

Improving the accuracy of all-electron calculations with alkaline earth atoms

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Introduction

In quantum chemistry, achieving numerical accuracy of the atomic systems with inexpensive computation cost has been desirable. Some widely-used methods include density functional theory (DFT), Hartree-Fock approach [1], and MP2/GW electron self-energies [2]. An important approximation that helps simplify the DFT calculation is pseudopotentials, which replace the nuclear Coulomb potential and the core electrons with a softened potential that agrees with the all-electron (AE) calculation [3]. AE calculation completely solves the core and valence electrons so it is not susceptible to pseudopotential approximation errors, but the basis set errors may become a trade-off. While the pseudopotentials achieve considerable efficiency, the ability of directly running AE calculation on molecular and periodic systems are appealing because of its accuracy.

Fritz Haber Institute “ab initio molecular simulations” (FHI-aims) is a computer program package that performs first principle, AE calculations with numerical atomic orbitals (NAOs) that is both computationally efficient and accurate for molecules and solids [4]. The numerically tabulated radial shape of the basis function allows flexibility to optimize the basis for each element and form a compact but accurate and transferable basis set up to meV-level. In developing the algorithm, Blum et al. [4] constructed a scheme that successfully captures the energies of free atoms by reproducing the behavior of wave functions near the core and generally describing bond formation. However, FHI-aims only focuses on training the basis sets to model one specific type of bond, the covalent bonds in homogenous dimers, so it is uncertain whether the same basis can accurately capture highly ionic bonds. Here, in a case study of Mg-containing systems, we assess whether considering the exact oxidation states and bond type during basis construction will improve the efficiency and accuracy of the calculation.

We have shown that the diatomic testing system of NAOs is flexible regardless of bond types and atoms, yielding basis sets with comparable accuracy and transferability. A variationally optimized basis fit to the MgO dimer shows a similar convergence trend as a basis fit to the Mg₂ dimer when applied to several ionic solids. The presence of a chemical bond in the testing system is necessary to correctly parameterize polarization-like orbitals, but solid-state systems are insensitive to the bonding character (covalent or ionic) in the testing system, as the overlap of basis functions from other atomic centers leads to a greater degree of flexibility. On the other hand, systems that show properties of isolated systems (gas phase molecules or ions) are more sensitive to the testing system: the standard basis trained on the Mg₂ dimer does not appropriately capture any ionic character present in many Mg-containing systems, so it performed poorly on the MgO dimer and Mg ionization energies compared with a

basis set that accounts for the ionic properties of Mg. In general, the transferability of dimer basis sets in ionic solids suggests that the testing method performs well as long as the applied system has a similar bonding character. Variationally optimizing the basis for specific systems can effectively improve the accuracy of partially isolated systems, such as ions and gaseous molecules.

This paper first provides an overview of the basis set generation scheme in FHI-aims, which sets up the fundamentals of this project.

Overview of FHI-aims method

FHI-aims uses NAO basis sets to define the Hilbert space of the electrons. The radial function $u_i(r)$ in the NAO allows for choosing highly flexible numerical solutions for Schrodinger-like radial equations:

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{cut}(r) \right] u_i(r) = \epsilon_i u_i(r) \quad (1)$$

where the potential is divided into $v_i(r)$, which defines the main behavior of the radial function, and $v_{cut}(r)$, a confining potential that smoothly decays the radial function to strictly zero outside a confining radius r_{cut} . l specifies the angular momentum of the orbital. FHI-aims includes a minimal basis that describes the core and valence functions of a free atom by setting $v_i(r)$ to the non-spin polarized free-atom radial potential. The confining potential begins to smoothly damp the radial function at a distance r_{onset} from the nucleus and gradually increases to infinity at r_{cut} over a width of w . The settings of r_{onset} and w impact the radial function and its second derivative, and hence the accuracy of the solution. In FHI-aims, $r_{onset} = 5 \text{ \AA}$ or more was used for basis optimization. The radial function was scaled by a Coulomb potential of z_{eff}/r with z_{eff} as an effective nuclear charge.

