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Push it to the limit: comparing periodic and local approaches to density functional theory for intermolecular interactions

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With the aim of systematically comparing two popular approaches to density functional theory – all-electron calculations with local basis sets, and periodic calculations employing plane wave basis sets and norm-conserving pseudopotentials – we have computed complete-basis binding energies across the S22 set of intermolecular interactions, a dataset consisting of noncovalent interactions of small- and medium-sized molecules containing first- and second-row atoms, using the Troullier-Martins norm-conserving pseudopotentials with SPW92, a local spin-density approximation; and PBE, a generalized gradient approximation. We have found that it is challenging to reach the basis set limit with these periodic calculations; for the methods and systems examined, a minimum vacuum distance of 30 Å between a system and its nearest images is necessary – unless some form of dipole correction is employed – as is a kinetic energy cutoff of at least 80 Ry. The trends in convergence with respect to vacuum size and kinetic energy cutoff are largely independent of the level of density functional approximation employed. A sense of the impact of each hyperparameter on basis set error provides a foundation for ensuring quality calculations in future studies and allows us to quantify the basis set errors incurred in existing studies on similar systems.

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I. INTRODUCTION

Although wavefunction-based methods dominated the electronic structure landscape for most of the twentieth century,[1–6] recent decades have seen a renewed interest in Kohn-Sham density functional theory (DFT).[7] In the early 1990s, state-of-the-art density functionals were generalized-gradient approximations (GGAs) with few, if any, nonempirical parameters.[8–12] Modern iterations of density functionals have involved exploration of vast – sometimes even combinatorially-optimized – parameter spaces;[13–23] the quest for the ultimate density functional is monumental, and tremendous effort continues to be dedicated towards its pursuit.[24]

The mere specification of a method, e.g. a particular density functional, does not uniquely define an electronic structure calculation; the choice of basis set, though often overlooked, is similarly important. In theory, a larger basis set is "better." As the size of the basis grows, the energy variationally converges toward the complete-basis-set (CBS) limit. The use of additional basis functions comes at a cost, however, as the size of the basis determines the computational effort of the method. Thus, in practice, finite basis sets are employed, and basis error is confounded with method error, sometimes fortuitiously,[25] though often unpredictably. In addition, matrix elements of the exchange-correlation functional typically must be obtained in the chosen finite basis by numerical quadrature, which typically is performed with atom-centered grids[26] in molecular codes, and uniform grids in condensed matter codes.

A key consideration is the type of basis set employed. In extended systems, plane waves are the most natural choice of basis function. The same periodic, delocalized nature that makes plane waves well-suited to describing extended systems renders them ineffective for localized densities, however, so plane wave codes tend to employ some form of additional approximation – often a pseudopotential or projector-augmented wave potential – to describe the effects of core electrons.[27] For more localized systems, such as molecular clusters, atomic orbital basis sets constructed from superpositions of Slater orbitals[28] or, more commonly, Gaussian-type orbitals (GTOs)[29] are the norm.[30–37] These are not ironclad rules, however: plane wave basis sets are often employed in calculations involving molecular clusters,[38–46] and Gaussian-type basis sets can be used in to describe extended systems.[47–51] Moreover, plane waves and GTOs are by no means the only options; real-space basis sets,[52,53] wavelets,[54] and

hybrid approaches, such as linearized augmented plane waves,[55] are all valid alternatives. Nevertheless, in this study we focus our attention on plane waves with pseudopotentials and GTOs, as they are the two most widely utilized approaches. We focus on intermolecular interaction energies, which have broad importance in chemistry and condensed matter, in areas including physi- and chemisorption, clustering, and supramolecular chemistry.

In this work, we calculate binding energies with DFT in two distinct ways: with an all-electron, GTO code, and with a periodic code that utilizes a plane wave basis set in conjunction with pseudopotentials. We systematically converge these binding energies to the basis set limit, which allows us to quantify the impact of each hyperparameter related to the size of the plane wave basis – the box size and the wavefunction kinetic energy cutoff – as well as the pseudopotential. A thorough understanding of these variables is vital, particularly when adapting functionals to different codes.

