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Benchmarking the performance of plane-wave *vs.* localized orbital basis set methods in DFT modeling of metal surface: a case study for Fe-(110)

Kapil Adhikari[a], Aurab Chakrabarty[b,c], Othmane Bouhali[d], Normand Mousseau[e], Charlotte S. Becquart[f], Fedwa El-Mellouhi[g,*]

[a] *Department of Physics, Prithvi Narayan Campus, Tribhuvan University, Pokhara, Nepal*
[b] *Physics Research Initiatives (PRI)-Pokhara, Nepal*
[c] *S. N. Bose National Centre for Basic Sciences, JD Block, Salt Lake Sector-III, Kolkata 700106, India*
[d] *Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar*
[e] *Département de physique and RQMP, Université de Montréal, Case postale 6128, succursale centre-ville, Montréal, QC, Canada H3C 3J7*
[f] *UMET, UMR CNRS 8207, ENSCL, Université Lille I, 59655 Villeneuve d'Ascq cédex, France*
[g] *Qatar Environment and Energy Research Institute (QEERI), Hamad Bin Khalifa University, P.O. Box 34110, Doha, Qatar*

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ABSTRACT

Reproducing electronic structure of extended metallic systems is computationally demanding with the cost efficiency of this approach heavily dependent on both the density functional and the basis function used to approximate the electronic orbitals. It is well known that the generalized gradient approximation functional (GGA) is the most suitable and reliable approach for the description of metallic systems. As for the basis functions, two approaches dominate: the linear combination of localized basis functions (LB) such as Gaussian functions and the linear combination of plane waves (PW). Both have their own advantages and disadvantages, that may impact the efficiency and accuracy of the simulations. In this work, we use the VASP and the CRYSTAL14 suites of codes that employ plane waves and localized Gaussian basis sets, respectively, to establish a benchmark on their computational efficiency for the modeling of metal surfaces. The PW basis technique requires that the entire simulation box including the vacuum space be filled with plane waves which reduces the computational efficiency and limits the vacuum space. For its part, the LB method is based on atomic localized orbitals and does not require vacuum to model surfaces. Therefore, for calculations that require relatively large vacuum thickness such as modeling of adsorption, the LB method might be superior in terms of computational expense while providing the comparable accuracy.

1. Introduction

Density functional theory (DFT) is one of the most widely used theoretical methods for simulating material properties at the atomic scale [1]. It rests on a few centrally important approximations including the exchange-correlation functional and the choice of basis sets. The selection of approximations must be done with care in order to obtain accurate results while, at the same time, attempting to optimize computational cost. The choice of exchange-correlation functional depends largely on the physics of system under study. Once a particular functional is chosen, a set of basis functions is used to develop the electronic density matrix. There are two major approaches available for the description of basis sets: the linear combination of localized basis functions (LB) and the linear combination of plane waves (PW). The linear combination of localized basis functions is particularly popular in molecular calculations whereas the plane waves are adopted more generally in periodic systems. However, there are a number of computer programs using localized orbital basis sets to perform DFT calculations on periodic systems [2–5]. Generally in periodic systems, plane wave basis sets are used in combination with effective core pseudo-potentials. One of the most useful features of plane wave basis set is their universality in the sense that they neither depend on the position of atoms in the unit cell nor on the nature of atoms. The same basis set can be used for any atomic

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* Corresponding author.
E-mail addresses: kapil.061@gmail.com (K. Adhikari), felmellouhi@hbku.edu.qa (F. El-Mellouhi).

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species and local environment. Moreover, the quality of its prediction can be arbitrarily improved by a single parameter, the cutoff energy, that determines the number of plane waves representing one-particle Kohn-Sham wave functions. Another advantage of plane wave basis sets is that they do not suffer from basis set superposition error (BSSE). This is particularly advantageous when one is studying the interaction between heterogeneous systems under periodic boundary condition, i.e. metal-gas catalytic reactions. However, the error from localized basis functions which greatly suffer from BSSE can be corrected by the well documented and widely used counterpoise method [6]. Despite their aforementioned advantages, however, plane wave basis sets have a major limitation; they must be expanded over the whole simulation box and therefore can only be strictly implemented in three dimensional (3D) fully periodic systems. Since a plane wave basis set is, by definition, uniform across the simulation box, a large number of plane waves are required to describe accurately localized inhomogeneous systems, and systems periodic along one or two directions. This is the case when modeling surfaces, for example, as the vacuum required to preclude interactions between slab supercells in perpendicular direction to the surface demands the same accuracy of description as the atomic layers. In this case, it is often preferable to use the LB methods, that can be more efficient when studying 2D periodic systems. The LB methods are also known to be hugely efficient with hybrid functionals in comparison with PW-based methods, where the large number of orbital wavefunctions means that expensive exchange matrix elements have to be computed for a more extended set of pairs of orbital wavefunctions [7].