The goal of FHI-aims is to objectively construct hierarchical basis sets up to meV-level energy convergence. To achieve this, a large pool of candidate radial functions that is as "open" as possible is considered, including hydrogen-like, cation-like, and atom-like functions. The construction strategy begins with a minimal basis, selecting different candidate basis functions from the pool and testing them on a simple chemical system, which in this case is the homogenous dimer. The procedures are iterated to generate a list of well-converged basis functions, which are then organized into hierarchical tiers of basis function groups with different angular momenta.

Methods

The all-electron, non-spin polarized calculations were performed in FHI-aims. The density of states of the electrons was converted to a gaussian broadening function to find the Fermi level of the system. The "tight" default setting was applied to all species. For Mg ion and Mg-contained dimers, the onset of confinement potential r_{onset} was chosen at 8 \AA and the potential smooths out over $w = 2 \text{ \AA}$. Within the dimers, H and

O atoms were set as $r_{onset} = 4\text{\AA}$, $w = 2\text{\AA}$. In solids, the r_{onset} for Mg was 4.75\AA and the width was 1.75\AA ; O had a r_{onset} of 3.75\AA and a width of 1.75\AA ; F, Cl, and S had the settings of $r_{onset} = 4\text{\AA}$, $w = 2\text{\AA}$. The k-points grid for periodic systems was set at (8, 8, 8).

The basis set was variationally optimized for the Mg ion (see Appendix, Table 1) and added on the default tier 2 basis. The charge was varied with a step of $0.01e$ with a range from 0 to $+2e$. Due to the spherically symmetric nature of the isolated ion, the basis pool only contains hydrogen-like s orbitals with z_{eff} in the range of $0 \leq z_{eff} \leq 16$. The continuous [4] parameter z_{eff} was varied with a step of 0.01 to maximize variational flexibility. We considered radial quantum numbers $n = 1, \dots, 7$. The minimal basis set contains the energy-converged solutions of the free atom, so the added basis primarily focuses on correcting Mg's ionic behavior without worrying about capturing the high-angular momentum orbitals.

The benchmark calculation for the ion-optimized basis was performed in the Open-Source Pseudopotential Interface/Unification Module (OPIUM) [5]. The nonrelativistic all-electron calculation solves the spherically symmetric atom on a radial grid to systematically converge the solution [3]. The charge of Mg ion varies at the same range and step as in FHI-aims. The total energy error of the NAOs relative to OPIUM was averaged over charges to give a root-mean-square error.

Another set of basis was variationally optimized for the MgO dimer (Appendix, Table 2). The testing system includes the dimer with varying bond lengths from 1.65\AA to 1.85\AA , covering the relaxed bond length of 1.75\AA . The radial function pool includes hydrogen-like functions with z_{eff} in the range $0 \leq z_{eff} \leq 16$ and a step of 0.01. We considered angular momenta $l = 0, \dots, 5$ for Mg, and radial quantum number $n = 1, \dots, 7$. Noted that Blum et al. only included $l = 0, \dots, 4$ for light elements before Ar [4], but we added *the h* function regardless because as Blum et al. shown, including high-angular momenta functions does not significantly increase the computational cost but has a non-negligible effect at reducing total energy error [4]. The $6h$ orbital was selected as the optimized basis (Appendix, Table 2). The high-angular momentum functions are less physical but more for fitting the optimization scheme [4]. The dimer-optimized basis substitutes Mg's default tier 3 basis and was applied to MgH and MgH₂ molecules; bulk MgCl₂, MgS, MgF₂, MgO, and Mg. Calculations using the default basis with matching basis sizes were performed for benchmarking.

Results and discussion

Ionization energies. Figure 1 shows the ionization energy errors corrected by the optimized bases. The default basis performs the worst because tier 3 (with 6 additional basis functions) hardly reduces the first ionization energy (Figure 1(a)) and slightly increases the error of the second ionization energy (1(b)), which might be caused by error cancellation between OPIUM and AIMS total energies at tier 2. Since the default

basis does not account for the ionic properties of Mg, the tier 4 basis (with 10 additional basis functions) generates a larger error than one optimized ion basis in both ionization energies. Compared to dimer-optimized basis, ion-optimized basis performs better because the basis has the exact testing system, showing that the isolated system is sensitive to the particular testing system in which the basis set is selected. The total energy difference offset between OPIUM and AIMS leads to the negative errors in 1(b).

