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Computational Analysis of Ethanol Dehydrogenation Reactions Occurring Over Extended Stepped Catalytic Metal Surfaces

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Abstract

As hydrocarbon fuel usage increases, so does the need for more renewable fuel sources. Pollutant greenhouse gases, such as water vapor, carbon dioxide, and methane, are released during the combustion of fossil fuels such as coal and natural gases. Hydrogen fuel, however, is a “clean” energy source in that it is a zero-emission fuel when it is reacted with oxygen in combustion or highly efficient fuel cell processes making it a more sustainable energy source for future generations. One way of synthesizing this from renewable plant based sources is by steam reformation whereby a simple hydrogen containing molecule, such as ethanol, may be cleaved in a dehydrogenation reaction over a metal catalyst. An ethanol dehydrogenation reaction will be studied to establish periodic trends using thirteen different metal interfaces over an extended unit cell on a stepped metal surface. Rhodium was the first surface investigated to observe this reaction and develop the computational model for stepped metal surfaces. Reaction energies were calculated using VASP (Vienna Abinitio Simulation Package) for density functional theory calculations and CrystalMaker for visualization. Following rhodium, a palladium and ruthenium catalyst were studied following the same computational method adapted for an extended, stepped metal surface. The next step for this project will be to investigate periodic trends across this row of metals involved in the ethanol dehydrogenation mechanism.

1. Introduction

The need for renewable fuel is constantly growing as the limited supply of hydrocarbon fossil fuels (such as crude oil, coal, and natural gas) continues to be the dominant source of energy throughout the world. Hydrogen fuel is becoming a more popular research topic as scientists look to expand alternative clean energy sources. Hydrogen fuel is “clean” in that it does not emit harmful greenhouse gases when it is reacted with oxygen in combustion or highly efficient fuel cell processes that produce water as the only by-product. This makes hydrogen fuel a more sustainable energy source for large scale use.

One way to produce hydrogen fuel is by steam reforming processes. Steam reforming uses fossil fuels to create cleaner products such as the highly sought after hydrogen fuel (H_2) as well as carbon monoxide.[1] A “cleaner” branch of steam reformation reactions is alcohol dehydrogenation. By alcohol dehydrogenation reactions, C-H and O-H bonds are cleaved. Alcohol dehydrogenation involves the removal of a hydrogen in order to produce products such as H_2 and acetaldehyde.[2] Ethanol dehydrogenation involving a metal catalyst interface is a reaction heavily studied within the field as ethanol is a simple alcohol to observe for hydrogen cleavage activity (Figure 1). The ethanol dehydrogenation reactions studied in Dr. Wasileski’s research group no longer focus on □C-H cleavage as it has been found that this is the last position for hydrogen cleavage to occur.

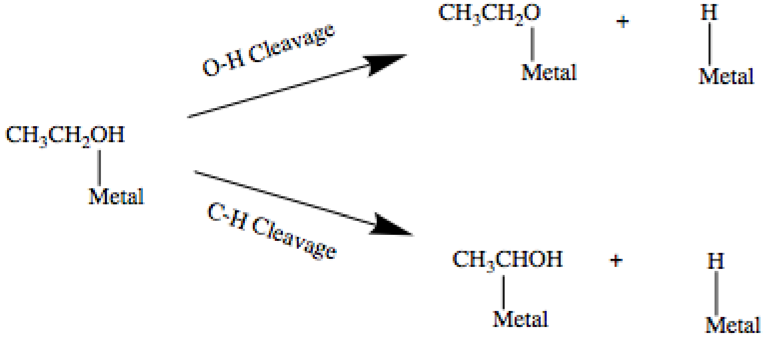
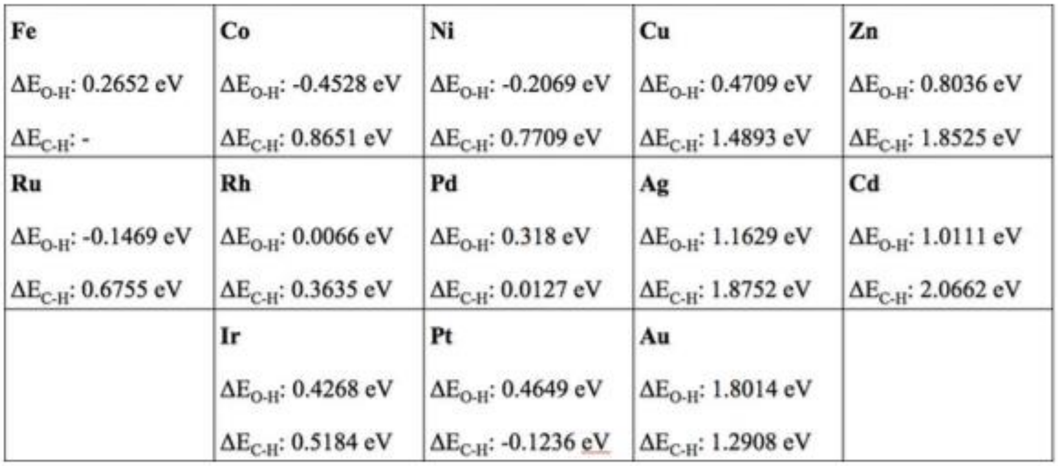


