Reinvestigating oxygen adsorption on Ag(111) by using strongly constrained and appropriately normed semi-local density functional with the revised Vydrov van Voorhis van der Waals force correction

Accepted Manuscript: This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination, and proofreading process, which may lead to differences between this version and the Version of Record.

Cite as: J. Chem. Phys. (in press) (2021); <https://doi.org/10.1063/5.0073407>

Submitted: 30 September 2021 • Accepted: 23 November 2021 • Accepted Manuscript Online: 23 November 2021

Jack Jon Hinsch, Junxian Liu and Yun Wang

View Online

Export Citation

CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[A consistent and accurate ab initio parametrization of density functional dispersion correction \(DFT-D\) for the 94 elements H-Pu](#)

The Journal of Chemical Physics **132**, 154104 (2010); <https://doi.org/10.1063/1.3382344>

[Note: Assessment of the SCAN+rVV10 functional for the structure of liquid water](#)

The Journal of Chemical Physics **147**, 216101 (2017); <https://doi.org/10.1063/1.5006146>

[Perspective on density functional theory](#)

The Journal of Chemical Physics **136**, 150901 (2012); <https://doi.org/10.1063/1.4704546>

Challenge us.

What are your needs for
periodic signal detection?

Zurich
Instruments

Reinvestigating oxygen adsorption on Ag(111) by using strongly constrained and appropriately normed semi-local density functional with the revised Vydrov van Voorhis van der Waals force correction

Jack J Hinsch ^a, Junxian Liu ^a, and Yun Wang ^{a*}

Author affiliations

^a School of Environment and Science, Centre for Catalysis and Clean Energy, Griffith University, Gold Coast, QLD 4222, Australia

E-mail: yun.wang@griffith.edu.au

Abstract

While density functional theory (DFT) at the generalized gradient approximation (GGA) level has made great success in catalysis, it fails in some important systems, such as the adsorption of the oxygen molecule on the Ag(111) surface. Previous DFT studies at the GGA level revealed theoretical inconsistencies on the adsorption energies and dissociation barriers of O₂ on Ag(111) in comparison with the experimental conclusion. In this study, the SCAN-rVV10 method at the meta-GGA level with the non-local van der Waals (vdW) force correction was used to reinvestigate the adsorption properties of O₂ on the Ag(111) surface. The SCAN-rVV10 results successfully confirm the experimental observation that both molecular and dissociative adsorption can exist for oxygen on Ag(111). The calculated adsorption energy for the physisorption state and the relevant dissociation energy barrier are close to the experimental data. It demonstrates that SCAN-rVV10 can outperform functionals at the GGA level for O₂/Ag(111). Therefore, our findings suggest that SCAN-rVV10 can be the desired method for systems where the correct description of intermediate ranged vdW forces are essential, such as the physisorption of small molecules on the solid surface.

I. Introduction

Density functional theory (DFT) based theoretical studies have delivered significant achievement in materials design for thermal and electrochemical catalysis^{1,2}. One of the recent DFT research focuses is to identify the active sites of electrocatalysts and further guide the design of high-performance materials for the hydrogen economy as to address the continuously growing energy consumption²⁻⁶. This technology allows for the direct conversion between chemical energy and electricity⁷. Due to their low environmental impact, they are desirable for a diverse range of applications. However, electrocatalysts for the cathodic oxygen reduction reaction (ORR) is far behind industry needs. Generally, these Pt-based catalysts are expensive, resulting in 36-56% of the fuel cell's cost coming from the electrocatalysts alone^{8,9}. Therefore, screening an alternative with a much lower price is imperative. Silver has been proposed as an alternative for electrocatalytic ORR in fuel cells as it has many similar properties to Pt and is more abundant¹⁰⁻¹³. Moreover, oxygen adsorption is also essential in many disciplines including epoxidation/oxidation for organic synthesis, reducing harmful substances and energy production/storage^{10, 13-15}. To this end, great efforts have been devoted to understanding the adsorption properties of O₂ on the Ag(111) surface, which is the most exposed facet of the Ag crystal due to its high thermodynamic stability^{16, 17}.

However, previous studies reveal inconsistent results about the adsorption properties of O₂ on the Ag(111) surface¹⁸. The calculated adsorption strengths via the DFT at the generalized gradient approximation (GGA) PBE level is -0.66 eV^{8, 19}, around 50.1% stronger than the experimental results of -0.4 eV through thermal-programmed desorption (TPD)²⁰⁻²². Through TPD experiments, the oxygen dissociation energy barrier was experimentally valued at 0.54 ± 0.26 eV²⁰⁻²². As a comparison, Xu et al. found that the corresponding theoretical dissociation energy barrier was 1.11 eV¹⁹. Such computational results are almost double the experimental data. Furthermore, the adsorbed state of O₂ on Ag(111) is also controversial¹⁸. While the experimental results indicate that both physisorption and chemisorption states can coexist on the surface^{21, 23, 24}, DFT-based calculations suggest only a chemisorbed species is present^{19, 21, 25}. Given that the adsorption of O₂ is weak, such interactions are greatly influenced by the vdW forces. However, DFT at the GGA level does not incorporate the vdW interactions²⁶⁻²⁹. Kim et al. showed that without a vdW correction, PBE calculations often generate incorrect cohesive energies, lattice parameters, adsorption energies and binding energies²⁷. Therefore, coupling a vdW correction method becomes an attractive solution. Mahlberg et al. and Alyssa et al. revealed that rPBE calculations combined with a vdW correction method can greatly

improve the accuracy of modelling physisorbed and chemisorbed species^{30,31}. Tsuzuki et al. also demonstrated that PW91, PBE and, rPBE calculations coupled with the D3 vdW correction method can better model intermolecular interactions³². However, Yan et al. used the PW91 functional with the D2 van der Waals (vdW) correction methods and found the O₂ dissociation energy was 1.07 eV³³, which is still much higher than the experimental data. Therefore, it is worthy to use recently developed exchange-correlation (XC) functionals at a higher level with better vdW correction to reinvestigate oxygen adsorption properties on Ag(111).

