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The Electronic Band Structure of Platinum Oxide (PtO)

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Abstract

We have performed the electronic band structure of the bulk and monolayer of PtO using the full potential linear muffin-tin orbital and the projector augmented wave method with the density functional theory. We applied the LDA and LDA+U scheme to both methods. It was found out that the LDA calculation of bulk PtO predicted a metallic nature in agreement with previous LDA and GGA calculations but in disagreement with the semiconductor nature favored by experiment. Our LDA+U calculation for both methods predicted PtO to be a semiconductor with a band gap value of 1.4 eV which is in reasonable agreement with experiment the experimental band gap value of 1.2 eV. The band structure of the monolayer PtO was found to be the same with the bulk in qualitative term. The position of the valence band maximum and the conduction band minimum are same as the bulk. The indirect band gap value of 1.4 eV is in agreement with the experimental value of 1.5 eV.

1.0 Introduction

PtO belongs to the technologically important group of noble-metal monoxides that includes species like NiO and PdO. It is an important technological material with application in gate electrodes in the fabrication of the next generation of large scale integrators and dynamic random access memories (DRAMs) [1]. It is of interest in experimental chemistry, for example, as dehydrogenation catalysts [2]. It has also being used in sensors and photocathode in water electrolysis [3]. Thin films of platinum oxides are promising candidates for electrode materials in ferroelectric memory capacitors [4]. It has also being shown in Lee and Lee [5]; and Grill and Brady [6] that PtO can improve the endurance properties of the ferroelectric capacitor.

Platinum oxide has received experimental and theoretical attention. The optical properties of PtO have been studied experimentally in [7,8,9]. McBride et al reported PtO to be a nonmagnetic semiconductor while Abe et al reported PtO to be metallic. The phonon spectra for PtO have also being reported [10]. A number of studies have been carried out on the electronic band structure of bulk PtO [1,3,11,12]. Previous band structure calculation of PtO have either failed to predict its semiconducting nature or have underestimate its band gap value.

In this paper, the electronic band structure of bulk and monolayer PtO have being studied using the LDA+U scheme to predict corrected the experimentally observed band gap value. To the best of my knowledge this is the first time the LDA+U scheme is applied to the electronic band structure of bulk PtO. Also this is the first time the electronic band structure of the nanosize PtO is carried out.

2.0 Computational Detail

PtO have the tetragonal structure with space group D_{4h}^{9} with two formula unit per unit cell. All calculations were performed with the experimental geometry taking from [8]. The lattice constants are a = 3.0777 Å and c = 5.3400 Å. The structure of PtO is shown in Figure 1.

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In this study, we have performed the electronic band structure of bulk and 2-d platinum oxide using the full potential linear muffin-tin orbital method (FP-LMTO) and projector augmented wave (PAW) [13] pseudopotential methods using the LDA+U [14] scheme within the density functional theory. The deficiency of the LDA can be overcome by the addition of an orbital-dependent correction to LDA potentials. The total energy functional is written as

$$\begin{aligned} E &= E_{LDA} - [UN(N-1)/2 - JN(N-2)/4 \\ &+ \frac{1}{2}\sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2}\sum_{m\neq m',m',\sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma} \end{aligned} \quad (1)$$

where U and J are the screened Coulomb and exchange parameter, $n_{m\sigma}$ is orbital occupancy, $U_{mm'}$ and $J_{mm'}$ are matrices given by

$$\begin{aligned} U_{mm'} &= \sum_k a_k F^k \\ J_{mm'} &= \sum_k b_k F^k \end{aligned} \quad (2)$$

where F^k are Slater integrals, and a_k and b_k are given by

$$\begin{aligned} a_k &= \frac{4\pi}{2k+1}\sum_{q=-k}^{k} \langle lm | Y_{kq} | lm \rangle \langle lm' | Y^*_{kq} | lm' \rangle \\ b_k &= \frac{4\pi}{2k+1}\sum_{q=-k}^{k} \left| \langle lm | Y^*_{kq} | lm' \rangle \right|^2 \end{aligned} \quad (3)$$