Figure 1. This figure shows the ethanol dehydrogenation reactions for different H cleavage locations (O-H and alpha C-H cleavage).

Metal catalysts have both planar and stepped surfaces. The activity rate of the metals used amongst dehydrogenation reactions depends on the surface structure involved in catalysis. Stepped and kinked surfaces have been found to be more reactive as these surfaces allow molecules to bind stronger to the metal surface. This is due to the increased electron density of these surfaces. Previous research students from Dr. Sally Wasileski's research team have studied the activity of alcohol dehydrogenation mechanism over planar, stepped, and kinked surfaces.[3,4]

Dr. Wasileski's research team previously studied thirteen pure metals using periodic density functional theory. Iron, cobalt, nickel, copper, zinc, ruthenium, rhodium, palladium, silver, cadmium, iridium, platinum, and gold were studied as planar 111 surfaces for an ethanol dehydrogenation mechanism. The RPBE functional in VASP was used to calculate the energy of the ethanol dehydrogenation reaction. This functional has been used for various chemisorption studies and has provided improved energetics over functionals such as PW91 and PBE.[3,4,5] Rhodium and silver were also observed as a stepped 211 surface. The reaction energies shown below are for the 111 surface catalysis (Figure 2).[4]



Fe $\Delta E_{O\text{-}H}$: 0.2652 eV $\Delta E_{C\text{-}H}$: -	**Co** $\Delta E_{O\text{-}H}$: -0.4528 eV $\Delta E_{C\text{-}H}$: 0.8651 eV	**Ni** $\Delta E_{O\text{-}H}$: -0.2069 eV $\Delta E_{C\text{-}H}$: 0.7709 eV	**Cu** $\Delta E_{O\text{-}H}$: 0.4709 eV $\Delta E_{C\text{-}H}$: 1.4893 eV	**Zn** $\Delta E_{O\text{-}H}$: 0.8036 eV $\Delta E_{C\text{-}H}$: 1.8525 eV
Ru $\Delta E_{O\text{-}H}$: -0.1469 eV $\Delta E_{C\text{-}H}$: 0.6755 eV	**Rh** $\Delta E_{O\text{-}H}$: 0.0066 eV $\Delta E_{C\text{-}H}$: 0.3635 eV	**Pd** $\Delta E_{O\text{-}H}$: 0.318 eV $\Delta E_{C\text{-}H}$: 0.0127 eV	**Ag** $\Delta E_{O\text{-}H}$: 1.1629 eV $\Delta E_{C\text{-}H}$: 1.8752 eV	**Cd** $\Delta E_{O\text{-}H}$: 1.0111 eV $\Delta E_{C\text{-}H}$: 2.0662 eV
	Ir $\Delta E_{O\text{-}H}$: 0.4268 eV $\Delta E_{C\text{-}H}$: 0.5184 eV	**Pt** $\Delta E_{O\text{-}H}$: 0.4649 eV $\Delta E_{C\text{-}H}$: -0.1236 eV	**Au** $\Delta E_{O\text{-}H}$: 1.8014 eV $\Delta E_{C\text{-}H}$: 1.2908 eV	

Figure 2. This figure, made by Mindy Schueneman, shows the reaction energies of C-H and O-H cleavage for ethanol dehydrogenation reaction over thirteen different pure metal interfaces.