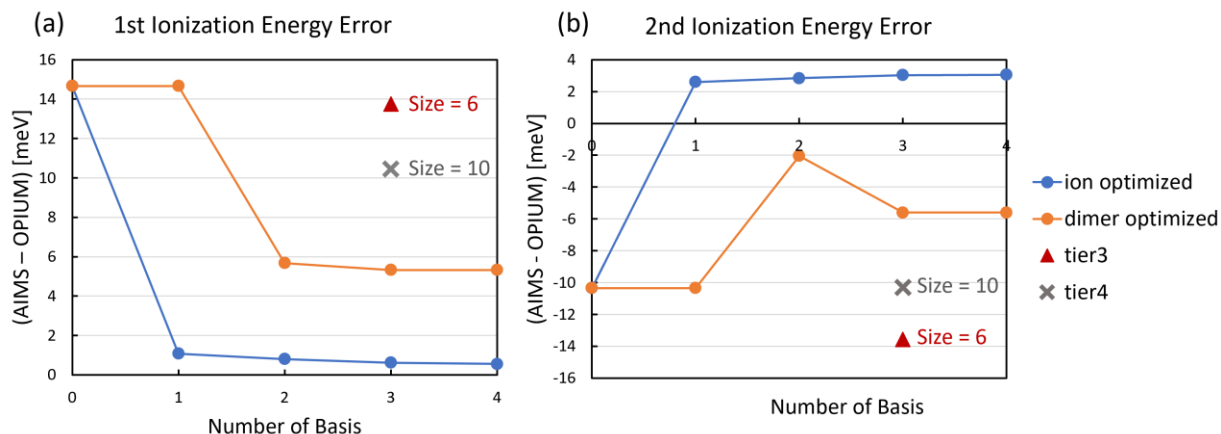


Figure 1. (a) The first ionization energy and (b) the second ionization energy of the Mg atom after adding different bases.

Molecules. Figure 2 considers two isolated systems, MgH and MgH₂ gaseous molecules. MgH exists at high temperatures such as the atmosphere of the Sun and stars [6] and can be produced by co-depositing pulsed laser-ablated Mg atoms with hydrogen on a substrate [7]. MgH₂ dimers are another predominant product of such reaction [7] and are observed in solid krypton and xenon using photoexcitation of Mg to initiate the reaction [8]. For both dimers, ion optimized basis is better than the default basis in the short term as it considers the dimers' ionic properties, but the other two dimer bases eventually outperform it because they capture the wave function changes to describe the chemical bonds. The MgO dimer basis is consistently better than the default basis for both molecules (Figure 2(a), 2(b)) by 1-2 meV because the testing system resembles the ionic dimers. The covalent bond that the default basis is selected on mismatches the weak ionic bonds of the magnesium hydrides, so the basis is less accurate.

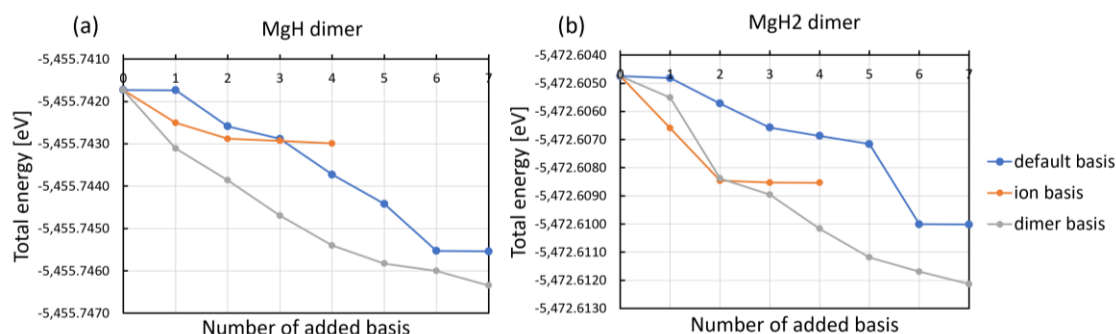


Figure 2. The total energy of (a) MgH dimer and (b) MgH₂ dimer after adding different bases
Solids. While the isolated systems are sensitive to the bond type of the testing system,