The expression for the orbital dependent one-electron potential is given by

$$\begin{aligned} V_{m\sigma}(\mathbf{r}) &= V_{LDA}(\mathbf{r}) + \sum_{m'} (U_{mm'} - U_{eff}) n_{m-\sigma} \\ &+ \sum_{m'\neq m} (U_{mm'} - J_{mm'} - U_{eff}) n_{m\sigma} \\ &+ U_{eff}\left(\frac{1}{2} - n_{m\sigma}\right) - \frac{1}{4}J \end{aligned} \quad (4)$$

where

$$U_{eff} = U - \frac{1}{2}J \quad (5)$$

To define all three integrals from U and J one needs to know only the ratio F^4/F^2. The expression for F^4 and F^2 are given as

$$F^2 = \frac{14}{1.625} J \quad (6)$$

$$F^4 = 0.625 F^2 \quad (7)$$

The screen coulomb interaction U and exchange parameter J used in the PAW calculation and the interpolation formula for the slater integral used in Bandlab calculation were taking from [20].

For exchange and correlation, the local density approximation (LDA) as parametrized in [15] was used for the FP-LMTO while the parametrization of [16] was used for the pseudopotential. The Abinit [17,18] and Bandlab [19] computer packages which implements pseudopotential and FP-LMTO method respectively were used in the calculations. For the brillouin zone integration, a k-point mesh of 45 was used for the bandlab calculation while a k-point mesh of 128 was used for the PAW calculation. The self-consistency calculation was assumed to have converged when the difference in energy between subsequent iteration was 1.0×10^{-10}. A kinetic energy cut-off of 20 Ha was used for the plane wave and PAW generation. Relativistic effect was also includes in the calculations. For the 2-d calculation, a mesh of (8x8x1) *k*-points generated by the method of [21] was used.

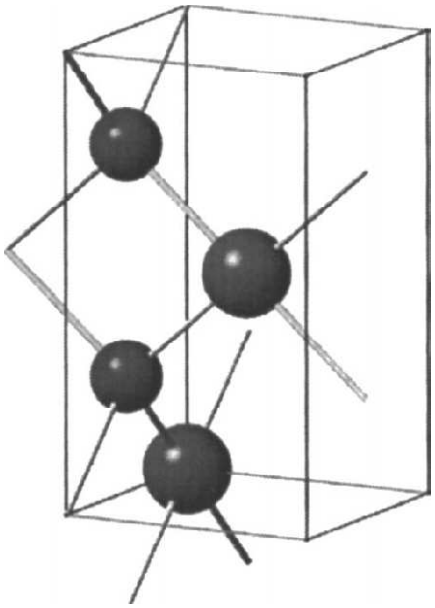

Figure 1: Tetragonal PtO unit cell. Platinum is shown in larger spheres [1]

3.0 Results and Discussion

The electronic band structure of bulk PtO of LDA calculation from PAW and FP-LMTO plotted along high symmetry point in the first Brillouin zone (BZ) are shown in Figures 2 and 3 respectively. The result from the Abinit (LDA) and Bandlab (LDA) calculations shown in Figures 2 and 3 respectively show the highest occupied band and the lowest unoccupied band crossing the Fermi level at the vicinity of the high symmetry point M. The results shown in Figures 2 and 3 also show agreement both in qualitative and quantitative term with result from previous LDA and GGA results [1,3]. They all predict PtO to be semi-metallic. The tetragonal crystal field symmetry in PtO splits the t_{2g} 5d states into the *xy*, *xz* and *yz* components, and the e_g states into the $\left(x^2 - y^2\right)$ and $\left(3z^2 - r^2\right)$ components. The *xz* and *yz* components hybridize especially strongly with the nearest four oxygen atoms. The other d states hybridization with O 2p orbitals is much weaker.

