Journal of Materials Science and Chemical Engineering, 2024, 12, 1-8
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

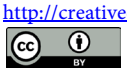
Convergence Issues Associated with Cutoff Energies and Ab Initio Studies of Adsorption of CO on W and Pt

Sathya Hanagud[1], Roussislava Zaharieva[2]

[1]School of Aerospace Engineering Georgia Institute of Technology, Atlanta, Georgia
[2]Bulgarian Academy of Sciences, Space Research Institute, "Acad. Georgy Bonchev" Str. Bl1 Sofia, Sofia, Bulgaria
Email: rsz@space.bas.bg

How to cite this paper: Hanagud, S. and Zaharieva, R. (2024) Convergence Issues Associated with Cutoff Energies and Ab Initio Studies of Adsorption of CO on W and Pt. *Journal of Materials Science and Chemical Engineering*, **12**, 1-8.
https://doi.org/10.4236/msce.2024.123001

Received: December13, 2023
Accepted: March 25, 2024
Published: March 28, 2024



Abstract

The experimental research programs of 1950s, to understand the adsorption of CO on W surfaces, changed to ab initio studies in 2000s. The goals were to seek improved practical applications. Most of the studies were based on density functional theory. Many studies also used programs, such as VASP (Vienna Abinitio simulation package) and CPMD. The computational procedures used plane wave approximations. This needed studies with selection of K points and cutoff energy selection to assure convergence in energy calculations. Observations and analysis of papers published from 2006 to 2022 indicate that the cutoff energies were selected arbitrarily without any needed convergence studies. By selecting a published 2006 paper, this paper has clearly showed that an arbitrary selection of cutoff energy, such as 460 eV, is not in the range of, cutoff energies that assure convergence of energy calculations, with ab initio methods and have indicated correction procedures.

Keywords

CO Adsorption, Tungsten and Pt surfaces, Cutoff Energy Selection, Convergence of Ab Initio Energy

1. Introduction

There are many published works on the ab initio studies of adsorption of CO on W(111) and Pt(111), starting with the work if Chen, Scholl and Johnson [1] in 2006 to publications in 2022 by Goonusooria [2] and J. C Tung *et al.* [3]. I have studied all these papers and noted discussions concerning inconsistency of ab

initio methods. I also have found one common issue in all these papers. In each of these papers, the cutoff energy has been arbitrarily selected to be approximately to be 460 eV, without any reference to any related convergence studies. Thus, I have selected the reference [1] by Chen *et al.* to illustrate the importance of convergence studies in selecting the cutoff energies as applied to Abinitio studies. This paper [1] is selected because the input variables are also clearly explained.

2. The Problem of Adsorption of CO on W(111)

Studies on the adsorption and chemisorption of CO on W started as research in experimental studies during late 1950s. Now, returning to the works of Chen, Scholl and Johnson, the objectives the paper are to focus on the mechanisms of adsorption of CO on W(111) by using density functional theory , that is based ab initio studies of the binding energy. Specifically they use VASP which is also known as Vienna Ab Initio Simulation Package. The publications in this area CO adsorption on W surfaces were relatively few. In a publication of 1999, Ryu *et al.* [4] present a study that uses molecular orbital theory, by using three layers. For a bcc metal three layers represent the minimum number of layers for W(111) surface studies. In 2006, Chen, Scholl and Johnson [1] present a density functional theory-based study of adsorption and disassociation of CO on W(111). In their studies, they calculate binding energies, vibrational frequencies and diffusion/disassociation pathways of CO on W. Specifically, they consider both clean and carbon-preadsorbed W(111) surfaces. They use Vienna ab initio simulation (VASP) package to perform the density functional theory-based calculations. They use revised Perdue-Burke-Ernzerhof (rPBE) exchange-correlation functional. Reasons for selecting rPBE, instead of PW91 are because of published results concerning prediction of binding energies that are compatible with experimental observations [1]. For electron-ion interactions, they use projector augmented wave (PAW) pseudo potentials. They also use a smearing technique, with a smearing width of 0.1 electron volts to minimize the errors in Hellmann-Feynman forces, due to electron free energy. The sampling of Brillouin zone is with 13 irreducible k-points ($5 \times 5 \times 1$) of Monkherst-Pack scheme. They also consider 6 to 11 layers of W-slab. Their calculations suggest that a consideration of 6 layers yield sufficient accuracy. However they do not perform any convergence studies with varying cutoff energies but they select 460 eV arbitrarily.

