

Accurate and efficient determination of chemisorption energies using pseudopotentials

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Abstract

The accuracy and efficiency of ab initio density functional theory calculations depend critically on the choice of pseudopotential. In this study, the merits of using large-core pseudopotentials for the dissociative chemisorption of oxygen on rhodium are discussed. The results show that these efficient pseudopotentials yield adsorption energies and bond distances of the oxygen atom to rhodium that are in close agreement with calculations performed with small-core pseudopotentials. However, to compute the dissociative chemisorption energy, a small-core calculation of the free O₂ molecule must also be performed to ensure accurate results. The use of pseudopotentials with different core radii for different aspects of the calculation leads to enhanced efficiency. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The chemistry and physics of molecules on metal surfaces is an area of great interest for many scientific and industrial fields, including catalyst development, epitaxial growth, and surface coatings. Ab initio pseudopotential methods within density functional theory are well suited to this class of systems due to the availability of efficient techniques. However, accurate first-principles calculations of adsorbate–surface interactions can still be quite costly if the right balance between rigor and approximation is not met.

On surfaces, the bonding of atoms and molecules differs from the gas phase. For instance, in dissociative oxygen adsorption, the bond between the surface and the oxygen atom tends to be much longer than the molecular bond. Because of this,

greater freedom can be used in creating the oxygen pseudopotential. Also, the inclusion of spin polarization is not necessary for the surface calculation since this effect tends to be small for most metals. These simplifications yield more efficient calculations of adsorption onto metal surfaces. These approximations are not valid for the free oxygen molecule, due to its short bond length and strong spin polarization. As demonstrated below, the combination of large-core pseudopotentials for unpolarized molecule–surface calculations and small-core pseudopotentials for spin-polarized calculations of the free molecule enhances efficiency significantly while retaining accuracy.

2. Method

This study uses density functional theory (DFT) [1,2] to compute the electronic structure of all

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systems considered. The single-particle wavefunctions are expanded using plane waves. This basis set is widely used for surface calculations due to its ability to represent periodic systems and because of the availability of efficient fast Fourier transforms. We use the direct minimization algorithm of Payne et al. [3] to find the electronic ground state.

Non-local pseudopotentials [4] are used to represent the nuclei and core electrons. We study the behavior of three types of oxygen pseudopotential. A large-core designed non-local (DNL) pseudopotential [5], a small-core optimized (OPT) pseudopotential [6], and the standard Bachelet–Hamann–Schlüter (BHS) potential are compared [7]. The rhodium atoms are represented by a DNL pseudopotential.

The local density approximation (LDA) [8] is used widely in DFT calculations. However, since LDA overestimates binding energies, the effects of the generalized gradient approximation (GGA) of Perdew et al. [9] will also be studied. In order to perform self-consistent GGA calculations, the discretization due to Bird and White [10] is invoked which gives accurate results with no increase in the real-space integration grid density.

3. Results and discussion

3.1. Pseudopotentials

Table 1 presents the parameters used in the construction of the oxygen pseudopotentials. Oxygen pseudopotentials with a range of core radii were generated, and the convergence properties for each pseudopotential were then tested. The DNL potential has a core radius of 0.81 Å, which gives significant overlap in the molecule but

requires the fewest plane waves. The optimized potential has a core radius of only 0.4 Å but requires many more plane waves. The BHS potential has the smallest core radius and requires the highest plane-wave cutoff. Table 1 lists the plane-wave cutoff required to compute total energies within 0.01 eV atom⁻¹ of the converged value for each potential. The transferability properties of each pseudopotential were gauged by comparing all-electron and pseudopotential calculations of the total-energy and eigenvalue differences between the ground state and various ionized and excited atomic states. We report the transferability as the error in the change in total energy for adding half an electron to the p orbital.

3.2. Atomic calculations

One source of error in computing the energy of the oxygen atom results from allowing the atom to evolve to a spherically symmetric ground state. Indeed, the DFT ground state is spherical with all three p orbitals degenerate. However, to obtain the observed ground state, the atom must be constrained to have integer fillings for each orbital [11]. This requires careful treatment of the orbital populations throughout the self-consistent calculation. Table 2 reports the non-spherical correction without spin polarization. As the results show, an error of about 0.3 eV is introduced without this constraint.

3.3. Molecular calculations

The existence of pseudopotential core overlap in the O₂ molecule causes an unpredictable error in the total energy. Although this error can be small, it is not systematic. Therefore, a reliable O₂ total energy can only be determined with a small-core pseudopotential.

Table 1

Parameters for the oxygen pseudopotentials. All potentials use the ground state as the reference configuration. See text for details

Pseudopotential method	Exchange correlation	r_c s (Å)	r_c p (Å)	E_{cut} (Ry)	Transferability error (meV)
DNL	LDA	0.62	0.81	50	−0.10
DNL	GGA	0.62	0.81	50	−0.01
OPT	LDA	0.40	0.40	183	−0.38
OPT	GGA	0.40	0.40	183	−0.41
BHS	LDA	0.25	0.14	350	−0.13
BHS	GGA	0.25	0.14	350	−0.16

Table 2

The non-spherical corrections to the total energy for the oxygen potentials: $E_{\text{non-spherical}} - E_{\text{spherical}}$. No spin polarization was used in these calculations. All results are in eV

Potential	LDA	GGA
DNL	0.342	0.316
OPT	0.299	0.253
BHS	0.295	0.251

It is also important to include spin polarization in calculations of the atom and the molecule. We computed the spin-polarized energies as a correction to the unpolarized energies. This was done by computing the difference in the exchange-correlation energies for the unpolarized ground-state charge density using polarized and unpolarized forms of the energy functionals. Based on fully self-consistent data [11] this introduces a minimal error which is constant for all of the pseudopotentials.