Previous studies suggest that the strongly constrained and appropriately normed (SCAN) semi-local XC functional at the meta-GGA level³⁴ with the revised Vydrov van Voorhis van der Waals correction functional (rVV10)³⁵ is promising. SCAN-rVV10 has outperformed many other comparable computational methods for molecular complexes, solids, benzene adsorption, 2D materials and layered materials^{27, 36}. Through a comparison with the Perdew–Burke–Ernzerhof (PBE) and PBE-D3 functionals³⁶, SCAN-rVV10 can calculate ground-state structures and geometric features exhibiting minimal bias towards metal-anion coordination environments. The results were also highly reproducible, facilitated by using constant local environments. Moreover, SCAN-rVV10 is sensitive to different types of bonding, which is critical for medium-ranged vdW interactions.

In this study, SCAN-rVV10 was employed to reinvestigate the oxygen adsorption properties on Ag(111) through comparison with the PBE, PBE-D3 and reported experimental results. Our results demonstrate that SCAN-rVV10 can be used to solve the long-standing theory-experiment discrepancy observed in the oxygen adsorption on Ag(111).

II. Computational details

All DFT computations were performed using Vienna Ab initio Simulation Package (VASP)³⁷ based on the projector augmented wave (PAW) method³⁸. For the electron-electron exchange and correlation interactions, the SCAN functional at the meta-GGA level was used³⁴. The PBE functional at the GGA level was also employed for comparative purposes³⁹. To better consider the vdW interaction, D3, rVV10, and two optimized versions of the vdW-DF, including optPBE and optB88 were employed^{34, 35, 39-42}. The electron-ion interaction was described using the PAW potentials, with 5s¹4d¹⁰, 6s¹5d⁹, 2s²2p⁴ and 2s²2p² valence electrons of Ag, Pt, O and C, respectively. The kinetic energy cut-off value for the plane waves was set to 520 eV to expand the smooth part of the wave function. During geometric optimization, atoms could relax until the Hellmann-Feynman forces were smaller than 1×10^{-3} eV/Å. The

convergence criterion for the electronic self-consistent loop was set to 1×10^{-5} eV. The gamma-centered k-point meshes utilized a reciprocal space resolution of $2\pi \times 0.02 \text{ \AA}^{-1}$.

The Ag(111) and Pt(111) surfaces were modeled by a $(2\sqrt{3} \times 3)$ supercell with a four-layer slab by using the theoretical lattice constants, separated by a vacuum of 15 Å to avoid interaction between the surfaces of neighboring slabs along the z-direction. When the surface structures were optimized, the top two layers of the (111) surfaces and the adsorbates were allowed to relax while the bottom two layers were fixed at the bulk position.

The binding energy of O₂ gas was calculated as the following equation:

$$E_b = E_{O_2} - 2 \times E_O \quad (1)$$

where E_{O_2} and E_O are the energies of the O₂ molecule and the isolated O atom, respectively.

The cohesive energy of cubic Ag metal was calculated using the equation below:

$$E_{coh} = (E_{bulk} - 4 \times E_{atom})/4 \quad (2)$$

where E_{bulk} and E_{atom} are the energies of the bulk Ag crystal and isolated Ag atom, respectively.

Meanwhile, the adsorption energies of O* and O₂* were calculated using the formula:

$$\Delta E_{ads} = \frac{1}{N} (E_{ad/surf} - E_{surf} - NE_{ads}) \quad (3)$$

where N is the number of adsorbates per unit cell, $E_{ad/surf}$, E_{surf} and E_{ads} are the energies of the Ag(111) surface with the adsorbate, the pristine silver surface and the isolated adsorbate, respectively. For the calculations of the isolated atoms and molecules, a $(20 \times 20 \times 20) \text{ \AA}^3$ unit cell and a Gamma-only k-point grid were used. The bonding strength of O-O bond of the adsorbed oxygen molecule was analyzed through the crystal orbital Hamilton population (COHP) analysis⁴⁰. The O₂ dissociation energy barrier was investigated using the climbing image nudged elastic band (CI-NEB) method with eight images between the initial and final states⁴³.

III. Results and Discussion

3.1 Oxygen molecule, Ag crystal and Ag(111)

The SCAN-rVV10 method was first evaluated by using the gaseous O₂, Ag crystal and a pristine Ag(111) surface as model systems. The structural and energetic properties were calculated and compared with the literature (see **Table 1**). Our PBE and PBE-D3 results were comparable to the reported data. The SCAN-rVV10, PBE-D3 and PBE calculations predicted similar binding energies, vibrational frequencies and O-O bond lengths. However, without the

rVV10 functional, the SCAN method predicted a large cohesive and binding energy. The binding energy of O₂ was at least 26.0% larger than the experimental data for all methods. Therefore, the SCAN-rVV10 method cannot solve this DFT problem on the isolated oxygen molecule^{19, 39, 44}. This over-binding mainly stems from the SCAN functional as seen in **Table 1**^{36, 45}. This method has shown to be on par with other semi-local functionals²⁷. Although, SCAN-rVV10 outperformed both GGA methods. The non-local rVV10 method is important to correct this overestimation as it adds the non-local element to the exchange calculations. The short-range dampening via the *b* parameter in the rVV10 method can counteract the assumptions of SCAN^{34, 36, 46}.