Calculations of binding energies (E_b) by Chen *et al.* [1] use the following definition.

$$E_b = E_a + E_{slab} - E_{a/slab}$$

By definition, a positive value of E_b corresponds to a stable adsorption $E_{a/slab}$.

All calculations are at the ground state or zero degrees Kelvin. In addition to the calculation of the binding energy, Chen, Scholl and Johnson also calculate vibrational frequencies by diagonalizing the Hessian matrix of selected atoms. The calculation of Hessian matrix also uses the VASP techniques. Their calcula-

tion of diffusion and disassociation pathways is by the use of nudged elastic band method.

Following the work of Chen, Scholl and Johnson, Scheijen *et al.* [5] Niemantsverdriet and Curulla-Ferre report a DFT-based study of the adsorption, Desorption and disassociation of CO on W(100) surface. Calculations in this paper follow the procedures of Chen, Scholl and Johnson for binding energies and vibrational frequencies. In the paper they also refer to an earlier theoretical work on adsorption of CO on W(100) by Lee *et al.*, [5] which uses extended molecular orbital by Huckel. The DFT-based theory for the adsorption of CO on W is still restricted to two papers.

In 2008, Yang *et al.* [6] report on experimental studies of the adsorption behavior of CO on W(110) [6] at elevated temperatures by using synchrotron radiation. Both the technique and observations at elevated temperatures pose new questions than answers, suggesting that additional ab initio studies are necessary to understand the mechanisms of adsorption, desorption and disassociation of CO on W.

3. Background of Binding Energy of Adsorption, and Cutoff Energy Convergence Study

The chemical reaction of CO with hydrogen is of interest in producing synthetic fuels [7] [8] [9]. The chemical reaction of interest involves the following types of chemical reactions.

$$(2n+1)H_2 + nCO = C_nH_{2n+2} + nH_2O$$

The resulting hydrocarbons are alkanes. All hydrocarbons other than n = 1 are of interest in producing synthetic fuels. The chemical mechanisms require conversion of CO to C-O bonds via possible initial formation of surface bound metal carbonyls. Thus, catalysts, such as cobalt, iron and ruthenium are necessary to complete the required chemical reaction through disassociation of CO, at temperatures varying between 150 to 300 degrees Celsius. Other catalyst, such as Nickel usually favors an undesirable product, such as methane (n = 1). During the past few years other catalysts, including tungsten, are subjects of investigation.

The original process is the result of studies by Franz Fischer and Hans Tropsch [8] during 1920s. Historically, the process benefits coal-rich geographical areas.

For example, Germany is the beneficiary of the process in producing fuel for trucks in 1930s. Other beneficiaries include South Africa. More recent exploration of the process is by U. S. Air force. Thus, the subject of adsorption is important.

There are many reported studies on the subject of the adsorption of CO on W since the 1960s. More specifically, CO adsorption on transition metal surfaces has been subject of significant interest from the point of view of understanding catalysis. Of special interest in studies related to W and CO is because of the opinion of many researchers that W is the borderline of disassociative adsorp-

tion as we move from left to right of the periodic table, of transition metals. There are significant amount of discussion concerning the disassociation and non disassociation of CO on W as a function of it's or different b states. Kim, Boo and Lee discuss this subject in 2009. Their discussions point in the direction of disassociative adsorption. In their paper, which is experimental in nature, they also display binding energies as a function of the temperature.