The effect of core overlap on the atomization energy is presented in Table 3 for calculations with and without spin polarization and using LDA or GGA. The fact that the atomization energy error for the LDA and GGA DNL potentials are of *different sign* reinforces the unpredictability of the core overlap effect.

3.4. Surface calculations

Since a small-core pseudopotential is necessary for calculations of the oxygen molecule, it may also seem that a surface calculation with oxygen would also require a potential with a small core. However, this greatly increases the required plane-

wave cutoff (and therefore computation time and memory). In surface calculations, oxygen frequently forms longer bonds, presenting less risk of core overlap. A large-core pseudopotential should yield results that are similar to small-core oxygen potentials in this environment.

Using each pseudopotential, we have calculated the binding energies of an oxygen atom approaching a three-fold site of a rhodium monolayer. In this calculation, we only use 1 k -point and about 4 Å of vacuum. Because k -point and thickness convergence errors are independent of pseudopotentials, they will not affect the comparisons between pseudopotentials made in this paper.

In fact, this is a much more rigorous test of this method than a standard surface calculation that has multiple atomic layers since a realistic multi-

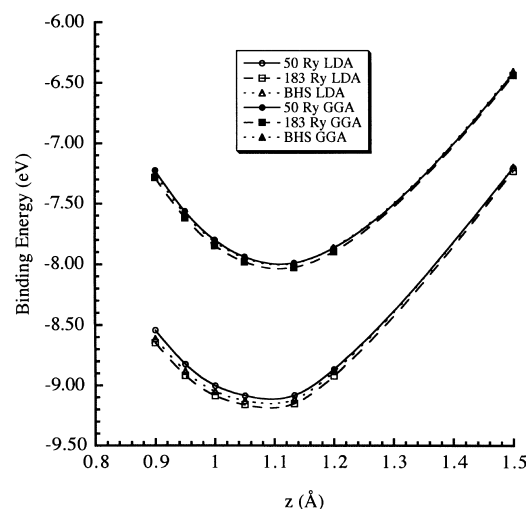


Fig. 1. Binding energies for oxygen approaching the rhodium (111) monolayer.

Table 3

The atomization energies for the oxygen pseudopotentials. All energies are in eV atom⁻¹

Potential	Unpolarized		Polarized	
	LDA	GGA	LDA	GGA
DNL	4.88	4.55	3.58	3.02
OPT	5.06	4.62	3.71	2.99
BHS	5.06	4.62	3.70	2.95
AE			3.74	2.95
			[12]	[12]
Exp.	2.56 [13]			

Table 4

Equilibrium distances and vibrational frequencies for oxygen bound to the rhodium monolayer. Distances are in Å and frequencies are in cm⁻¹

Potential	LDA		GGA	
	z_0	ν	z_0	ν
DNL	1.082	779	1.109	743
OPT	1.077	784	1.107	743
BHS	1.077	784	1.107	743

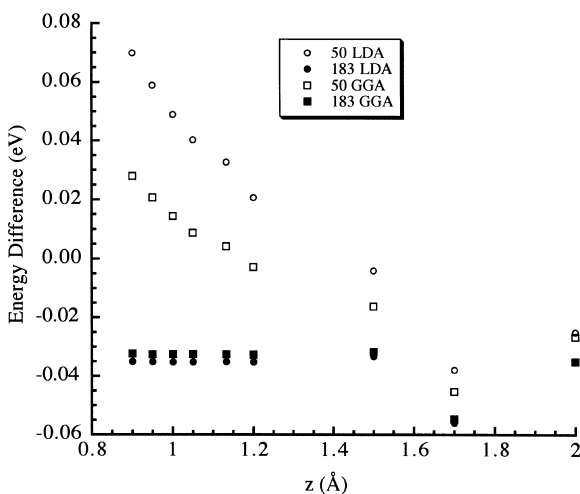


Fig. 2. Plot of binding energy error relative to the BHS potential.

layer slab allows much less penetration of the oxygen atoms. Table 4 shows the equilibrium distance and vibrational frequencies for an oxygen monolayer adsorbed to a rhodium (111) monolayer. There is close agreement for all potentials considered.

Fig. 1 shows the binding energy as a function of distance between the oxygen and rhodium layers along the surface normal using LDA and GGA. For all of the pseudopotentials, the binding energies differ from the BHS values by less than 0.07 eV. We can compute the chemisorption energy of the oxygen atom by using:

$$\begin{aligned}
 E_{\text{chem}} &= E_{\text{atom-bind}} - E_{\text{atomization}} \\
 &= (E_{\text{O}(50\text{Ry})+\text{surface}} - E_{\text{surface}} - E_{\text{O}(50\text{Ry})\text{spherical}} \\
 &\quad + E_{\text{O}(183\text{Ry})\text{spherical}} - E_{\text{O}(183\text{Ry})\text{non-spherical}}) \\
 &\quad - \left(\frac{1}{2} E_{\text{O}_2(183\text{Ry})} - E_{\text{O}(183\text{Ry})\text{non-spherical}}\right)
 \end{aligned}$$

and expect the maximum error to be of the order of 0.05 eV as shown in Fig. 2. However, the error will be much less for *relative* chemisorption energies since the discrepancy between the two potentials will tend to cancel.

4. Conclusions

In this paper, we have shown that accurate chemisorption energies for oxygen on surfaces can

be performed using a pseudopotential with larger core radii than is appropriate in the calculation of the oxygen molecule. This allows for more efficient calculations involving the adsorption of oxygen. However, the molecular atomization energy should be computed separately using a pseudopotential with smaller core radii. This paper shows that this hybrid approach is able to yield accurate chemisorption energies without requiring an extremely large plane-wave cutoff in the surface calculation.

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