periodic systems have many overlaps of the basis functions from other atomic centers that compensate for the basis set errors. The presence of a bond in the testing system is necessary to correctly parameterize polarization-like orbitals, but the bond type is less critical. Figure 3 shows the total energies of Mg metal and MgO solid. The ion-optimized basis produces comparable accuracy to the default basis by the size of 3 (Figure 3(a)), perhaps due to the properties of positively charged ions in the metallic bonds. Additional ion basis generates larger errors than the default basis because it does not account for the presence of bonds. Except for the second dimer basis that reduces 1.3 meV of total energy more than the default basis, the two bases perform similarly as their total energies differ at sub-meV levels (3(a)), which is insignificant due to the error contribution from DFT functionals [9].

The downside of discounting chemical bonds becomes prominent in MgO solid. As shown in Figure 3(b), the ion-optimized basis consistently generates more than 8 meV of energy error from the default basis at each size because it does not contain nonsymmetrical orbitals that describe bond formation. For a better comparison of energy convergence, the default tier 3 basis was reranked based on their reduction of the MgO solid total energy. The resultant total energies calculated from the default basis and the dimer basis deviate at the sub-meV level until the sixth dimer basis outperforms by 2.7 meV (3(b)). Hence, the dimer-optimized basis has a slight advantage over the default basis in an ionic solid but is negligible when the basis size is small (< 6).

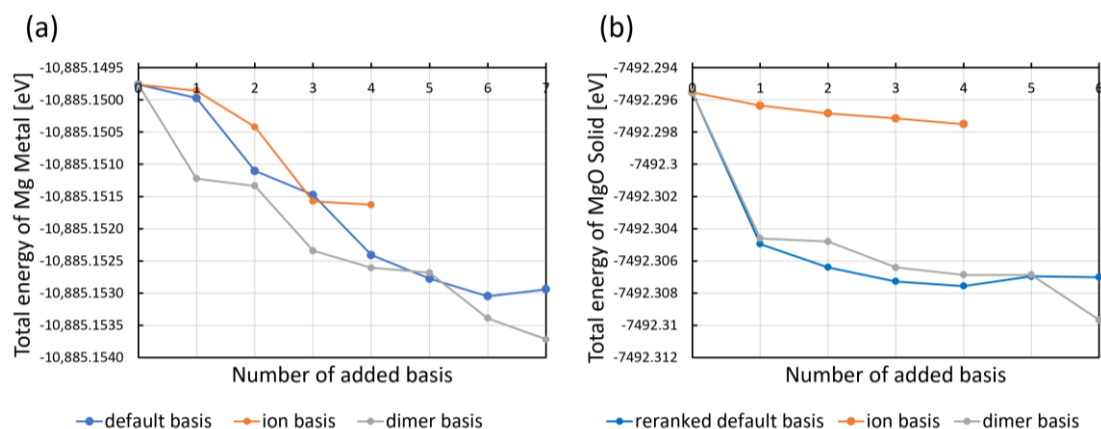


Figure 3. The total energy of (a) bulk Mg and (b) MgO solid after adding different bases

A comparison of basis performance in Mg-contained salts shows a similar trend of a short-term advantage (size < 5) of the default basis and long-run precedence of the dimer basis (size > 5) (Figure 4). In MgO solid, as discussed, both bases have competing performance until the sixth basis function where the dimer basis reduces the total energy by 2.7 meV more (4(a)). Similarly, in MgCl_2 , the dimer basis produces a 10.8 meV larger error in its second basis, but it surpasses the default basis by the fourth NAO, and eventually outperforms the default basis by 5.8 meV (4(c)). MgF_2 and MgS show a larger scale of energy difference. The second NAO in the dimer basis leads to an 11.3 meV disadvantage than the default in MgF_2 (4(b)) and an 18.7 meV

larger error in MgS (4(d)). The dimer basis reaches the default by the fifth NAO and achieves energy convergence at the sixth, which exceeds the last default basis that can converge by 4.3 meV (4(b)). MgS is the most challenging to converge, but the dimer basis shows a similar tendency to reach the default after the second NAO: the third basis reduces the energy difference by 15.0 meV, leaving a 3.6 meV error from the default basis (4(d)).