To make such an assessment, we must choose a specific pseudopotential for the working calculations, and for this purpose we select a common choice: the Troullier-Martins pseudopotentials from the Fritz-Haber-Institute[56,57]. These pseudopotentials are norm-conserving, and at the basis set and grid limits, we will be able to assess the errors associated with their use. We note that conclusions drawn from our calculations with regard to the rate of convergence to the basis set limit, as well as errors at the limit, are specific to this choice. This pseudopotential, and its Quantum Espresso implementation[58] have been quite widely used for calculations of intermolecular interactions using Van der Waals density functionals, including the following recent examples[59–62] Other choices will have different convergence rates (e.g. ultra-soft pseudopotentials should be faster converging), and will reach different limits.

The systems for which we calculate binding energies are 22 molecular interaction energies that comprise the S22 data set[63]. The S22 set includes dispersion-dominated systems, hydrogen-bonded systems, and some where binding is controlled by a mixture of dispersion and electrostatics. It has become widely used in testing the ability of electronic structure methods to treat a basic range of intermolecular interaction energies,[64–66] including our own work on approaching the CBS limit using a range of Gaussian basis sets[67]

II. COMPUTATIONAL METHODS

We have compared binding energies obtained with density functional theory calculations based on two approaches: all-electron calculations with local, GTO basis sets; and periodic pseudopotential calculations with a plane wave basis. Specifically, we have utilized two density functional approximations – SPW92,[7,68–70] a local spin-density approximation; and PBE,[12] a generalized gradient approximation – to calculate binding energies for the S22 set of molecules,[63] depicted in Figure 1.

The all-electron, GTO calculations were performed with a development version of Q-Chem 5.0.[71] For these calculations, the DIIS error was converged to 10^{-8}, integral threshholds of 10^{-14} were used, no symmetry was exploited, and a fine Lebedev integration grid consisting of 99 radial shells – each with 590 angular points – was utilized. For all systems, binding energies were calculated by applying the Boys and Bernardi counterpoise correction for basis set superposition error (BSSE)[72] in the pc-4 basis set.[33,34] It is worth noting that BSSE does not affect plane wave calculations, which is an advantage in computing intramolecular interactions where the counterpoise correction is not available[73].

The periodic, pseudopotential-employing calculations were performed with version 5.3 of Quantum Espresso.[58] Troullier-Martins pseudopotentials from the Fritz-Haber-Institute were utilized,[56,57]. A convergence threshold of 10^{-8} was used. Plane-wave methods use a uniform grid for numerical quadrature which is not translationally invariant, and the resulting origin-dependence of the energy is termed the egg-box effect.[74] In order to minimize this egg-box effect, calculations on isolated monomers were performed with the atoms kept at the same absolute positions as in the dimer calculations. Molecular structures were generated with Avogadro.[75]

III. RESULTS AND DISCUSSION

The principal objective of this study is the comparison of two distinct electronic structure approaches for calculating intermolecular interaction energies, namely an all-electron calculation using local, GTO basis sets, and a periodic calculation employing a plane wave basis set in conjunction with a pseudopotential. In order to isolate differences due to the use of a pseudopotential, binding energies obtained via both approaches are converged to