Calculations of binding energies (E_b) by Chen *et al.* use the following definition.

$$E_b = E_a + E_{slab} - E_{a/slab}$$

In this equation, E_a is the energy of the isolated molecule of CO. The term E_{slab} is energy of the W(111) slab and the term $E_{a/slab}$ is the energy of the slab with adsorbed CO. With this definition, a positive value of E_b corresponds to a stable adsorption. All calculations are at the ground state or zero degrees Kelvin in addition to the calculation of the binding energy.

Chen, Scholl and Johnson also calculate vibrational frequencies by diagonalizing the Hessian matrix of selected atoms. The calculation of Hessian matrix also uses the VASP techniques. Their calculation of diffusion and disassociation pathways is by the use of nudged elastic band method.

Following the work of Chen, Scholl and Johnson, Scheijen, Niemantsverdriet and Curulla-Ferre [8] report a DFT-based study of the adsorption, Desorption and disassociation of CO on W(100) surface. Calculations in this paper follow the procedures of Chen, Scholl and Johnson for binding energies and vibrational frequencies. In the paper they also refer to an earlier theoretical work on adsorption of CO on W(100) by Lee *et al.*, which uses extended molecular orbital by Huckel. The DFT-based theory for the adsorption of CO on W is still restricted to two papers.

4. The Issue of Convergence and Cutoff Energy Selection

To illustrate the point, we selected the adsorption CO on W(111) surface. In this paper, the adsorption of CO In the first part, the needed convergence studies are presented to select the cut-off energy and the K-points, (K point convergence's been discussed in [1]). The calculations are based on plane wave based density functional theory calculations. The specific numerical procedure is based on VASP and CPMD. Following the convergence studies, the next item of discussion is the accuracy of the presented binding energy. The binding energy calculation follows the standard procedure.

Density functional theory by Hohenberg and Kohn is the foundation for energy calculations in this paper. Specifically, the Kohn-Sham (KS) approach forms the basis for numerical calculations. The KS approach modifies the Hatree-Fock (HF) approach, to benefit from the single electron wave function approach of HF and leads to the following calculation of the ground state energy. In addition, the calculations use plane waves as the basis functions, for use with

metallic catalyst W and associated periodic boundary conditions. Because it is necessary to use finite number of plane waves in any practical calculation of energies, it is necessary to ensure that the selection of a finite number of plane waves. (For the corresponding k-point grid in the reciprocal space) and the associated cut-off energy leads to a satisfactory convergence of the calculated energies by the KS approach. Such convergence studies are especially important. Thus, first series of our calculation is to select the cut-off energy and the k-point grid. In the calculations, the exchange-correlation functional is the revised Perdue-Burke Ernzerhof functional. The k-point grid is 5 × 5 × 1 of Monkherst-Pack Scheme. Further finer grid does not improve the accuracy. Following Chen *et al.*, we select 8 layers. In the calculations by Chen *et al.*, The CO is on the top of W(111) surface, with use of (1 × 1) rhomboidal cell as the primitive cell.

In all the present calculations, in this paper, the unit cell is rectangular 2 × $\sqrt{3}$ unit cell (or 2 × 2 for convenience in presentation). There are 4 W atoms per layer, in comparison to one W atom of the paper by Chen *et al.* Then, we proceed to discuss the convergence studies as a function of the cut-off energy. Without any strain, Figure 1 illustrates the variation of binding energy with the cut-off energy.

Some details of the calculations are as follows. A first step is the geometry optimization.

Figure 2 illustrates the BCC sections that were used in the convergence studies.