Figures 4 and 5 present the band structure of bulk PtO along high symmetry point in the first BZ of LDA+U calculation from PAW and FP-LMTO respectively. The results from both methods are in qualitative and quantitative agreement. As seen from Figure 4 and 5, the top of the valence band is at the M high symmetry point while the bottom of the conduction band is at the Γ high symmetry point. This implies that the nature of the band gap is indirect. The failure of the LDA in underestimation of the band gap of this transition metal oxide is due to the absence of the potential jump which appears for the exact density functional [14]. Gunnarsson and Schonhammer [22] showed that the discontinuity in the one-electron potential can give a large contribution to the band gap. To overcome this deficiency, an orbital dependent correction is added to the LDA potential. This induces an upward shift of the unoccupied 5d state and a downward shift of the occupied states. For both calculations a band gap value of 1.4 eV was obtained, this is in agreement with the experimental value of 1.2 eV [23]. Uddin et al [1] using the hybrid functional (HSE) obtained a direct band gap value of 0.86 eV at the M symmetry point. Also Hass and Carlsson [11] in their augmented spherical wave (ASW) method obtained a band gap value of 0.7 eV while Ahuja et al [12] using linear-muffin-tin orbital method in the atomic-sphere approximation (LMTO-ASA) found a band gap value of 0.6 eV. These studies have all underestimated the band gap value of PtO.

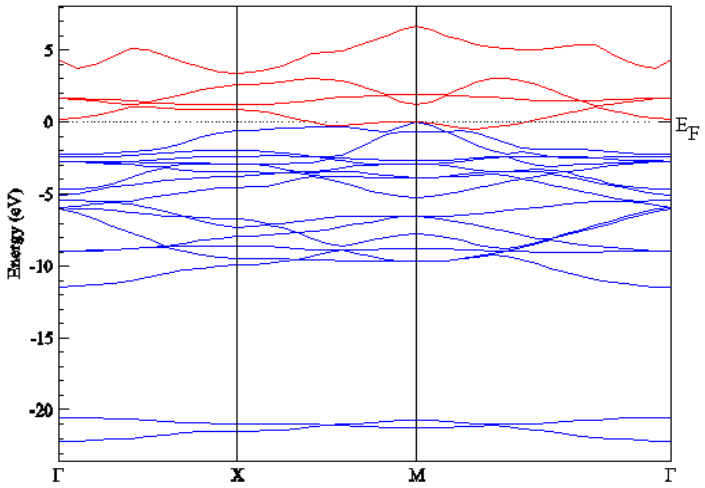

Figure 2: The band structure of PtO from PAW. E_F indicates the Fermi energy.

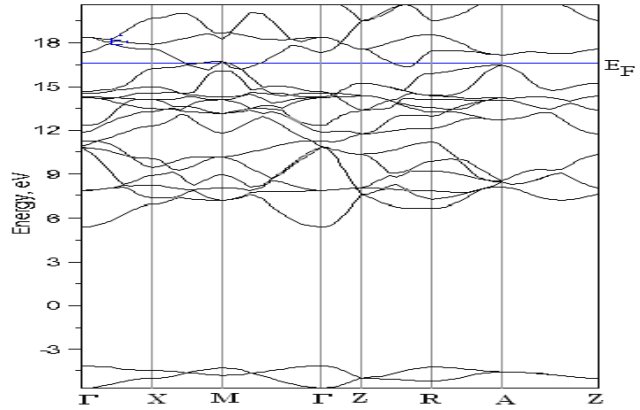

Figure 3: The band structure of PtO from FP-LMTO (LDA). E_F indicates the Fermi energy.

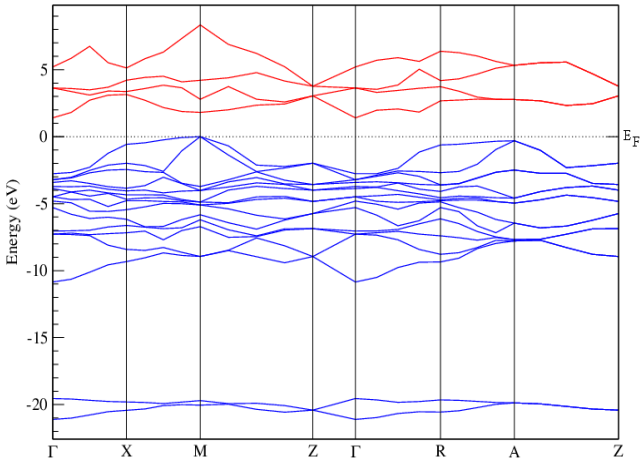

Figure 4: The band structure of PtO from PAW (LDA+U). E_F indicates the Fermi energy.