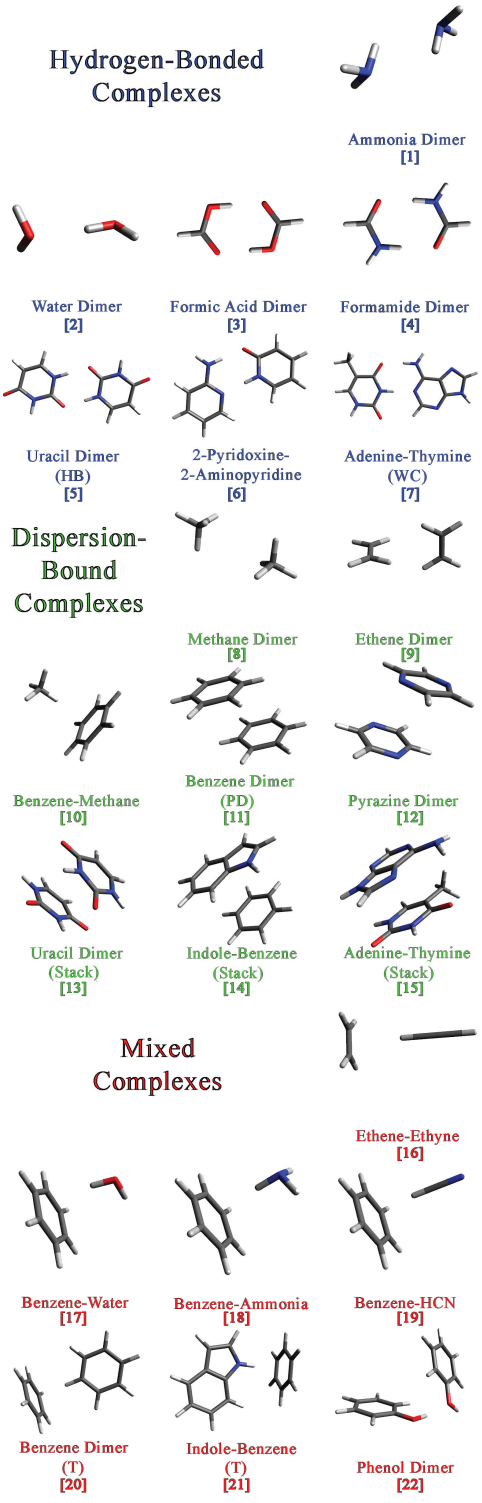

FIG. 1. Structures of the systems in the S22 dataset. The systems are classified by interaction type as per the original work.[63] The numbers in brackets are used to reference each system throughout this study.

the complete-basis (CBS) limit. For the all-electron calculations, it has been established that counterpoise-corrected binding energies across S22 in the pc-4 basis set are converged within 0.01 kcal/mol, which is roughly the limit imposed by the constraints of double precision floating point numbers and linear-dependencies in large basis sets;[67,76] thus, this level of theory has been chosen for calculating CBS all-electron values. Such studies have not been conducted for periodic codes, however, and so we must begin by developing a protocol for converging the plane wave calculations to this same level of accuracy.

Since these are zero-dimensional calculations, we need only consider the Γ-point. The two relevant degrees of freedom are thus the wavefunction kinetic energy cutoff and the size of the cubic lattice, i.e. the amount of vacuum separating a system from its periodic images. The first of these hyperparameters is explored in Figure 2, in which the impact of the kinetic energy cutoff with the PBE functional is demonstrated.

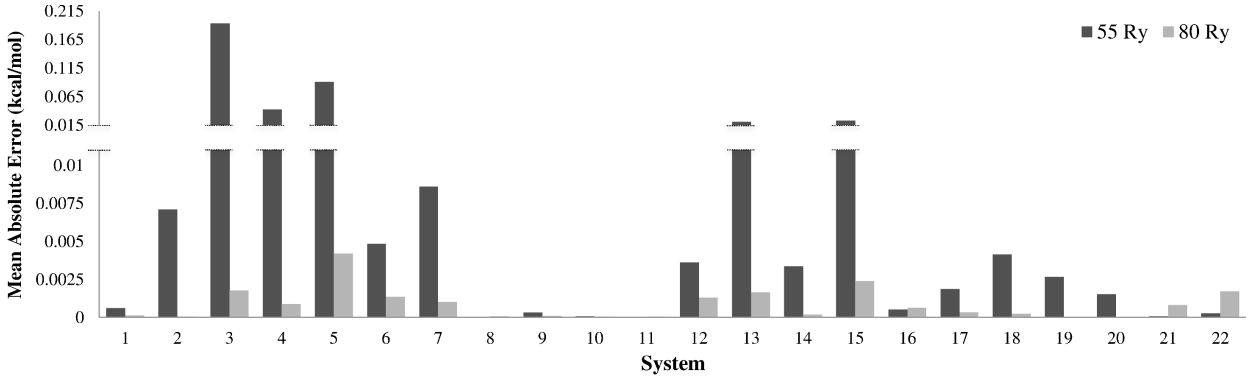

FIG. 2. Convergence of PBE plane wave binding energies with respect to wavefunction kinetic energy cutoff. Errors are expressed relative to binding energies computed with a 110 Ry cutoff. System numbers are defined in Figure 1.

From Figure 2, it is evident that a 55 Ry energy cutoff – a popular choice for the S22 dataset[42–45] – is insufficient, particularly for those systems containing electronagetive atoms, yielding a root-mean-square error at the PBE level of theory of 0.05 kcal/mol. A larger kinetic energy cutoff of 80 Ry, however, is sufficient to converge everything well below the desired level of precision. This error incurred by the choice of a 55 Ry cutoff may seem small, but it is on the same order of magnitude as the differences in S22 binding energies predicted by two popular density functionals, B97M-V[19] and ωB97M-V,[20] and as such is non-negligible in the context of functional development. It is worth noting the same behavior is seen for

the SPW92 functional, as can be observed in the Supplemental Material.