SCAN-rVV10 outperformed PBE, SCAN and PBE-D3 when calculating the cohesive energy of the Ag crystal. The PBE-D3 and PBE data were 11.2% and 21.1% smaller than the empirical result, respectively. Here, the SCAN method does the majority of the work in SCAN-rVV10 as such systems have insignificant vdW forces³⁶. The 17 exact constraints that guided SCAN's development allow for excellent error cancellation between correlation and exchange energies, which is important for metals^{27, 36, 46, 47}. SCAN-rVV10 and SCAN also performed well at predicting the Ag lattice constant. It suggests that the SCAN-rVV10 can improve the calculation accuracy in terms of the energetic properties of crystals³⁶.

Table 1: The calculated properties of the O₂ molecule, bulk Ag and pristine Ag(111). The binding energy of O₂ is E_b , the bond length is $do-o$, and the vibrational frequency is $vo-o$. The properties of the Ag crystal including, the lattice constant (a) and cohesive energy (E_{coh}). The Ag(111) surface's $\Delta 12$ and $\Delta 23$ interlayer relaxation are also shown.

	E_b (eV)	$do-o$ (Å)	$vo-o$ (cm ⁻¹)	a (Å)	E_{coh} (eV)	$\Delta 12$	$\Delta 23$
SCAN-rVV10	-6.65	1.225	1612	4.06	2.517	-0.87%	-0.37%
SCAN	-6.93	1.244	1628	4.08	3.059	-0.80%	-0.30%
PBE-D3	-6.75	1.233	1568	4.07	2.149	-0.80%	-0.81%
PBE	-6.75	1.233	1562	4.145	1.908	-0.18%	-0.52%
PBE ^{16, 39, 48}	-6.24	1.21		4.17	2.52	-0.3%	0.04
rPBE ^{15, 19, 49}		1.24		4.125			
PW91 ^{19, 34, 39}	-6.20	1.24	1551	4.12			
EXP. ^{10, 38, 39, 50}	-5.12	1.207	1580	4.09	2.420	-1.0%	-0.2%

The total density of states (TDOS) of the Ag crystal was calculated using different methods to understand the impact of SCAN-rVV10 on the electronic properties (see **Figure 1**). The PBE results were almost identical to the reported data^{51, 52}. However, SCAN-rVV10 and SCAN downshift by roughly 0.5 eV. The shift in DOS peaks matched the trend of the cohesive energy of the Ag crystal by using different computational methods. Again, for this metal system, the SCAN functional is causing the greatest change due to a larger contribution by its exchange term at the meta-GGA level^{17, 34, 36, 46, 47}.

Figure 1: Total density of states of bulk Ag using SCAN-rVV10, SCAN, PBE-D3 and PBE.

The relaxation of the clean Ag(111) surface differs with each functional. All the computational results agree with the experimental observations that the close-packed Ag(111) surface exhibits minimal relaxation⁵⁰. The PBE calculations found a small Δ_{12} and Δ_{23} interlayer relaxation of -0.18% and -0.52%, correspondingly. Meanwhile, PBE-D3 predicted a Δ_{12} and Δ_{23} distance of -0.80% and -0.81%, respectively. SCAN-rVV10 results revealed a Δ_{12} and Δ_{23} relaxation of -0.87% and -0.37%, respectively. SCAN predicted a similar Δ_{12} and Δ_{23} relaxation of -0.80 and -0.30%, correspondingly. The interlayer distance is strongly governed by the vdW interactions⁵³. As PBE does not describe the vdW forces, its results differ from other methods^{18, 39}. The methods with vdW correction can predict more accurate surface properties.

3.2 Molecular adsorption

For the molecular adsorption, the hollow (H), long-bridge (LB) and short-bridge (SB) sites were investigated based on previous studies^{10, 15, 54}. All O-O bonds were parallel to the (111) surface and interacted with three, four and, two Ag atoms at the H, LB and SB sites, respectively (see **Figure 2**). At the LB adsorption site, two O atoms were above the surface on the hcp and fcc sites, respectively. As a comparison, the O₂ molecule orientation at the SB site was perpendicular to that at the LB site. At the H site, the O₂ molecule was above the surface at the fcc site.

The molecular oxygen adsorption properties varied at the adsorption sites. The O-O bond lengths are listed in **Table 2** because the bond distance is an important indicator of bond strength⁵⁵. The SCAN-rVV10 results reveal that two O atoms were 1.48 Å above the surface at the LB adsorption site. The O-O bond length increased by 17.8%. The O-O bond length at the SB site was almost identical to the isolated O₂ molecule, which suggests a weak adsorption strength. The weak adsorption was further supported by a distance between O₂* and the (111) surface of 1.57 Å. At the H site, the O-O bond length was similar to the LB site. However, O₂* has the largest distance to the surface of 1.77 Å at the H site. SCAN-rVV10 predicted the adsorption energy of the LB and SB sites at -0.23 eV and 0.85 eV, respectively (see **Table 2**). The O₂ has the lowest adsorption energy at the H site of -0.38 eV, which matches the TPD experimental value of -0.4 eV.

Figure 2: The cross-sectional (bottom) and top (above) view of molecular adsorption configurations on the Ag(111) surface at **a)** hollow (H), **b)** short-bridge (SB), and **c)** long-bridge (LB) sites. Color code: silver, Ag; red, O.

