrt{\pi}} & \text{for } |\mathbf{r}| = 0 \end{cases}$$

We have found that this kernel gives very high accuracy, even for highly non-cubic supercells. Other kernel definitions are possible. Kawai, in his PSPW codes uses a short and long range decomposition based on a Lorentzian[20].

III. Accuracy of the Free-Space Algorithm

The free-space algorithm presented in the preceding section is an improvement over other reported implementations because it is extremely accurate. A necessary (but not sufficient) test of the free space algorithm is that, for a neutral centrosymmetric system, the total energies produced from a modified free-space PSPW code and a regular periodic PSPW code should be nearly the same.

To demonstrate this accuracy, we present in Table I total energies obtained from a regular periodic PSPW code and a modified free-space PSPW code for atoms and dimers of aluminum and oxygen. In these calculations the ion-electron energy parameters used to define the local pseudopotential were chosen to be $\alpha=1/1.65\ a_0^{-1}$ for Al and $\alpha=1/0.7\ a_0^{-1}$ O. Eq. 17 was used to represent the Coulomb kernel with $\varepsilon=1.0\ a_0^{-1}$. The ability to get the same energies with these two different codes represents an important improvement for PSPW algorithms because it allows systems calculated with a modified free-space code to be directly compared to periodic systems such as slabs or bulk solids calculated with a conventional periodic PSPW code.

IV. Parallel Performance of a Free-Space PSPW Code

The cost of typical PSPW calculations, as well as their inherent parallelism, makes them suitable for running on parallel computers. As a result most PSPW codes in use today are parallel codes. These codes are usually parallelized in two different ways. One way is to distribute the one-electron orbitals across processors[21], and the other is to do a spatial decomposition[22]. The free-space algorithm can be implemented in either scheme. However, the additional costs associated with calculating the electron-electron energy and its associated Hartree potential are difficult to make parallel efficient. This is especially true when parallelism is done via distributing one-electron orbitals in a straightforward way, because the extra computations associated with calculating the Hartree potential must be done sequentially. On the other hand, the extra computations in a spatial decomposition algorithm do not have to be done sequentially. Nevertheless, parallel efficiency is difficult to obtain, because the majority of time spent in calculating Hartree potentials is in calculating fast-Fourier transforms on the extended grid, and spatially decomposed fast Fourier transforms are hard to parallelize.

In Table II the parallel performance of a regular periodic PSPW code and a modified free-space PSPW code are shown. Both of these codes are written in Fortran 77 and MPI, and are parallelized using a spatial decomposition algorithm. The required parallel Fast Fourier Transform was implemented using a slab decomposition of the 3-dimensional space.

V. Hexaqua Complexes of Al^{3+}, Ga^{3+}, and In^{3+}: Comparison of PSPW and Gaussian Basis Set Calculations

There are several contexts in which it is desirable to move smoothly between molecular systems and periodic systems (such as slabs or bulk solids). For example, it has been previously demonstrated that the first hydrolysis constant of a variety of aqueous metal ions correlates well with the gas-phase deprotonation energy for some trivalent hexaaquo complexes using Gaussian based DFT methods[23]. Such a correlation serves as an excellent validation of the particular combination of methods used, and would provide a convincing basis for understanding the much more complex hydrolysis reactions occurring on the surface functional groups of the analogous metal oxide minerals. It is well known that Gaussian-based methods have very different basis set requirements for gas and solid phase applications [24], complicating the transferability of these methods. PSPW methods, on the other hand, have been shown to work quite well on some of the oxyhydroxide minerals of interest[25], and have been recently applied to aqueous metal complexes [26-28]. It is therefore of interest to test whether the PSPW methods are capable of reproducing the gas-phase deprotonation energy vs. solution pK_{11} observed in reference[23]. The efficacy of molecular-solid state transferability will be crucial in the investigation of oxide interfaces, which share both molecular and solid state characteristics.

An additional aspect of the accuracy of the PSPW method is, of course, in the choice of pseudopotential. Reliable pseudopotentials do not exist for the transition metal ions, which comprise the bulk of the study in reference[23]. To avoid complications due to the pseudopotential and focus on the implementation of the free-space PSPW code, we have restricted our calculations to Al^{3+}, Ga^{3+}, and In^{3+} hexaaqua species. The extent to which the free-space PSPW method can reproduce the results of the Gaussian based calculations is a stringent test of the accuracy of the method.