The effect of the second hyperparameter in the plane wave calculations, the box size, is visualized for the PBE density functional in Figure 3. From Figure 3, it is evident that in order to reach the desired level of accuracy – 0.01 kcal/mol – a box size of at least 40 Å is necessary. Significant spurious interactions between adjacent cells are observed when the length of each cell is reduced to 20-25 Å, which is notable, as such box sizes have been utilized in previous benchmarking studies on the S22 dataset.[42–46] The basis-related errors incurred through the use of a 20 Å cell are similar to the differences between many modern density functionals.[18–20,77]

From Figure 3, it is evident that hydrogen-bonded systems are the most slowly convergent class of systems with respect to the size of the simulation cell. We postulate that this is largely a consequence of spurious dipole interactions between images; as such, it should be capable of being mitigated with some sort of dipole correction. Figure 4 demonstrates the convergence pattern of PBE binding energies employing the Makov-Payne correction[78] with respect to box size. Relative to the uncorrected binding energies, these dipole-corrected binding energies are much more quickly convergent, being fully converged to 0.01 kcal/mol with a cell length of 35 Å. This same sort of accelerated convergence is observed when the Martyna-Tuckerman correction is employed, as can be seen in the Supplemental Material. Note that these corrections alter only the rate of convergence, not the converged binding energies themselves; the root-mean-square difference between the converged uncorrected and corrected binding energies is less than 0.005 kcal/mol, i.e. well below our desired level of precision.

It is clear from Figures 3 and 4 that the simulation cell size is a highly system-dependent hyperparameter; perhaps a more transferable metric is the minimum contact distance between a system and its nearest images, i.e. the minimum amount of vacuum space separating a molecule from its images. The box-related errors in both uncorrected and dipole-corrected PBE binding energies across the S22 dataset with box sizes of 20, 25, 30, 35, and 40 Å are visualized with respect to the minimum system-image separation in Figure 5. From this plot, the accelerated convergence of the dipole-corrected calculations is immediately evident. Moreover, Figure 5 allows us to make more transferable recommendations. For instance, to achieve box-related errors smaller than 0.1 kcal/mol, one should allow at least 15 Å of vacuum to separate a molecule from each of its nearest images; to reach the level

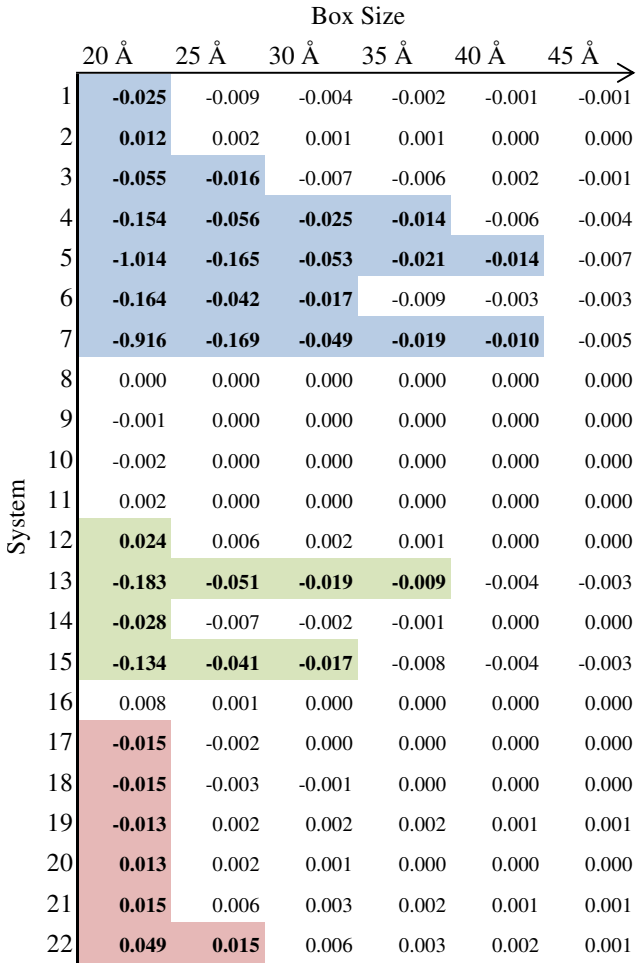

FIG. 3. Convergence of PBE plane wave binding energies with respect to box size. The number in each cell corresponds to the change in binding energy (in kcal/mol) on increasing the box size by 5 Å to the listed size. Errors greater in magnitude than 0.009 kcal/mol are bold-faced and colored, with the cell color corresponding to the type of interaction, as per Figure 1. All calculations utilize a wavefunction kinetic energy cutoff of 80 Ry. System numbers are defined in Figure 1.