The adsorption strength of molecular oxygen on Ag(111) was also investigated using the PBE, SCAN, PBE-optB88, PBE-optPBE and PBE-D3 methods. The PBE, SCAN and PBE-optPBE results indicate that there is no molecular adsorption state for O₂ on Ag(111), which is the same as similar studies at the same level^{8, 10, 18, 19, 31, 54, 56-58}. However, both molecular and dissociative adsorption states were suggested from experiments^{21, 23, 24}. PBE-D3 and PBE-optB88 results can qualitatively match the experimental observation. However, their adsorption strength is 72.5% and 32.5% weaker than the empirical value, respectively. It suggests that some correction methods, such as D3 and optB88, can improve the intermediate-ranged vdW predictions. However, only SCAN-rVV10 here can correctly replicate the experiment. The success of SCAN-rVV10 may be because SCAN can accurately predict surface properties (See **Table 1**), while the long-range rVV10 correction method is suitable for the description of weak O₂ adsorption^{42, 59}. Additionally, rVV10 models the interactions between electron clouds, which is more reflective of O₂^{35, 36}. Therefore, our comparative results further reaffirm the proficiency of SCAN-rVV10 as a cost-effective approach for this type of intermediate-ranged adsorption. To this end, only SCAN-rVV10 is used in modeling O₂ dissociation, along with the most widely used PBE and PBE-D3 calculations for comparative purposes.

The magnetic moment and vibrational frequency for all sites were within expected values. The vibrational frequency was larger than experiments have shown, but this was an already well-understood limitation of DFT^{22, 51, 60, 61}. The calculated magnetic moments suggest that the oxygen molecule becomes peroxo with a charge of -2 after adsorption in all our considered systems except at the SB site when using the SCAN-rVV10 method. Our theoretical results are, again, consistent with the experimental observation that the peroxo species was present in the molecular adsorption state⁶².

Table 2: Calculated adsorption energy (ΔE_{ads}), O-O bond length (d_{o-o}), O-O vibration frequency (ν_{o-o}), and magnetic moment (m) of molecular O₂ on Ag(111) at different sites along with the reported theoretical results and experimental data by using the electron energy loss spectroscopy (EELS) and TPD.

	Surface cell	Adsorption site	ΔE_{ads} (eV)	d_{o-o} (Å)	ν_{o-o} (cm ⁻¹)	m (μ_B)
SCAN-rVV10	$(2\sqrt{3}\times 3)$	H	-0.38	1.42	827	0
		LB	-0.23	1.44	815	0
		SB	0.85	1.23	1565	1
SCAN	$(2\sqrt{3}\times 3)$	H	0.02	1.41	723	0
		LB	0.12	1.48	691	0
PBE-optB88	$(2\sqrt{3}\times 3)$	H	-0.27	1.39	810	0
PBE-optBE	$(2\sqrt{3}\times 3)$	H	0.071	1.30	1141	1
PBE-D3	$(2\sqrt{3}\times 3)$	H	-0.11	1.38	846	0
		LB	0.23	1.47	690	0
PBE	$(2\sqrt{3}\times 3)$	H	0.10	1.41	692	0
		LB	0.43	1.50	690	0
PW91 ^{19, 33, 63}	(2×2)	SB	-0.17	1.30	1149	1
PW91-D2 ³³	(3×3)	H	0.19	1.35		0
EELS. ⁶²					685	0
TPD ^{21, 64}			-0.4			

The partial density of states (PDOS) of the O₂/Ag(111) system are shown in **Figure 3**. The substantial overlap between Ag 4d and O 2p states was presented. Interestingly, the SCAN-rVV10 PDOS images are more asymmetric (see **Figure 3a**), which suggests the stronger adsorption causes the charge density polarization of oxygen molecules. The peaks of O 2p states also moved away from the Fermi level with SCAN-rVV10 in comparison with the PBE or PBE-D3 PDOS peaks. Specifically, at the $E - E_F$ range of -8 eV to -6 eV, the overlap was a prominent feature. As expected, the proper incorporation of vdW interactions will influence and enhance the adsorption strength. However, SCAN-rVV10 results show broader Ag 4d peaks in comparison to PBE-D3/PBE. The adsorption of O₂ causes strong charge transfers as supported by the change of the magnetic moments, which are preferential to the electronegative O₂ molecules⁶⁵. Thus, the PDOS of the adsorbed O₂ was more significantly affected by using different XC functionals (see **Figures 3a** and **b**). When comparing the PDOS of the adsorbed oxygen molecule at the H site with and without rVV10, there were minimal differences (see

Figure 3c). Therefore, this downshift observed in **Figures 3a** and **b** after using the SCAN-rVV10 method is mainly ascribed to the contribution from the SCAN functional. There was also a change in the anti-bonding range by using different methods. SCAN-rVV10 produced an apex far into the anti-bonding region. The PBE-D3/PBE methods had an anti-bonding peak closer to the Fermi level. Again, it supports that there is a stronger adsorption strength when the SCAN-rVV10 method is used.

Figure 3: The PDOS of Ag 4d and O 2p states for Ag-O₂ at the H site using **a)** SCAN-rVV10 and **b)** PBE-D3/PBE, respectively. **c)** the PDOS of O 2p from SCAN and SCAN-rVV10 calculations at the H site. **d)** the -pCOHP analysis for the O-O bond at the H site on the Ag(111) surface using SCAN-rVV10 and PBE-D3/PBE along with the corresponding -IpCOHP value.

The -pCOHP analysis was used for further investigation on bonding mechanisms of O₂ on Ag(111). **Figure 3d** showed the -pCOHP for the O-O bond after the adsorption when using SCAN-rVV10 or PBE/PBE-D3. The -pCOHP results with both methods were almost identical. To quantitatively identify the subtle difference, the -IpCOHP was calculated by integrating -pCOHP up to the Fermi energy level. The -IpCOHP of O-O bond was -8.00 eV/bond, which is -0.10 eV higher than the PBE/PBE-D3 value. It suggests that the O-O bonding strength is weaker when the SCAN-rVV10 method is used. It further supports the stronger adsorption of O₂ on Ag(111) revealed by SCAN-rVV10 calculations.