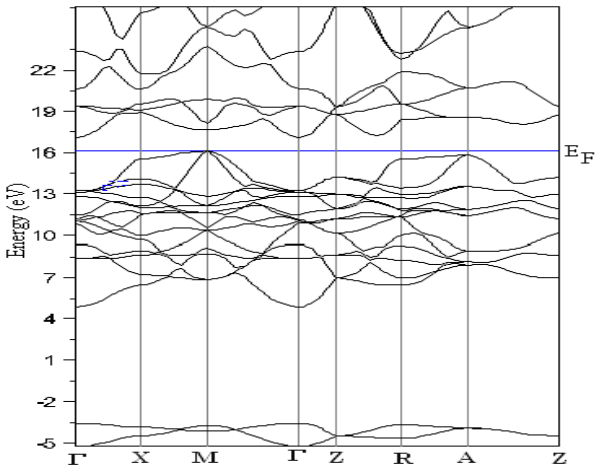

Figure 5: The band structure of PtO from FP-LMTO (LDA). E_F indicates the Fermi energy.

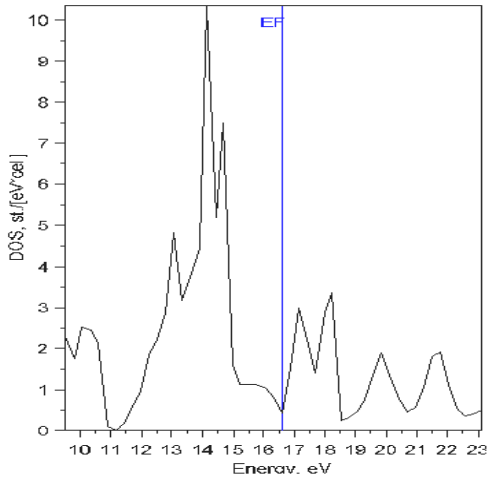

Figure 6: The density of states of PtO from FP-LMTO (LDA). E_F indicates the Fermi energy. The Fermi energy is at 16.6 eV.

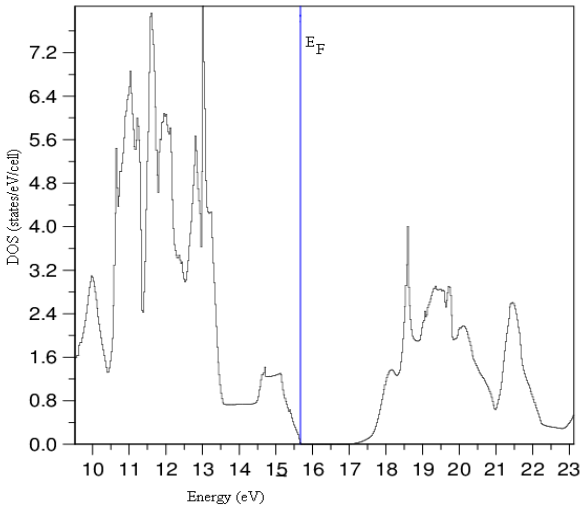

Figure 7: The density of states of PtO from FP-LMTO (LDA+U). E_F indicates the Fermi energy. The Fermi energy is at 15.7 eV.

The total density of states (DOS) for PtO from FP-LMTO (LDA) and (LDA+U) are shown in Figures 6 and 7 respectively. Figure 6 show that PtO is metallic which agrees with the LSDA result of [1]. The main feature of the LDA DOS is the d dominated valence band and the hybridization of the 5d of Pt with the 2p of oxygen. In Figure 7, the band gap opening is well reproduced in the LDA+U calculation of the FP-LMTO method. Again it is seen that the introduction of the orbital dependent correction to the LDA has caused an upward shift of the conduction band and a downward shift of the valence band which leads to a gap opening up around the Fermi energy.