Cobalt was found to react strongly when cleaving O-H bonds, while platinum was found to react strongly when cleaving C-H bonds. Rhodium was found to react well when cleaving either type of bonds over a planar metal surface. The results from Mindy Schueneman's study with planar metal surfaces can be applied to future research in the group as stepped surfaces are studied further.

This project will combine the knowledge gained from Mindy Schueneman's work with planar metal surfaces and Ganjina Nagzibekova's work with stepped metal catalyst surfaces to investigate the effects of extended, stepped metal catalysts for ethanol dehydrogenation reactions. Rhodium has been found amongst researchers to have the best outcomes for alcohol dehydrogenation reactions.[7] By using periodic density functional theory, the goal of this project is to study the reaction mechanisms for breaking both the αC-H bond and O-H bond of ethanol in an alcohol dehydrogenation reaction catalyzed by metals, beginning with rhodium.

2. Methods

Periodic Density Functional Theory (DFT) is the computational method used to investigate metal-molecule interactions in a catalytic reaction by describing the electron density as waves with repeating unit cells to create an extended metal surface.[8] By utilizing periodic DFT and a plane wave basis set, this method models an infinitely repeating system with mathematical approximations involving electron density.[9] Applying an RPBE functional to the electron density, an energy may be calculated describing the reaction of this study. Using computational programs, Crystalmaker and VASP (Vienna Abinitio Simulation Package),[10,11,12,13,14] the activity of metal interfaces can be studied utilizing periodic DFT and visualization models. Using CrystalMaker, an extended rhodium unit cell was produced for the purpose of visualizing the metal interface interactions with the reactants and products of the ethanol dehydrogenation reaction being studied.

After obtaining the structural results from CrystalMaker, the coordinates are used in VASP to calculate the optimal bonding geometries using an estimated optimization. This was done using a Monkhorst-Pack resolution of 3x3x1 (k points). The 331 approximation optimized the geometry to find the lowest energy conformation for each binding site on the extended step rhodium surface. Then, using a more extensive 5x5x1 optimization, a more accurate energy calculation was completed. There are several potential binding sites for a stepped (211) rhodium surface (Figure 3).[7]

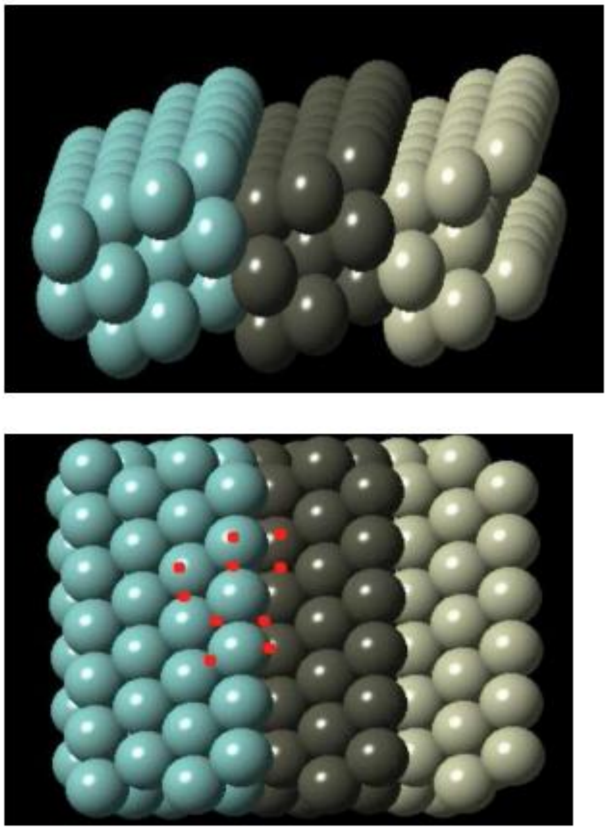


Figure 3. Possible binding sites on a stepped rhodium (211) surface: atop, bridge, and hollow. Atop occurs over one atom, bridge occurs between two atoms, and a hollow is an interaction between 3 atoms. These positions can be oriented upper, lower, and on the edge of the metal surface.[7]

The optimal interactions of unreacted ethanol, hydroxyethyl (C-H cleavage), and ethoxy (O-H cleavage) are atop on the extended, stepped rhodium surface. Hydrogen interacts favorably with this same surface in an edge bridge orientation.