The free-space PSPW electronic structure calculations for the hexaaqua and hydroxopentaaquo complexes were carried out using Hamann norm-conserving pseudopotentials[29] in Kleinman-Bylander seperable form[30], and a plane-wave basis set with a kinetic energy cutoff of 60 Ry and a 26 a.u. simple cubic supercell. The lattice constant was chosen to be sufficiently large so as to ensure that the density decayed to zero by the supercell edges. Here only the local density approximation (LDA) parameterized by Vosko *et al* [31] was used. The Hamann pseudopotentials used in these calculations have a single length parameter for each (l=s,p,d) angular component, r_{cs}, r_{cp}, r_{cd} called core radii. The values used for these core radii can be found in Table III.

The Gaussian based electronic structure calculations were done using the NWChem program package[32,33]. Again, only the local density approximation (LDA) parameterized by Vosko *et al* [31] was used for the exchange-correlation functional. The Kohn-Sham orbitals were expanded using the DZVP DFT orbital basis set [34]. The exchange-correlation energy and potential were evaluated on a numerical grid. The integration scheme that we chose to use partitions the density into atomic contributions [35] with the partitioned density integrated using an Euler-McLaurin radial quadrature and a Gauss-Legendre angular quadrature as described in reference[36]

Both the hexaaqua and hydroxopentaaqua complexes were optimized and proton binding energies were obtained by taking their total energy differences.

$$\Delta E_{\mathrm{H}^+} = E\left\{\mathrm{MOH(H_2O)_5^{2+}}\right\} - E\left\{\mathrm{M(H_2O)_6^{3+}}\right\} \text{ where M} = \text{Al, Ga, and In}$$

Table IV shows that results for the proton binding energies of the hexaaqua species of Al^{3+}, Ga^{3+}, and In^{3+} are nearly identical between the two ab initio methods.

VI. Conclusion

In this paper, a method for implementing free-space boundary conditions into an existing periodic PSPW code was described. Equations providing a highly accurate implementation were given. It was shown for problems in which the choice of boundary conditions was not important that the energies calculated using a modified free-space PSPW code could be directly compared to a conventional periodic PSPW code. Furthermore, it was shown that implementing free-space boundary conditions into an existing parallel periodic PSPW code would not significantly degrade its parallel efficiency.

The accuracy of our free-space PSPW code was also demonstrated by calculating the proton binding energies of a series of Group IIIB hexaaqua complexes. The energies obtained with our free-space PSPW code were shown to agree quite well with standard Gaussian basis set methods. These simulations demonstrate that free-space PSPW codes can provide accuracy similar to more traditional Gaussian based first principles methods in non-trivial charged complexes. This accuracy lends further justification for using free-space PSPW molecular dynamic codes to look at solvation and hydrolysis of highly charged metal cation complexes.

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Table I: Total energies from a periodic PSPW code and a free-space PSPW code for an oxygen atom and dimer. The distance of the aluminum dimer was fixed at 4.660 a_0, and the distance of the oxygen dimer was fixed at 2.282 a_0. All calculations in this table were done in a simple cubic unit cell with a side length of 20.0 a_0. All values are in a.u..

	Periodic Boundary Condition	Free-Space Boundary Condition	Cutoff Energy
Al_1 (^2P)	-1.954609	-1.954688	25 Ry
	-1.954675	-1.954754	57 Ry
	-1.954676	-1.954755	101 Ry
Al_2 ($^3\Sigma_g^-$)	-3.981827	-3.981937	25 Ry
	-3.981958	-3.982068	57 Ry
	-3.981959	-3.982069	101 Ry
O_1 (^3P)	-15.725014	-15.725011	101 Ry
O_2 ($^3\Sigma_g^-$)	-31.724185	-31.724174	101 Ry

Table II: Parallel performance of a periodic PSPW code and a free-space PSPW code on PNNL's IBM-SP. Results in this table are for 16 waters at a cutoff energy of 100 Ry.