3.3 Dissociative Adsorption

Previous studies suggested the fcc, hcp, bridge and atop sites would be viable for O adsorption^{8, 10, 54}. As such, the adsorption properties of the oxygen atom from the dissociated oxygen molecules at these four sites were investigated. Here, the adsorption energy was calculated from $\Delta E_{ads} = E_{O/surf} - E_{surf} - 1/2E_{O_2}$, where $E_{O/surf}$ is the total energy of the surface with the adsorbed atomic O. And E_{O_2} is the energy of the isolated O₂ molecule. The adsorption configurations are shown in **Figure 4**. The O* atoms were located at the fcc and hcp sites at similar heights from the metal surface. The atop site was unstable for the O* species and would transition to fcc after structural optimization (see **Table 3**). The SCAN-rVV10 results predicted that the fcc site had the lowest adsorption energy (-0.74 eV) and the most transferred charge densities (1.18 eV/Å³) among all the considered adsorption configurations, which was followed by the hcp site with the adsorption energy and transferred charge densities of -0.64 eV and 1.16 eV/Å³, respectively (see **Table 3**). PBE and PBE-D3 adsorption energies at the fcc site were -0.47 eV and -0.41 eV, respectively. These results for PBE and PBE-D3 align with that reported by Zhang et al.⁸. The SCAN-rVV10 result was the closest to the experimental data with a difference of 17.3%⁵⁸. Both PBE-D3 and PBE results underestimated the adsorption strength, which was 60.7% and 72.9% higher than that experimental data, respectively. The difference between methods with and without vdW correction functionals was less prominent. The SCAN data is identical to SCAN-rVV10 which, proved minimal contributing vdW forces were present^{36, 66}. The exchange part of the XC functional is the main contributor to these differences between the GGA and meta-GGA methods.

Figure 4: The cross-sectional (bottom) and top (above) view of the oxygen atom adsorption site on the Ag(111) surface in a $(2\sqrt{3}\times 3)$ unit cell. **a)** atop, **b)** bridge, **c)** fcc, **d)** hcp. Color code: silver; Ag, red; O.

Table 3: Calculated atomic dissociative adsorption properties of O on Ag(111) using different methods. ΔE_{ads} (eV) is the adsorption energy of both O* atoms after dissociation. $|q_{Ag-O}|$ is the absolute charge transfer between Ag and O*.

	Surface cell	Adsorption site	ΔE_{ads} (eV)	d_{Ag-O} (Å)	$ q_{Ag-O} $
SCAN-rVV10	$(2\sqrt{3}\times 3)$	fcc	-0.74	2.10	1.18
		hcp	-0.64	2.13	1.16
		bridge	-0.43	2.10	1.15
		atop	-	-	-
SCAN	$(2\sqrt{3}\times 3)$	fcc	-0.74	2.12	1.17
		hcp	-0.64	2.12	1.17
PBE-D3	$(2\sqrt{3}\times 3)$	fcc	-0.47	2.16	1.15
PBE	$(2\sqrt{3}\times 3)$	fcc	-0.41	2.14	1.15
PW91 ¹⁰	(2×2)	fcc	-0.47		
		hcp	-0.35		
PBE ⁸	(2×2)	fcc	-0.28		
TPD ^{21, 58}		fcc	-0.88		

The PDOS of O 2p and Ag 4d states for each method were shown in **Figure 5**. There were subtle differences between the PDOS of the meta-GGA and GGA methods for atomic O adsorption systems (see **Figure 5**). However, there were only negligible differences between methods with the same XC functional (e.g., SCAN and SCAN-rVV10). Again, it suggests that the vdW forces have a small impact on their electronic structures. The SCAN/SCAN-rVV10 peaks exhibited stronger overlap, were broader at the apex and shifted further away from the Fermi level, which was similar to the trend observed in O₂/Ag(111) systems (see **Figure 3**). There was also a smaller difference between the GGA and meta-GGA methods in terms of the molecular oxygen adsorption system. They even became almost indistinguishable at the $E - E_F$ range between -2 eV and 0 eV. Therefore, it reflects the similar adsorption energies, bond distance and charge transfer by all methods.

Figure 5: PDOS of Ag 4d and 2p O states of O adsorption on Ag(111) at the fcc site using different methods. a) and b) are SCAN-rVV10 and SCAN, respectively. c) and d) are PBE-D3 and PBE, respectively.