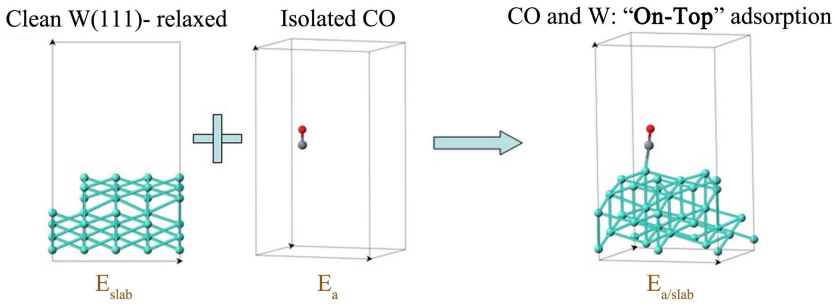


Figure 1. Geometry optimization.

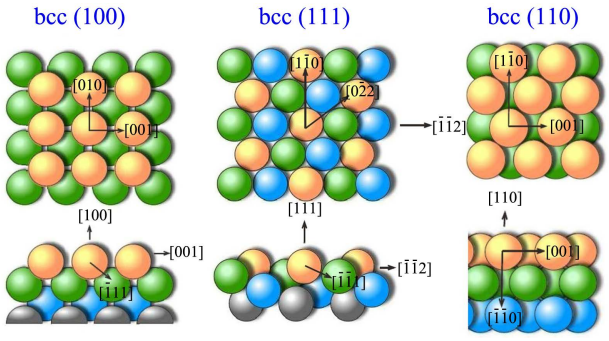


Figure 2. Three different surfaces of Tungsten (BCC).

Figure 3 illustrates the comprehensive results of the calculated energies as a function of selected cutoff energies. The different methods that were used are also indicated in the figure.

In Figure 3, 8 means 800 eV. Also In the paper by Chen *et al.*, the cut-off energy is only 400 eV (or approximately 29.4 Ry), which is not in the range of convergence. Yet, the resulting binding energy calculations are within 5%. Figure 3 clearly indicates that, for convergence of the binding energy, at least 700 eV or 50 Ry is necessary. The figure illustrates a summary of convergence of VASP/CPMD energy convergence, with increase in the selection of cutoff energy, Before the calculations were done for Figure 3, it was necessary to study convergence on W surfaces, convergence if CO alone, convergence of combined W and CO and the location of adsorption sites on W. Some details of the calculation are illustrated in Figures 4-7.

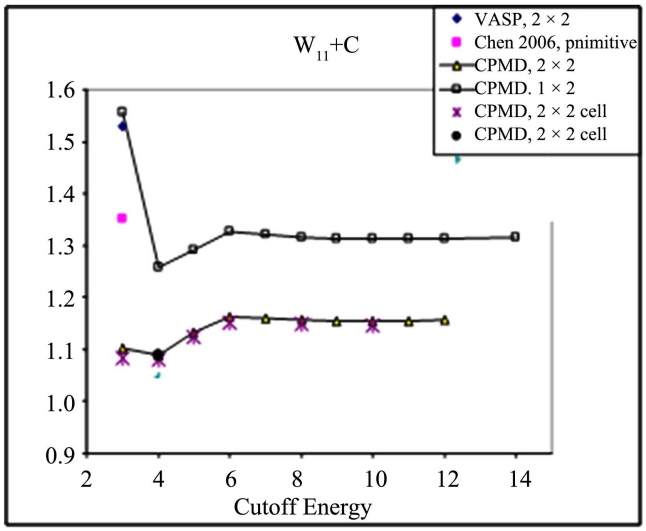


Figure 3. Calculated energy for selected cutoff energy.

E_{CUT} [Ry]	E_{TOT} [A.U.]
30	-214.859954
40	-214.884989
50	-214 885893
60	-214.886345
70	-214.886464
80	-214.886736
90	-214.887082
100	-214.887242
110	-214.887156
120	-214.886798