The computational study of metallic surfaces is important to improve our understanding of the metal surface itself and of its interaction with adsorbates [8]. In recent decades a significant number of experimental and computational studies on metallic surfaces have been produced, in particular to understand the processes of contrasting homogeneous and heterogeneous catalysis [9–15]. Fe surface is particularly relevant for surface science communities interested in the modeling heterogeneous catalytic reactions. For example carbon monoxide (CO) adsorption on Fe attracted particular attention because of its fundamental importance in Fischer-Tropsch synthesis (FTS)[16] and the initiation of metal dusting corrosion in Fe. While other bcc metals such as Cr, Mo, and W show similar abilities to capture and dissociate CO, Fe surface is peculiar in terms of its strong ferromagnetic character often challenging DFT code in terms of slow convergence and high computational cost. Over the years, slab-supercell models as well as zero dimensional finite cluster approximations have been used to study quantum metallic thin films and their interaction with molecules. The finite cluster approximations are particularly useful both to model the catalytically active centers on the metal surface and for providing in depth information regarding the geometry at these centers. However the finite cluster approximations are best suited for processes in which small clusters are catalytically active or for the interaction of adsorbates with ideal surface or the surfaces with defects at low surface coverages [8,17,18]. Yet, to obtain realistic results from computational modeling, the size of the model should be sufficiently large or should at least "mimic" an infinitely large system from the atomic standpoint, a goal that is out of reach of routine finite cluster approximation approaches [17,19,20]. This is why slab-supercell approach has often be preferred for a realistic and comprehensive modeling of metal surfaces and their interactions with adsorbates.

A correct computation of the work function or absorption energy relies strongly on whether slabs have been rigorously chosen to minimize artefacts coming from periodic boundary conditions while at the same time keeping the computational cost affordable. Our previous work rigorously addressed the finite size effects on the CO adsorption energies and diffusion barrier [21], emphasizing on the need of simulating large surface areas to avoid such errors. Next, we studied the effect of point and extended defects on the adsorption of CO molecules and their dissociation barrier. [22,23] All the above investigations stressed on the need of the community to move to larger Fe slabs. Hence the current work helps to assess whether sufficiently converged computational settings and large enough slabs have been carefully selected without compromising the CPU time.

In the present work we report on a comparative assessment of the performance of plane wave basis set and localized basis functions to study bcc iron surfaces, more precisely the Fe-(110) surface within a slab-supercell environment. Though there have been some attempts to compare these two kinds of basis sets in the past [24–29], the authors believe that the literature is insufficient and inconclusive, especially in the case of metal surfaces. The aim of this preliminary study is to set ground for further full fledged studies on performance comparison of these basis sets not only on bare metal surfaces but also on metal assisted catalytic processes.

2. Computational methods

In the present work, the Fe(110) surface is studied using density functional theory as implemented in two widely used computer code: local-basis CRYSTAL14 [2] and the plane wave Vienna *Ab initio* simulation package (VASP) [30]. Optimized geometry of Fe *bcc* crystal with space group $Im\bar{3}m$ was obtained in both the suites of programs, and respective optimized bulk geometries are used to cleave the (110) surface. The optimal lattice parameter is found to be 2.783Å and 2.831Å with the LB and PW methods, respectively. Single-point calculations are performed on the slabs thus obtained and energetics and computational costs for the slabs with respect to the supercell size are determined. The supercells dimensions for the selected slabs range from 1×1 to 5×5 with up to seven atomic layers of thickness. Although an exact one to one correspondence between all the numerical parameters in the two approaches is not possible, parameters such as smearing factor, k-points, etc. are kept similar to the extent possible and the same density functional, PBE-GGA [31], is used. For localized basis function calculation in CRYSTAL14, a consistent basis set of double-zeta valence with polarization, i.e. POV-DZVP [32], is selected. This basis set is based on def2-DZVP basis sets [33] developed for molecules. PW calculations, for their part, are performed using the projector augmented wave pseudopotential (PAW-PP) method implemented in VASP [30]. Total energies are calculated with a kinetic energy cutoff fixed at 400 eV for all calculations. Convergence criteria of 10^{-6} eV/atom were selected for total energy calculations.