The dissociation mechanism of adsorbed oxygen molecules on Ag(111) was explored. Our results reveal a novel dissociation pathway (see **Figure 6**). The O₂ first adsorb at the H site, which then shifted to the neighboring LB site. After that, the O-O bond length increases till the two atoms are separated and move to the fcc and hcp sites. The energy barrier is the energy difference between the transition state and the initial state. The energy barrier from SCAN-rVV10 calculations is 0.78 eV. For comparison, PBE and PBE-D3 results predict a higher dissociation barrier as 1.58 eV and 1.02 eV, respectively. Our GGA results match the reported data at the same level. Xu et al. and Yan et al. used PW91 and PBE-D2 and found that the dissociation energy barrier was 1.11 eV and 1.07 eV, respectively^{19, 33}. The much lower energy barrier when using the SCAN-rVV10 method can be ascribed to the stronger adsorption energy of molecular oxygen on Ag(111). As suggested by our -pCOHP analysis, the O-O bond strength weakens after the adsorption from the SCAN-rVV10 calculations, which can benefit the dissociation. The theoretical O₂ dissociation energy barrier on Ag(111) using SCAN-rVV10 is also within the TPD energy barrier range of 0.54 ± 0.26 eV^{23, 63}. Our results demonstrate that O₂ dissociation is strongly influenced by vdW forces due to the intermolecular ranges. Additionally, rVV10 predicts pairwise interactions between electron clouds^{35, 36}. This added sensitivity better predicts the weak forces during dissociation and how each atom will relocate. Furthermore, SCAN can describe the intermediate-range attractions between overlapped but nonbonded densities due to its semi-local nature^{34, 46}. SCAN can also accurately describe the surface properties due to excellent error cancellation. These factors enable SCAN-rVV10 to surpass the DFT methods of the past. The success of SCAN-rVV10 on this long-term experiment-theory puzzle indicates the importance of the accurate description of intermediate-range vdW interactions for correctly understanding the O₂/Ag(111) system.

Figure 6: The molecular oxygen dissociation energy profile using SCAN-rVV10, PBE-D3 and PBE with each species represented along with experimental data and reported PW91 results ^{18, 19, 23, 33, 64}.

SCAN-rVV10 was also used to investigate CO adsorption on Pt(111) because of its well-known site preference issue ⁶⁷⁻⁷⁰. The experiments reveal that the CO adsorbed at the atop site. However, fcc sites were preferred based on the DFT calculations at the GGA level (see **Figure 7**). Our PBE and PBE-D3 calculations are also preferential to the fcc site while the addition of the D3 correctional can reduce the energy difference between two sites. As a comparison, SCAN-rVV10 results confirmed the experimental observation that the atop site is more energetically favorable (see **Table 4**). It supports that the SCAN-rVV10 can outperform other widely used DFT methods for the system in which the intermediate ranged vdW force is important.

Figure 7: The cross-sectional (bottom) and top (above) view of CO adsorption configurations on the Pt(111) surface at **a)** atop and **b)** fcc sites. Color code: grey = Pt, red = O and brown = C.

Table 4: Calculated CO adsorption on Pt(111) using different methods. d_{C-O} (Å) is the bond distance between the C and O atoms in the CO molecule.

	Adsorption site	ΔE_{ads} (eV)	d_{C-O} (Å)
SCAN-rVV10	fcc	-2.09	1.19
	atop	-2.21	1.15
PBE-D3	fcc	-1.94	1.20
	atop	-1.56	1.15
PBE	fcc	-1.75	1.20
	atop	-0.82	1.18
PBE ⁶⁸	fcc	-1.67	
	atop	-1.57	
TPD ⁶⁹	atop	-1.37 ± 0.13	

IV. Conclusion

In this study, the recently developed SCAN-rVV10 functional at the meta-GGA level with the consideration of vdW force correction was used to reinvestigate the adsorption

properties of oxygen molecules on the Ag(111) surface, which were inadequately treated in previous DFT studies. Our results demonstrate that the SCAN-rVV10 calculations can reproduce the adsorption energy of O₂ derived from the experiments. Both molecular and dissociative adsorptions can exist based on the SCAN-rVV10 results, which matches the experimental data while being different from the conclusion from previous DFT studies. The molecular adsorption energy is -0.38 eV, which is very close to the experimental data of -0.4 eV from the TPD measurement. A novel dissociation pathway was found as it capitalized on the stability of the H and LB adsorption sites. The dissociative energy barrier of the oxygen molecule through this pathway is 0.78 eV, which is within the experimental range of 0.54 ± 0.26 eV. Our results demonstrate that SCAN-rVV10 can outperform PBE, PBE-D3 and SCAN for the O₂/Ag(111) systems because it has demonstrated better performance for describing intermediate-ranged vdW forces. This improved performance was further confirmed by using SCAN-rVV10 to correctly predict the preferred CO adsorption site on Pt(111).

However, our results also suggest that the SCAN-rVV10 is not a panacea. SCAN-rVV10 faces a great difficulty when the short-ranged interactions become dominant, as evidenced by the big theory-experiment gap of gaseous O₂. Additionally, this problem encompasses other systems such as CO adsorption as the adsorption energy was stronger than the experimental values (see **Table 5**)^{67, 68}. Recent works have highlighted numerical issues with the SCAN functional in certain circumstances and would be present in SCAN-rVV10^{46, 71}. The "regularized" SCAN (rSCAN) and r²SCAN functionals have recently been introduced to overcome these issues while replicating the success of SCAN^{46, 47}. The investigation on the performance of these regularized SCAN methods combined with the non-local vdW correction is worthy to be conducted in the future.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

This research was undertaken on the supercomputers in National Computational Infrastructure (NCI) in Canberra, Australia, which is supported by the Australian Commonwealth Government, and Pawsey Supercomputing Centre in Perth with funding from the Australian government and the Government of Western Australia.

Data Availability

The data that supports the findings of this study are available within the article.