Following the reactions below, reaction energies were calculated for the ethanol dehydrogenation reaction over a stepped, extended rhodium catalyst.

$$\Delta E_{reaction} = E_{products} - E_{reactants}$$

$$\Delta E_{reaction} = (E_{Hydrogen\text{-}Metal} + E_{Hydroxyethyl\text{-}Metal\ or\ Ethoxy\text{-}Metal}) - (E_{Bare\ surface} + E_{Ethanol\text{-}Metal})$$

The equations above give the energy results for C-H and O-H bond cleavage in an ethanol dehydrogenation reaction over a metal catalyst. Using the optimized geometries of each molecule bound to a metal surface (and the metal surface itself), the energy of the reaction was then calculated.

3. Results and Discussion

Following the works of Mindy Schueneman and Ganjina Nagzibekova, member of Dr. Wasileski's research team, it was evident which positions might be more favorable for the products and reactants of the ethanol dehydrogenation reaction involving a rhodium metal catalyst.[4,7] This directed the current project as optimized binding trends were established. By using CrystalMaker, Figures 4, 5, 6, and 7 were generated to show the interactions between the rhodium surface and the molecules being studied. The figures below show the optimized binding positions for the molecules involved in the ethanol dehydrogenation reaction over a metal catalyst surface.

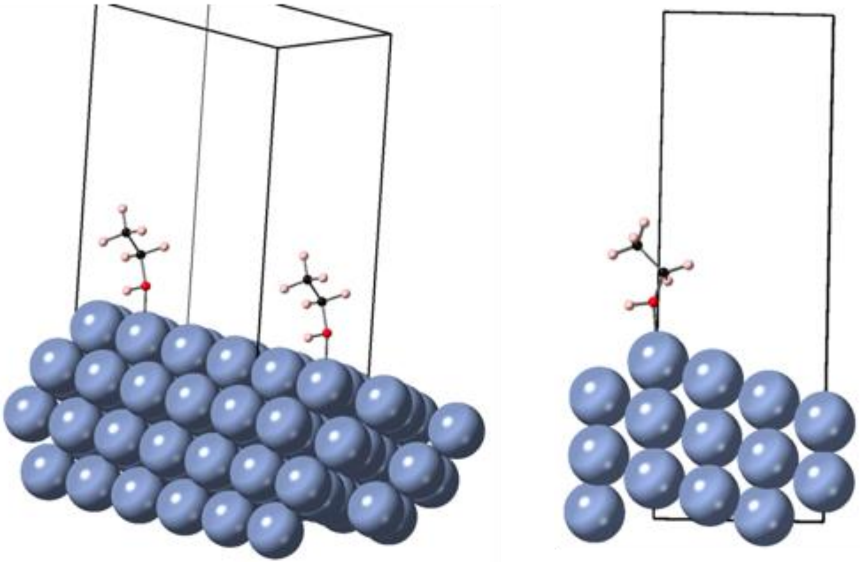


Figure 4. The unreacted ethanol molecule interacts with the extended (211) stepped rhodium surface in an atop step position.