3. Results and discussion

Due to the sharp drop in the electronic occupation at the Fermi level at 0 K in metallic systems, it is imperative to use a finite temperature smearing of the Fermi surface to avoid the unphysical oscillations in the charge density of the system which leads to non-convergence. Therefore, for such systems, a finite non zero temperature distribution is used to get a better convergence rate of the self consistent field (SCF) calculation.

However, with a high smearing temperature, magnetic states of the system are not represented accurately. Therefore, the first benchmarking should be done to get an optimized value of smearing factor while performing calculation of metallic systems. Among several smearing schemes, two major schemes are implemented in our calculations: Fermi and Methfessel-Paxton smearing [34] (Fig. 1). Fig. 2 shows the comparison of these two schemes tested with PW calculations. We find that a Fermi smearing factor of less

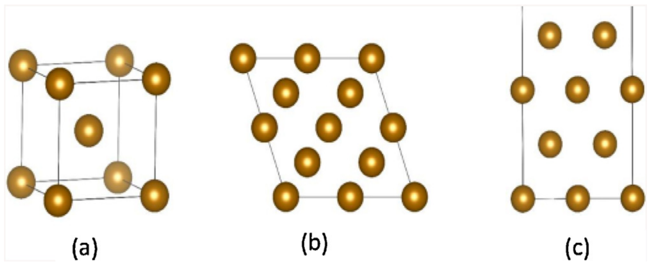

Fig. 1. Atomic structures of (a) the bulk structure of Fe bcc, (b) the (110) surface (top view), and (c) the ABAB stacking of (110) surface (side-view).

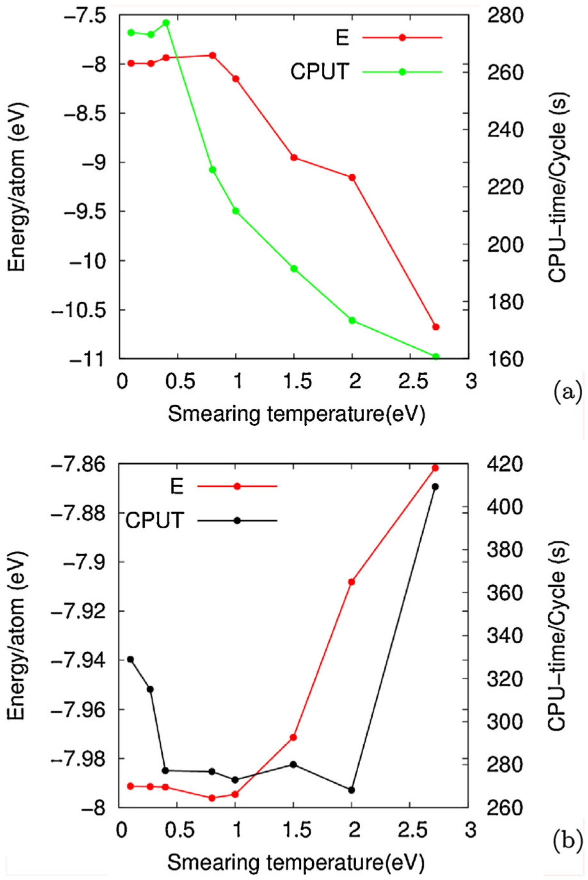

Fig. 2. Energy and CPU time for PW calculations as functions of smearing temperature using (a) the Fermi and (b) the Methfessel-Paxton methods.

than 0.3 eV and a Methfessel-Paxton smearing factor between 0.5 and 1.0 eV yield stable energy with similar computational costs. A comparison of the Fermi and the Methfessel-Paxton smearing (Fig. 2(a) and (b)) shows, moreover, that the later yields better energy stability for plane wave calculations in wider range of temperature (note the energy scale). Therefore, we use a Methfessel-Paxton smearing factor of 0.8 eV in plane-wave calculations. Unlike the VASP code which is used for PW calculations, CRYSTAL14 offers only the Fermi smearing scheme with a recommendation to prefer low smearing temperature [2]. Since a Fermi smearing factor of less than 0.3 eV is stable and comparable to an 0.8 eV Methfessel-Paxton smearing in terms of CPU time and the total energy, a Fermi smearing factor of 0.27 eV is used in the localized basis set calculations.