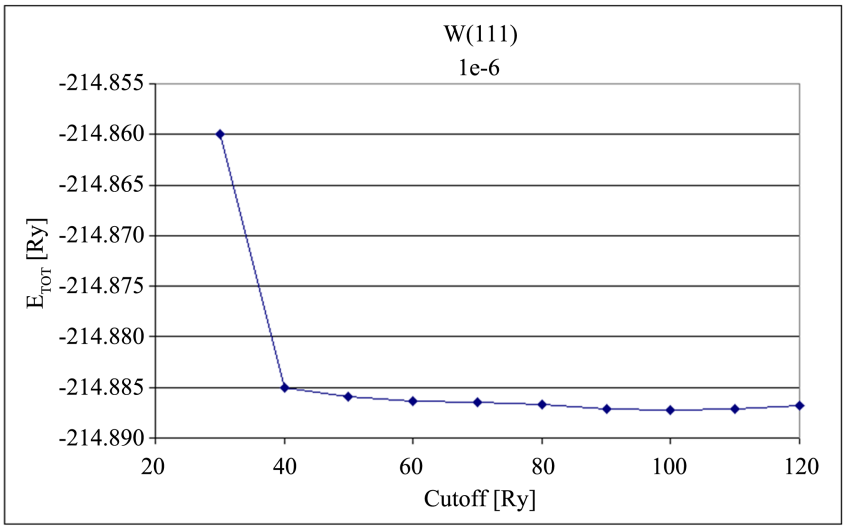


Figure 4. Energy convergence of W(111) with Cutoff energy selection.

E_{CUT} [Ry]	E_{TOT} [A.U.]	bond-length
30	-20.988396	1.215224
40	-21.325701	1.154511
50	-21.506361	1.140757
60	-21.600847	1.141831
70	-21.646731	1.138271
80	-21.666691	1.136239
90	-21.674822	1.135798
100	-21.677581	1.135590
110	-21.678292	1.135265
120	-21.678414	1.135335

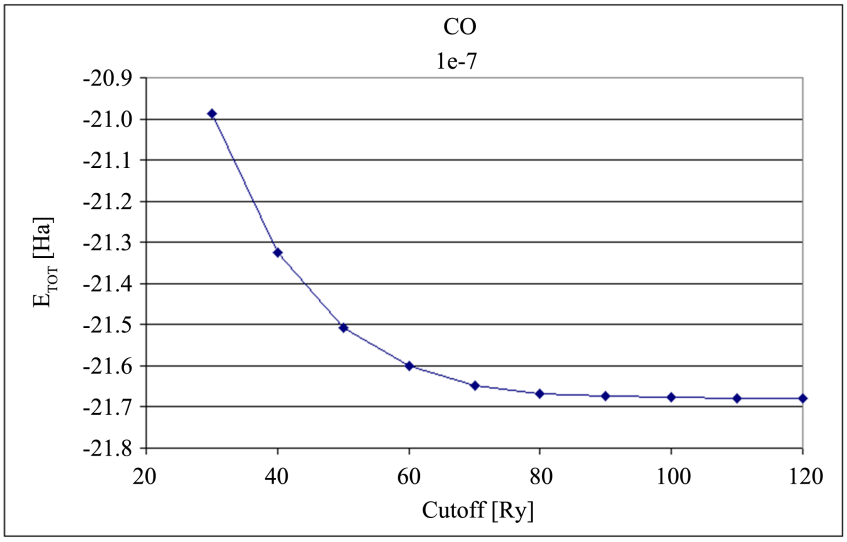


Figure 5. Energy convergence of CO with cutoff energy selection.

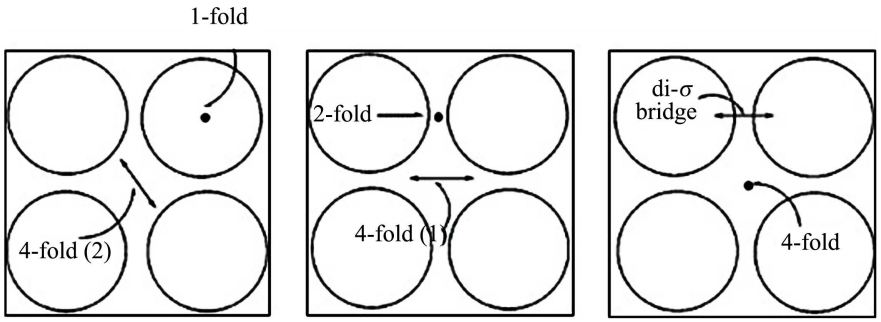


Figure 6. W(100) adsorption sites studies.