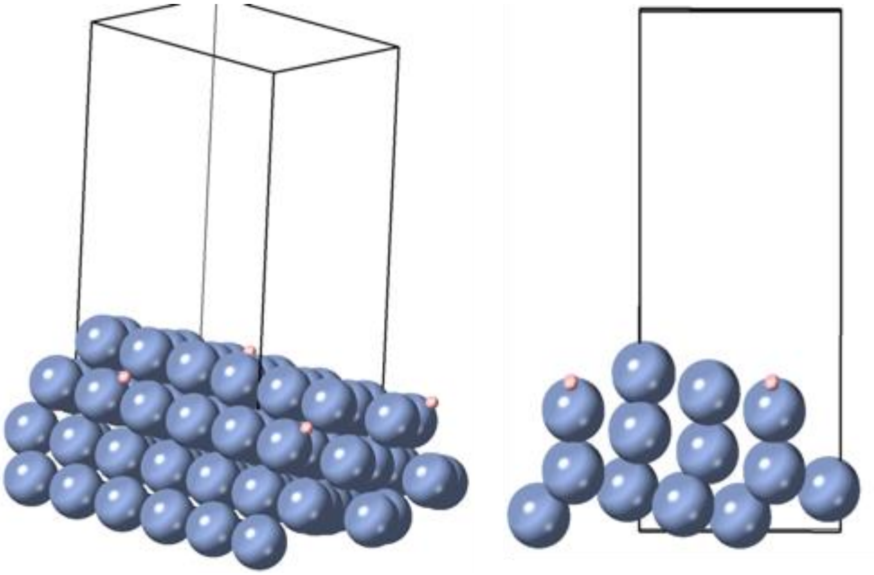


Figure 5. The removed hydrogen molecule interacts with the extended (211) stepped rhodium surface in an edge bridge position. *Results are pending for this interaction (the rhodium surface was buckled upon further inspection and did not give accurate results for an extended stepped rhodium surface).

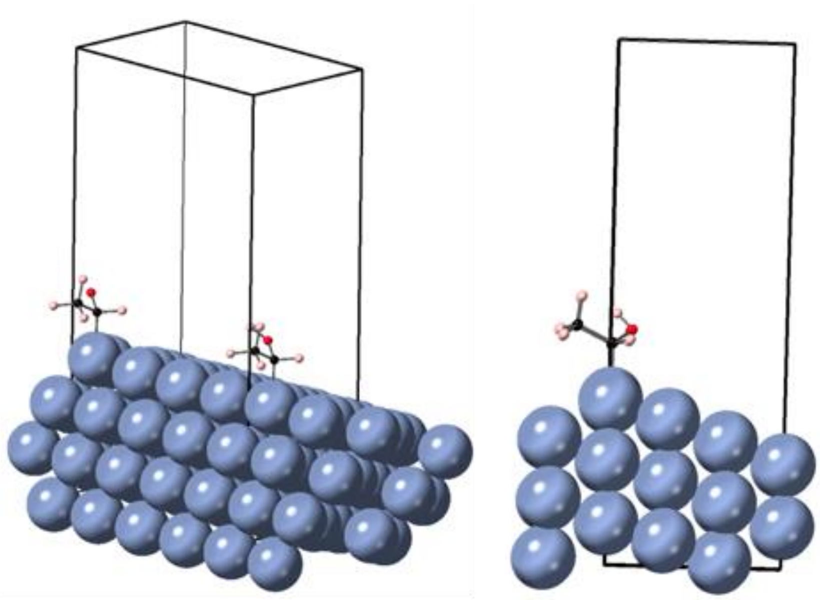


Figure 6. The hydroxyethyl molecule interacts with the extended (211) stepped rhodium surface in an atop step position.

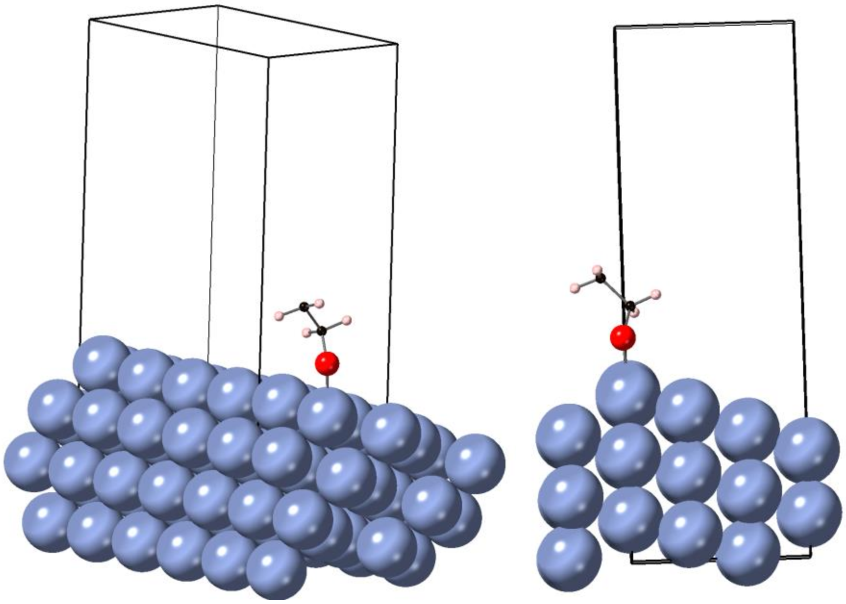


Figure 7. This geometry optimization shows the ethoxy molecule interacts with the extended (211) stepped rhodium surface in an atop step position.