Figure 8 show the band structure of 2-d monolayer PtO from the PAW calculation. It is observed that the band structure for bulk and surface PtO are qualitatively the same. In otherwords, the position of the valence band maximum and the conduction band minimum are same as in the bulk. The band gap value of 1.4 eV obtained for the monolayer is in agreement with the optical experiment of [24] where an indirect band gap of 1.5 eV was obtained as measured from their graph. The density of states for the monolayer is presented in figure 9. It is seen that the band gap of the monolayer of PtO is well reproduced in the density of states calculation.

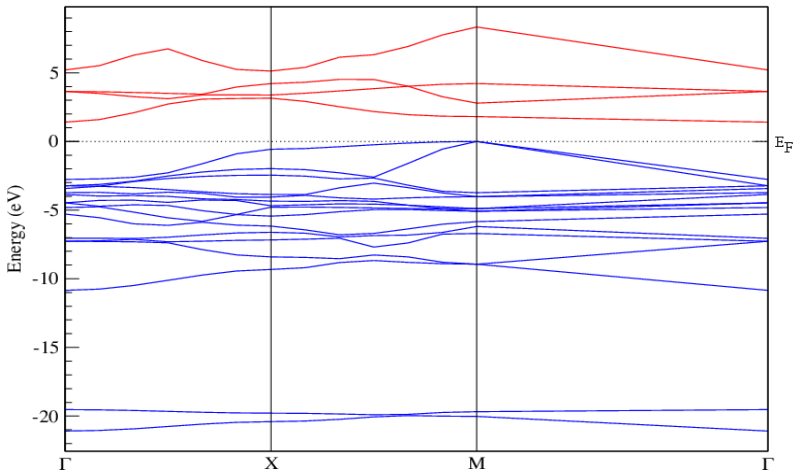

Figure 8: The band structure of monolayer PtO. E_F indicates the Fermi energy. A band gap of 1.4 eV was obtained.

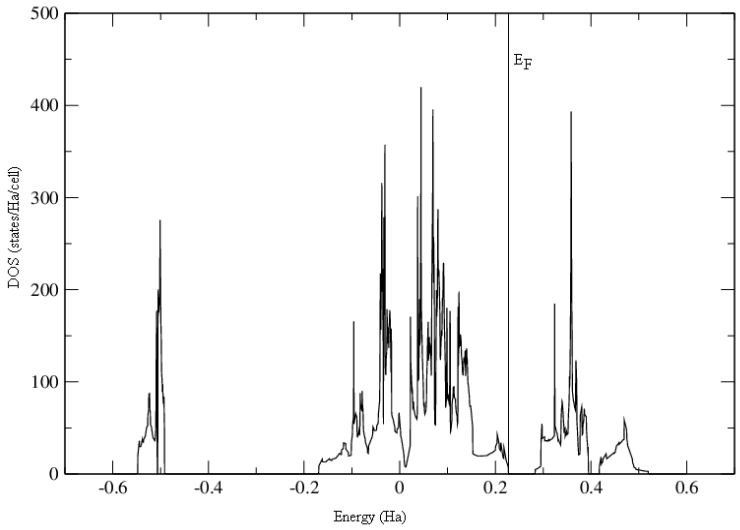

Figure 9: density of states of monolayer PtO. E_F indicates the Fermi energy. The Fermi energy is at 0.21 Ha

Conclusion

We have performed the electronic band structure of the bulk and monolayer of PtO using the full potential linear muffin-tin orbital and the projector augmented wave method with the density functional theory. We applied the LDA+U scheme to both methods. It was found out that the LDA calculation of bulk PtO predicted a metallic nature. This is in agreement with previous LDA and GGA calculations. Our LDA+U calculation for both methods predicted PtO to be a semiconductor. This is in reasonable agreement with experiment. The band structure of the monolayer PtO was found to be in agreement with experiment.

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