# of processors	Periodic PSPW code Seconds per iteration	Free-Space PSPW code Seconds per iteration
2	105.4	
4	54.0	
8	30.9	42.4
16	16.4	23.3
32	8.4	9.8
64	4.9	5.8

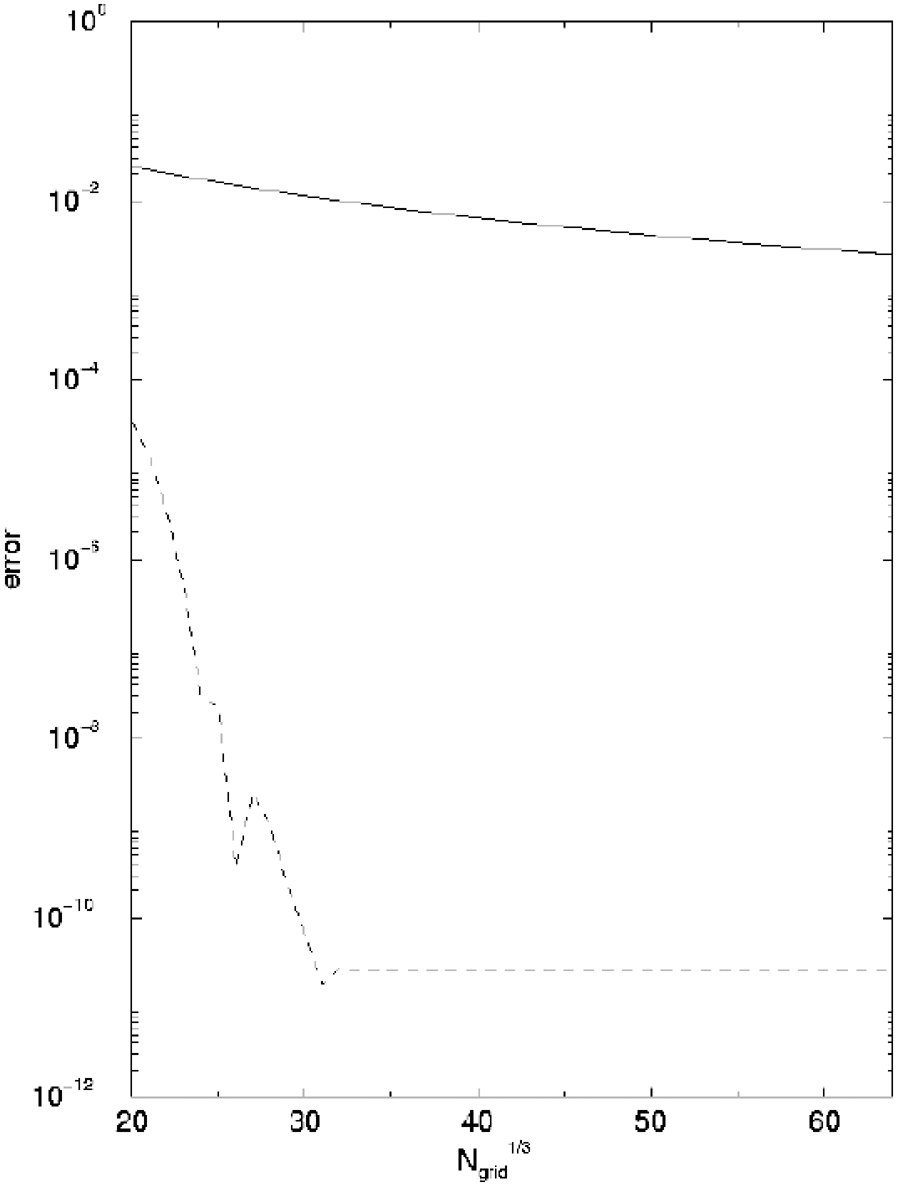
Table III: Hamann pseudopotential parameters. All values are in a.u..

Atom	r_{cs}	r_{cp}	r_{cd}
H	0.8	0.8	
O	0.7	0.7	0.7
Al	1.214	1.549	1.549
Ga	1.128	1.506	2.118
In	1.285	1.690	1.690

Table IV: Calculated Proton binding energies. Zero-point energies are not included. All values are in kcal/mol.

	ΔE_{H+}(kcal/mol)	Method
Al^{3+}	35.0	PSPW-LDA/60 Ry
	34.5	LDA/DZVP
Ga^{3+}	31.7	PSPW-LDA/60 Ry
	30.9	LDA/DZVP
In^{3+}	43.0	PSPW-LDA/60 Ry
	42.3	LDA/DZVP

Figure 1: Error in calculating the electron-electron Coulomb energy for a test density composed of 3 normalized Gaussian functions located at (8.0,8.0,10.0), (12.0,12.0,12.0), and (8.0,13.0,10.0) on the $\Omega=[0.0,20.0)^3$ domain. The normalized Gaussians have decay rates of 0.4, 0.4, and 0.5 respectively. The solid line used Eq. 12 to represent the kernel, and the dashed line used Eq. 15 to represent the kernel.



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