References

1. A. Jain, Y. Shin and K. A. Persson, *Nat. Rev. Mater.* **1** (1), 15004 (2016).
2. Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Norskov and T. F. Jaramillo, *Science* **355** (6321) (2017).
3. J. K. Norskov, T. Bligaard, J. Rossmeisl and C. H. Christensen, *Nat. Chem.* **1** (1), 37-46 (2009).
4. B. Liu, Y. Wang, H. Q. Peng, R. O. Yang, Z. Jiang, X. T. Zhou, C. S. Lee, H. J. Zhao and W. J. Zhang, *Adv. Mater.* **30** (36), 1803144 (2018).
5. Z. C. Lai, A. Chaturvedi, Y. Wang, T. H. Tran, X. Z. Liu, C. L. Tan, Z. M. Luo, B. Chen, Y. Huang, G. H. Nam, Z. C. Zhang, Y. Chen, Z. N. Hu, B. Li, S. B. Xi, Q. H. Zhang, Y. Zong, L. Gu, C. Kloc, Y. H. Du and H. Zhang, *J. Am. Chem. Soc.* **140** (27), 8563-8568 (2018).
6. S. Zhao, Y. Wang, J. Dong, C.-T. He, H. Yin, P. An, K. Zhao, X. Zhang, C. Gao, L. Zhang, J. Lv, J. Wang, J. Zhang, A. M. Khatkhat, N. A. Khan, Z. Wei, J. Zhang, S. Liu, H. Zhao and Z. Tang, *Nat. Energy* **1**, 16184 (2016).
7. S. Chu and A. Majumdar, *Nature* **488** (7411), 294-303 (2012).
8. N. Zhang, F. Chen, D. Liu and Z. Xia, *ACS Appl. Energy Mater.* **1** (8), 4385-4394 (2018).
9. R. Ma, G. Lin, Y. Zhou, Q. Liu, T. Zhang, G. Shan, M. Yang and J. Wang, *npj Comput. Mater.* **5** (1), 78 (2019).
10. B. W. J. Chen, D. Kirvassilis, Y. Bai and M. Mavrikakis, *J. Phys. Chem. C* **123** (13), 7551-7566 (2018).
11. M. G. Sensoy and M. M. Montemore, *J. Phys. Chem. C* **124** (16), 8843-8853 (2020).
12. Y. Yang, H. Zhang, J. Wang, S. Yang, T. Liu, K. Tao and H. Chang, *J. Mater. Chem. A* **7** (18), 11497-11505 (2019).
13. L. Zhu, H. Xu, Y. Nan, Y. Xie, J. Zhu and D. Cheng, *Appl. Surf. Sci.* **476**, 115-122 (2019).
14. Q. Yu, C. Guo, J. Ge, Y. Zhao, Q. Liu, P. Gao, J. Xiao and H. Li, *J. Power Sources* **453**, 227846 (2020).
15. Z. Zhang, X. Li, C. Zhong, N. Zhao, Y. Deng, X. Han and W. Hu, *Angew. Chem. Int. Ed.* **59** (18), 7245-7250 (2020).
16. Y. Wang, W. Wang, K.-N. Fan and J. Deng, *Surfaces Science* **490**, 125-132 (2001).
17. A. Michaelides, K. Reuter and M. Scheffler, *J. Vac. Sci. Technol. A* **23** (6), 1487 (2005).
18. M. M. Montemore, M. A. van Spronsen, R. J. Madix and C. M. Friend, *Chem. Rev.* **118** (5), 2816-2862 (2018).
19. Y. Xu, J. Greeley and M. Mavrikakis, *J. Am. Chem. Soc.* **127** (37), 12823-12827 (2004).
20. B. V. Andryushechkin, V. M. Shevlyuga, T. V. Pavlova, G. M. Zhidomirov and K. N. Eltsov, *J. Chem. Phys.* **148** (24), 244702 (2018).
21. C. T. Campbell, *Surf. Sci.* **157**, 43-60 (1985).
22. A. Raukema, D. A. Butler, F. M. A. Box and A. W. Kleyn, *Surf. Sci.* **347** (1-2), 151-168 (1995).