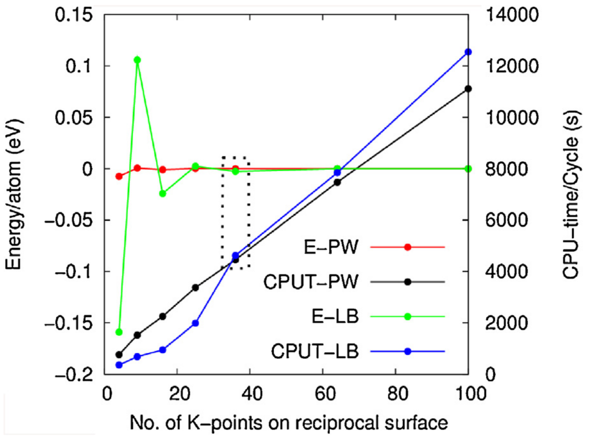

Fig. 3. Energy and CPU time for PW and the LB methods as function of number of k-points on the reciprocal space.

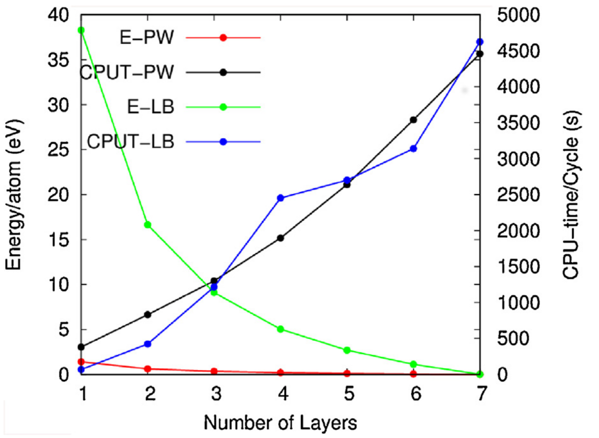

Fig. 4. Total energy (scaled to converged value) and CPU time as functions of number of layers in a 4×4 slab.

The same k-point grid, auto generated by the Monkhorst-Pack scheme [35], is used for both the LB and PW calculations. There are both qualitative and quantitative differences in k-point convergence. Fig. 3 shows the energy per atom and the CPU time for different k-point grids in the LB and PW methods. For both methods, $4 \times 4 \times 7$ slabs were used. At a lower k-point density the energy fluctuation is much higher with the LB as compared to the PW method. With a k-point grid of $6 \times 6 \times 1$ the energy per atom is converged for both approaches. At a lower k-point grid, CPU time per SCF cycle with the LB method is slightly less than that with the PW method. However at the convergence threshold (highlighted by the dotted rectangle) and beyond, the computational cost of the LB method is higher than with the PW method, and the difference in computational cost increases with the k-point grid density. Comparable Accuracy and CPU time are achieved using both methods at k-point grid of $6 \times 6 \times 1$.

In surface studies, convergence of energetics with respect to surface thickness and area are of paramount importance to model slabs with optimum dimensions. It is therefore necessary to benchmark the two methods with respect to slab thickness and area. Figs. 4 and 5 show the energy and computational cost of the surface calculation with simulation model size. Fig. 4 shows the computational cost of the calculations with respect to the number of layers.

With the increase in periodic surface area the CPU time increases almost linearly in both methods. For the PW method, larger surface areas correspond to larger simulation box volumes requiring a greater number of plane waves. With the increase in number of atoms computational time for the LB method increases almost linearly, similar to that for the PW method. As a result, it can be

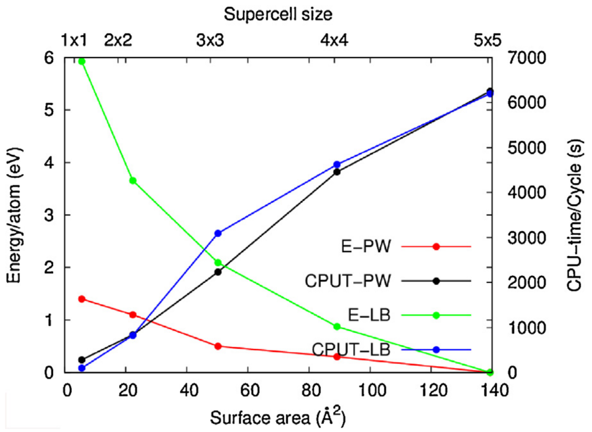

Fig. 5. Scaled energy (to converged) and CPU time as functions of surface area of seven-layer-thick slab.