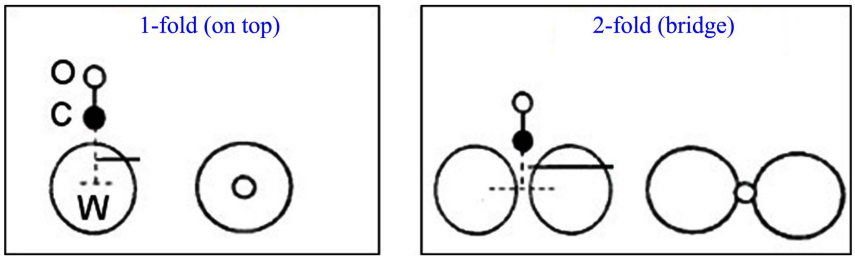


Figure 7. Adsorption site studies with CO and W surfaces.

5. Conclusion

This paper discusses the issue of selection of the cut-off energy when we use program packages, such as VASP or CPMD, that uses plane wave expansion. It is important that we check if the selected cut-off energy leads to converging energy solutions or we need to change the selection kf the cut-off energy. In the selected paper, the selected cut-off energy was approximately 400 eV while the needed cut-off energy is at least 700 eV for converging energy solution. The same conclusion applies to all other papers, in the period from 2006 to 2022 where cut-off energy was selected without investigating for convergence.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Chen, L., Scholl, D.S. and Karl-Johnson, J. (2006) First Principles Study of Adsorption and Disassociation of CO on W(111). *Journal of Physical Chemistry B*, **110**, 1344-1349. https://doi.org/10.1021/jp055374z

[2] Tung, J.C., *et al.* (2022) Ab Initio Studies of Work Function Changes of CO Adsorption Changes on Clean and Pd-Doped Zn Ga_2O_4 (111) Surfaces of Gas Sensors, *Applied Sciences*, **12**, 5978. https://doi.org/10.3390/app12125978

[3] Goonasooriya, G.T.K.K. and Saeys, M. (2018) CO Adsorption on Pt(111): From Isolated Molecules to Ordered High-Coverage Structures. *ACS Catalysis*, **11**, 1022-10233. https://doi.org/10.1021/acscatal.8b02371

[4] Ryu, G.H., *et al.* (1999) Molecular Orbital Study of the Interactions of CO Molecules Adsorbed on a W(111) Surface. *Surface Science*, **427-428**, 419-425. https://doi.org/10.1016/S0039-6028(99)00314-3

[5] Lee, Y., Lee, W. and Chun, K. (2000) Calculation of Surface Potential and Beam Deflection due to Charging Effects in Electron Beam Lithography. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, **18**, 3095. https://doi.org/10.1116/1.1319822

[6] Scheijen, F.E., *et al.* (2008) Adsorption, Desorptionband of CO on Tungsten (100), a DFT Study. *The Journal of Physical Chemistry C*, **112**, 7436-7444. https://doi.org/10.1021/jp711995d

[7] Yang, T.-S., Boo, J.-H., Lee, G.-H. and Lee, S.-B. (2008) Adsorption and Desorption of CO on W(110) Surfaces. *Bulletin of the Korean Chemical Society*, **29**, 1115-1120. https://doi.org/10.5012/bkcs.2008.29.6.1115

[8] Somorjai, G.A. (1994) Introduction to Surface Chemistry and Catalysis. Wiley, New York.

[9] Claridge, J.B., *et al.* (1998) New Catalysts for the Conversion of Methane to Synthesis Gas: Molybdenum and Tungsten Carbide. *Journal of Catalysis*, **180**, 85-100. https://doi.org/10.1006/jcat.1998.2260