23. R. B. Grant and R. M. Lambert, *Surf. Sci.* **146** (1), 256-268 (1984).
24. D. Schmeisser and K. Jacobi, *Surf. Sci.* **156**, 911-919 (1985).
25. D. C. Ford, A. U. Nilekar, Y. Xu and M. Mavrikakis, *Surf. Sci.* **604** (19-20), 1565-1575 (2010).
26. B. Santra, J. Klimes, A. Tkatchenko, D. Alfe, B. Slater, A. Michaelides, R. Car and M. Scheffler, *J. Chem. Phys.* **139** (15), 154702 (2013).
27. M. Kim, W. J. Kim, T. Gould, E. K. Lee, S. Lebegue and H. Kim, *J. Am. Chem. Soc.* **142** (5), 2346-2354 (2020).
28. A. J. Cohen, P. Mori-Sanchez and W. T. Yang, *Science* **321** (5890), 792-794 (2008).
29. A. Santosh., T. Hong., N. Bimal., C. Gabor. and R. Adrienn., *Phys. Rev. Mater.* **4** (2), 25005-25015 (2020).
30. D. Mahlberg, S. Sakong, K. Forster-Tonigold and A. Gross, *J. Chem. Theo. Comput.* **15** (5), 3250-3259 (2019).
31. A. J. R. Hensley, K. Ghale, C. Rieg, T. Dang, E. Anderst, F. Studt, C. T. Campbell, J.-S. McEwen and Y. Xu, *J. Phys. Chem. C* **121** (9), 4937-4945 (2017).
32. S. Tsuzuki and H. P. Lüthi, *J. Chem. Phys.* **114** (9), 3949-3957 (2001).
33. M. Yan, Z.-Q. Huang, Y. Zhang and C.-R. Chang, *Phys. Chem. Chem. Phys.* **19** (3), 2364-2371 (2017).
34. J. Sun, A. Ruzsinszky and J. P. Perdew, *Phys. Rev. Lett.* **115** (3), 036402 (2015).
35. R. Sabatini, T. Gorni and S. de Gironcoli, *Phys. Rev. B* **87** (4), 41108-41112 (2013).
36. H. Peng, Z.-H. Yang, J. P. Perdew and J. Sun, *Phys. Rev. X* **6** (4), 41005-41020 (2016).
37. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6** (1), 15-50 (1996).
38. P. E. Blochl, *Phys. Rev. B* **50** (24), 17953-17979 (1994).
39. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* **77** (18), 3865-3868 (1996).
40. V. L. Deringer, A. L. Tchougreeff and R. Dronskowski, *J. Phys. Chem. A* **115** (21), 5461-5466 (2011).
41. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* **132** (15), 154104 (2010).
42. J. Klimeš, D. R. Bowler and A. Michaelides, *J. Phys.: Condens. Matter* **22** (2) (2009).
43. G. Henkelman, *J. Chem. Phys.* **113** (22), 9901-9904 (2000).
44. M. E. Turano, R. G. Farber, E. C. N. Oskorep, R. A. Rosenberg and D. R. Killelea, *J. Phys. Chem. C* **124** (2), 1382-1389 (2019).
45. J. G. Brandenburg, J. E. Bates, A. Ruzsinszky, J. Sun and J. P. Perdew, *Phys. Rev. B* **94**, 115114 (2016).
46. A. P. Bartok and J. R. Yates, *J. Chem. Phys.* **150** (16), 161101 (2019).
47. S. Ehlert, U. Huniar, J. Ning, J. W. Furness, J. Sun, A. D. Kaplan, J. P. Perdew and J. G. Brandenburg, *J. Chem. Phys.* **154** (6), 061101 (2021).
48. P. Mkhonto, H. Chauke and P. Ngoepe *Minerals* **5** (4), 665-678 (2015).
49. Y. Xu and M. Mavrikakis, *J. Phys. Chem. B* **107** (35), 9298-9307 (2003).
50. J. Xie, S. d. Gironcoli, S. Baroni and M. Scheffler, *Phys. Rev. B* **59** (2), 970-974 (1999).
51. H. Oughaddou, S. Sawaya, J. Goniakowski, B. Aufray, G. Le Lay, J. M. Gay, G. Trégliat, J. P. Bibérian, N. Barrett, C. Guillot, A. Mayne and G. Dujardin, *Phys. Rev. B* **62** (24), 16653-16656 (2000).
52. P. Quaino, E. Santos, G. Soldano and W. Schmickler, *Adv. Phys. Chem.* **2011**, 1-14 (2011).
53. T. Björkman, A. Gulans, A. V. Krashenninnikov and R. M. Nieminen, *Phys. Rev. Lett.* **108** (23), 235502 (2012).
54. S. Liu, M. G. White and P. Liu, *ChemCatChem* **10** (3), 540-549 (2018).

55. Z. Y. Gao, W. J. Yang, X. L. Ding, G. Lv and W. P. Yan, *Phys. Chem. Chem. Phys.* **20** (10), 7333-7341 (2018).
56. S. Gautier, S. N. Steinmann, C. Michel, P. Fleurat-Lessard and P. Sautet, *Phys. Chem. Chem. Phys.* **17** (43), 28921-28930 (2015).
57. B. Vlasisavljevich, J. Huck, Z. Hulvey, K. Lee, J. A. Mason, J. B. Neaton, J. R. Long, C. M. Brown, D. Alfe, A. Michaelides and B. Smit, *J. Phys. Chem. A* **121** (21), 4139-4151 (2017).
58. W.-X. Li, C. Stampfl and M. Scheffler, *Physical Review B* **65** (7), 75407 (2002).
59. B.-T. Teng, X.-D. Wen, M. Fan, F.-M. Wua and Y. Zhangd, *Phys. Chem. Chem. Phys.* **16** (34), 18563-18569 (2014).
60. A. W. Czanderna, *J. Phys. Chem.* **68** (10), 2765-2771 (1964).
61. I. Goikoetxea, J. Beltrán, J. Meyer, J. Iñaki Juaristi, M. Alducin and K. Reuter, *New J. Phys.* **14** (1), 013050 (2012).
62. A. F. Carley, P. R. Davies, M. W. Roberts and K. K. Thomas, *Surf. Sci.* **238** (1-3), L467-L472 (1990).
63. M. Endo, T. Matsumoto, J. Kubota, K. Domen and C. Hirose, *J. Phys. Chem. B* **104** (20), 4916-4922 (2000).
64. A. W. Kleyn, D. A. Butler and A. Raukenma, *Surf. Sci.* **363** (1-3), 29-41 (1996).
65. M. Poberžnik and A. Kokalj, *J. Phys. Chem. C* **120** (45), 25915-25922 (2016).
66. S. Alvarez, *Dalton Transactions* **42** (24), 8617-8636 (2013).
67. P. J. Feibelman, B. Hammer, J. K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe and J. Dumesic, *J. Phys. Chem. B* **105** (1), 4025 (2001).
68. P. Lazić, M. Alaei, N. Atodiresei, V. Caciuc, R. Brako and S. Blügel, *Phys. Rev. B* **81** (4) (2010).
69. F. Abild-Pedersen and M. P. Andersson, *Surf. Sci.* **601** (7), 1747-1753 (2007).
70. Y. Wang, S. de Gironcoli, N. S. Hush and J. R. Reimers, *J. Am. Chem. Soc.* **129** (34), 10402-10407 (2007).
71. T. Gould, E. R. Johnson and S. A. Tawfik, *Beilstein J. Org. Chem.* **14**, 1181-1191 (2018).

TDOS (a.u.)

— SCAN-rVV10
— SCAN
— PBE-D3
— PBE

-8

-6

-4

-2

0

2

4

6

8

$E-E_F$ (eV)

a)

b)

c)

a)

b)

c)

d)

a)

b)