Using previous models from Wasilski's team, the computational methods were implemented using a rhodium catalyst in an ethanol dehydrogenation reaction. These methods were adjusted to develop a new model for an extended, stepped metal surface. The results for the hydrogen edge bridge interaction with the extended rhodium (211) surface are still pending, but the current calculated energy (using the best estimate with current results) for C-H cleavage and O-H cleavage of ethanol can be seen below. The results of other researchers from the group are also included in Table 1. to make future comparisons and establish trends.

Table 1. The reaction energy results for O-H and C-H bond cleavage for ethanol dehydrogenation over a rhodium surface in comparison to previous works.

Molecule (w/ Rhodium)	**Energy (211)** **RPBE functional**	**Energy (111)[4]** **RPBE functional**	**Energy (211)[7]** **PW91 functional**
Hydroxyethyl E= -261.28 eV	$\Delta E_{C\text{-}H}$: -0.43 eV	$\Delta E_{C\text{-}H}$: 0.36 eV	(Hydroxy alkyl) $\Delta E_{C\text{-}H}$: -0.55 eV
Ethoxy E= -261.66 eV	$\Delta E_{O\text{-}H}$: -0.81 eV	$\Delta E_{O\text{-}H}$: 0.01 eV	(Alcoxy) $\Delta E_{O\text{-}H}$: -0.97 eV
Hydrogen E= -214.16 eV *new $E_{Hydrogen}$ pending **Bare Surface** E= -209.57 **Ethanol** E= -265.43 eV			

By comparing results of this project (highlighted in blue) to the works of previous projects, it can be determined that the results of the new extended, stepped rhodium (211) surface closely resemble those of Ganjina Nagzibekova's results with a stepped Rh (211) surface for alcohol dehydrogenation reactions. One difference is that Gangina used a PW91 functional, while this study was done using an RPBE functional in VASP. RPBE functional results have been found to match closer to experimental results, so it can be assumed that Gangina's stepped Rh (211) results may be an overestimate of reaction energies. In comparison with the O-H and C-H cleavage data of Mindy Schueneman, the results are as expected. Mindy's study used a planar Rh (111) surface, which has been shown to be less reactive than stepped and kinked metal surfaces.

The method established in this paper will be further applied across this row of metals to both ruthenium and palladium.

4. Acknowledgements

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5. Cited Sources

1. Yoon, Y.; Kim, H.; Lee, J. Enhanced catalytic behavior of Ni alloys in steam methane reforming. *J. of Power Sources*. **2017**, *359*, 450-457.
2. Wang, Y.; Tang, Y.; Shao, Y. Theoretical investigation of the selective dehydration and dehydrogenation of ethanol catalyzed by small molecules. *J. of Molecular Graphics and Modelling*. **2017**, *76*, 521-534.
3. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865.
4. Schueneman, M.; Catalytic Ability of non Precious Metals on a (111) and (211) Metal Surface and Periodic Trends. *Wasileski Research Group*. UNC Asheville **2017**.
5. Hammer, B.; Hansen, L.; Nørskov, J. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B*, **1999**, *59(11)*, 7413-7421.
6. G. Nagzibekova, "Computational Investigation of Alcohol Dehydrogenation on an Extended Stepped Rhodium Surface Using Density Functional Theory." Wasileski Research Group. UNC Asheville **2018**.
7. Gross, E. K. U; Dreizler, R. M. Density Functional Theory. **1995**, *42*, 3.
8. *Shan, N.; Zhou, M.; Hanchett, M.K.; Chen J.; Liu, B. Practical principles of density functional theory for catalytic reaction simulations on metal surfaces – from theory to applications, *Molecular Simulation*, **2017**, *43:10-11*, 861-885.
9. G. Kresse and J. Hafner. Ab initio molecular dynamics for liquid metals. Phys. Rev. B, 47:558, **1993**.
10. G. Kresse and J. Hafner. Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. Phys. Rev. B, 49:14251, **1994**.
11. G. Kresse and J. Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mat. Sci., 6:15, **1996**.
12. G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B, 54:11169, **1996**.