of 0.01 kcal/mol, a separation of 30 Å is necessary, unless a dipole correction is employed. These findings are consistent with those of two recent studies.[40,41] As noted by a referee, in the absence of a dipole correction, it is also possible to use results for two different box sizes to extrapolate the binding energy against $1/V$ (the volume of the unit cell), to accelerate convergence.

Now that prescriptions for convergence have been established, we can compare CBS binding energies obtained with all-electron, GTO-based calculations those obtained with periodic calculations involving plane waves and pseudopotentials. In so doing, we are able

FIG. 4. Convergence of PBE plane wave binding energies employing the Makov-Payne dipole correction with respect to box size. For further details, see Figure 3.

to isolate the effect of the pseudopotential. Such complete-basis binding energies may be found in Table I for the LSDA level of theory, and in Table II for the GGA level of theory.

From Tables I and II, it is clear there are significant differences between the all-electron and pseudopotential results – an RMSD of 0.08 kcal/mol for SPW92, and 0.10 kcal/mol for PBE. These differences are large in some contexts, and they may manifest themselves e.g. when optimizing a functional that was designed for an all-electron code in a pseudopotential-employing code. Nevertheless, for standard applications – where the desired level of accuracy is on the order of 1 kcal/mol – these differences are relatively small, roughly the sort of deviation expected when running a method optimized at the CBS limit in a non-augmented triple-zeta basis with counterpoise-correction.

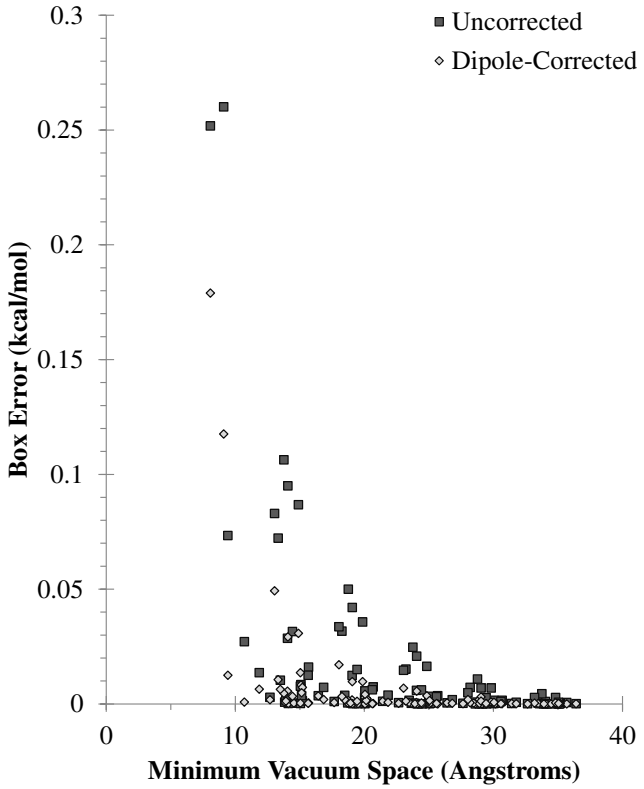

FIG. 5. Convergence of PBE plane wave binding energies with and without the Makov-Payne dipole correction with respect to the closest system-image contact distances.

IV. CONCLUSIONS

In this work, we have examined the convergence of plane wave pseudopotential density functional theory towards complete-basis binding energies across the S22 set of intermolecular interactions. Specifically, we have converged binding energies with respect to box size and kinetic energy cutoff for two distinctly different density functional approximations – SPW92, a form of local spin-density approximation; and PBE, a generalized-gradient approximation – and compared these to complete-basis energies obtained via all-electron calculations with local, GTO basis functions. We have used the norm-conserving Troullier-Martins pseudopotential, and thus our conclusions are restricted to this family of pseudopotentials.