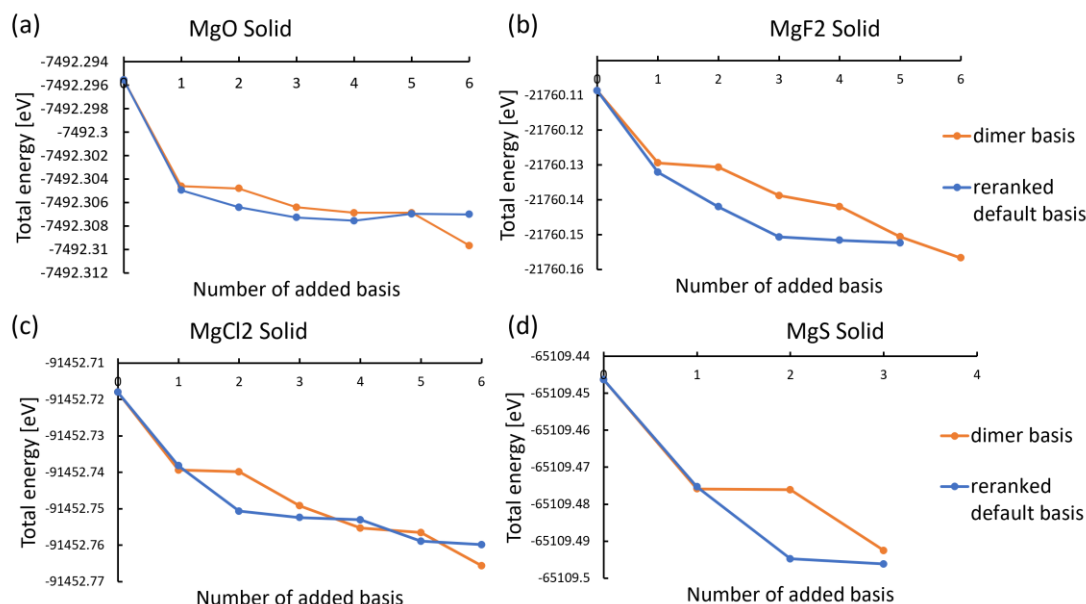


Figure 4. The total energy of (a) MgO solid, (b) MgF₂ solid, (c) MgCl₂ solid, and (d) MgS solid after adding different basis

In this study, the default tier 3 basis is reordered for each solid based on their energy reduction to benchmark. In reality, however, the entire tier 3 basis is designed to add altogether [4], so the sixth NAO perhaps shows the most visible difference of the basis sets. The dimer basis consistently reaches lower energy by the sixth and is easier to converge than the default basis in MgCl₂. Hence, though the periodic system is less susceptible to the various bond types in the basis testing system, an ionic dimer still achieves a subtle but non-negligible advantage over the homogenous dimer testing system.

Conclusion

In periodic systems, variationally optimized NAOs are insensitive to the diatomic testing system that the basis set is selected based on; that the testing system includes a chemical bond, regardless of the bond type, is critical in accurately modeling bulk materials. We have presented a case study on Mg to show that the NAO basis sets optimized for a covalent bond and an ionic bond perform comparably well in salts and metal. In systems that showcase isolated system properties (ions and molecules), however, a testing system that captures the Mg ionic bond produces a more accurate basis set. The MgO dimer optimized basis reduces ~ 8 meV in the ionization energies with a smaller basis size than the Mg₂ dimer basis and it performs consistently better

by 1-2 meV at every size in gaseous molecules. The transferability of dimer basis sets in solids suggests that the diatomic testing system can be chosen based on computation simplicity, whereas variationally optimizing basis sets for particular systems can tailor basis functions to describe partially isolated systems with higher accuracy.

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Appendix

Table 1. Optimized basis based on a testing system of Mg ion

Order	Basis
1	4 s 6.0
2	3 s 3.3
3	1 s 0.5
4	5 s 13.5

Table 2. Optimized basis based on a testing system of MgO dimer

Order	Basis
1	5 g 5.6
2	5 s 6.2
3	2 p 3.8
4	3 d 2.2
5	5 f 8.0
6	6 h 7.4
7	3 d 6.8