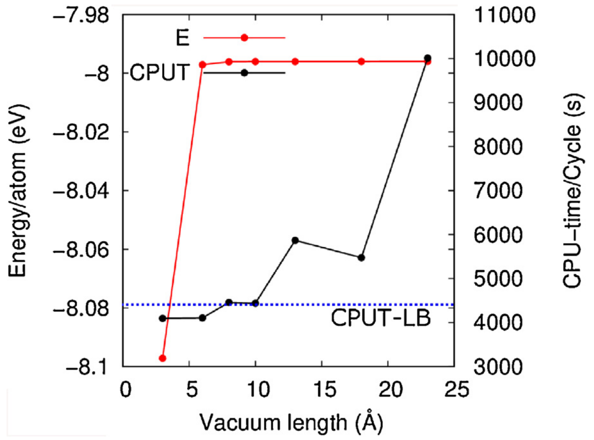

Fig. 6. Effect of increasing vacuum thickness in PW calculation on CPU time and energy, the best converged 4 × 4 ×7 slab was taken as benchmark. The dotted blue line shows the CPU time for the same system with localized orbital basis set.

inferred from Fig. 5 that both methods consume a similar computational time per SCF cycle with increase in surface area. Worth noting that the above analysis suggests that total energies might converge faster for small slabs in PW, with comparable CPU time compared to LB. However, the LB becomes as efficient as PW methods for sufficiently large and thick slabs which are in general desired to avoid numerical errors arising from finite size effects.

Since the major motivation to undertake slab calculations is to model catalytic reactions on metallic surfaces; evaluating the energetics of adsorbates such as CO or hydrocarbons would greatly benefit from minimizing numerical artefact caused by finite size effects. Ideally, large and thick slabs would lead to better converged energies compared to experiment but remain prohibitly expensive to simulate. Since the PW method strictly applies to 3D systems, any low-dimensional system (*i.e.* 2D, 1D, and 0D) must be defined by a three dimensional simulation box with sufficient vacuum space defined. The vacuum is necessary to avoid interactions caused by the periodic boundary conditions that lead, as mentioned earlier, to an unnecessarily large number of functions to be computed for < 3D systems. The LB method, on the other hand, introduces basis functions bound to atomic sites that do not require a finite vacuum space to be defined. This becomes computationally advantageous when one is interested in surface adsorption calculations. It is worth noting that according to Figs. 4 and 5, both LB and PW methods showed a satisfactory converged total energies with a comparable computational cost. The optimized k-point grid of 6 × 6 × 1 with smearing temperature of 0.8 eV is used for comparison.

Fig. 6 shows the total energy and CPU time as a function of vacuum thickness for the PW calculation on a 4 × 4 ×7 slab. The energy converges well at a relatively narrow (≈8Å) vacuum thickness. As expected, the PW computational cost increases drastically as the vacuum thickness increases. However, the CPU time for the LB method depicted in Fig. 6 (blue dots and line) remains constant. This suggests that for calculations that require relatively large vacuum thickness such as modeling surface adsorption and other catalytic reactions, the LB method might be superior in terms of computational expense. While the computational cost of LB increases with increasing the number of basis functions used in the LB method, it compensates quickly for the same number of atoms by a non-requirement of vacuum space. In the PW method, which requires a finite vacuum space, the computational cost increases with the simulation box size. This increment, on the other hand, is compensated by the universal nature of plane wave basis functions. Still overall, for large slabs the LB is superior if vacuum thickness greater than (≈8Å) vacuum is required.

4. Conclusions

CRYSTAL14 and VASP DFT codes were used to carry out a comparative benchmarking study of plane-wave (PW) versus localized basis set (LB) methods for modeling the Fe-110 slab. Total energy convergence and computational cost for both methods as a function of supercell dimensions, both parallel (surface area) and perpendicular (thickness) to the surface plane, is assessed.

We find that PW converges faster and might be more appropriate for small slab calculations while a more stable and computational efficiency could be achieved from LB for large slabs. In conclusion, once the setting are well optimised and carefully taken care of, the localized basis set becomes more suitable than plane-wave for a sufficiency large slab lifting the computational burden associated with increasing the vacuum in PW calculations to accommodate large adsorbates. A more detailed study of the performance comparison of these basis sets, on metal assisted catalytic processes, is in progress.

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