Although there has been a recent surge in the number of studies comparing different DFT codes and approaches,[79–82] these studies are most often confined to solid-state calculations, and those rare studies that consider both all-electron and pseudopotential calculations are focused exclusively on thermochemical properties. To our knowledge, this is the first study

TABLE I. Complete basis set (CBS) binding energies (in kcal/mol) at the SPW92 level of theory for each system in S22 obtained using GTO and plane wave basis sets. For the local basis set, counterpoise-corrected pc-4 constitutes the CBS limit. For the plane wave basis set, the CBS limit is reached with an energy cutoff of 80 Ry and a box size of 45 Å.

System	GTO[a]	Plane Wave
1	-5.07	-5.12
2	-7.81	-7.90
3	-26.98	-27.19
4	-21.92	-22.03
5	-26.27	-26.37
6	-22.89	-23.06
7	-22.08	-22.23
8	-0.83	-0.82
9	-2.47	-2.47
10	-2.02	-2.01
11	-2.60	-2.56
12	-4.43	-4.43
13	-10.14	-10.14
14	-4.36	-4.31
15	-11.95	-11.94
16	-2.27	-2.30
17	-4.44	-4.48
18	-3.04	-3.07
19	-5.82	-5.88
20	-3.05	-3.06
21	-6.27	-6.32
22	-9.01	-9.12

[a] GTO CBS values taken from Ref. 67

in which the gap between all-electron, GTO-based and plane wave pseudopotential DFT calculations on noncovalent interactions is bridged at the respective basis set limits of each approach.

In the course of this study, we have established that it is remarkably difficult to truly reach the basis set limit. For the all-electron, GTO-based calculations, use of the massive pc-4 basis set is necessary to obtain binding energies converged to within 0.01 kcal/mol across the S22 dataset.[67] For the plane wave pseudopotential calculations, a kinetic energy cutoff of 80 Ry in conjunction with a 40 Å box yields this same level of precision; use of some form of dipole correction accelerates the convergence with respect to box size. Although this level of precision is necessary for certain purposes – most notably functional development, where

TABLE II. Complete basis set (CBS) binding energies (in kcal/mol) at the PBE level of theory for each system in S22 obtained using GTO and plane wave basis sets. For further details, see Table I.

System	GTO	Plane Wave
1	-2.81	-2.87
2	-4.95	-5.05
3	-18.26	-18.53
4	-14.80	-14.94
5	-18.58	-18.71
6	-15.39	-15.58
7	-14.39	-14.57
8	-0.09	-0.10
9	-0.33	-0.34
10	-0.05	-0.06
11	1.85	1.85
12	0.69	0.66
13	-2.74	-2.78
14	2.18	2.18
15	-1.41	-1.46
16	-1.17	-1.20
17	-2.02	-2.07
18	-0.93	-0.96
19	-2.82	-2.89
20	-0.13	-0.15
21	-2.05	-2.11
22	-3.90	-4.02

differences between modern functionals on standard noncovalent interactions are minimal – for standard applications, significantly larger errors are acceptable. Nevertheless, in order to ensure the basis set error is no larger than the pseudopotential error, a minimum vacuum distance of 15 Å is recommended, as is kinetic energy cutoff of 80 Ry – at least for those molecules containing electronegative atoms, i.e. N and O.

The fact that the differences between binding energies computed at the CBS limit using an all-electron, GTO-based approach and a plane wave, pseudopotential approach are generally small – on the order of 0.1 kcal/mol – is quite encouraging. These differences are consistent with those observed, albeit not at the CBS limit, in a recent study by Pestana et al.,[83] and our broader findings of transferability between different codes and different approaches to DFT reinforce the existing literature.[80,82] Nevertheless, care should be taken when porting a functional optimized for all-electron calculations to a pseudopotential code, or vice versa, as

certain parameters may need to be re-tuned. In the future, it would be interesting to extend the assessment presented here to classes of pseudopotentials other than our choice of the Troullier-Martins norm-conserving form, such as ultrasoft pseudopotentials, which should converge more rapidly.

V. SUPPLEMENTARY MATERIAL

Supplemental material contains tables of binding energies, as well as convergence figures with the SPW92 functional, and a spreadsheet with raw binding energies.

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