First principles study on solid oxygen using van der Waals density functional

Masao Obata¹, Ikutaro Hamada², and Tatsuki Oda¹,³

¹ Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan obata@cphys.s.kanazawa-u.ac.jp
² International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan
³ Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

Abstract

We introduce scaling parameters for the spin-polarization dependent gradient correction to the local correlation in the van der Waals density functional, which enable us to tune the magnetic interaction between atoms and molecules. We have applied the method to solid oxygen and found that by using an optimal choice of the parameters, the structural parameters are significantly improved over the ones obtained in the previous work. We discuss the generic features of the proposed approach.

Keywords: Oxygen, Magnetism, van der Waals Force, Density Functional Theory

1 Introduction

The oxygen molecule has the spin triplet ground state, and the solid oxygen shows a rich variety of crystal and magnetic structures in a wide range of temperature and pressure, and under applied magnetic field[1, 2, 3, 4, 5, 6]. The magnetism of the solid oxygen under pressure is of particular interest, because it is sensitive to the distance and relative angle between molecules, and as a result, it has been shown that oxygen molecular systems have complex magnetic interaction potential depending on the structure [7, 8, 9, 10, 11, 12]. In addition, there is a competition between magnetic and inter-molecular interactions in the solid oxygen[12], which may give rise to a rich phase diagram of solid oxygen under various conditions. Thus, the accurate description of the potential energy surface is a key to understanding of the crystal and magnetic structures of solid oxygen.

Density functional theory (DFT) within the local density approximation (LDA) and generalized gradient approximation (GGA) has been used successfully to understand and predict various materials properties. However, LDA and GGA are known to fail to properly describe the dispersion forces, which are responsible for the binding of the molecular crystals, including the solid oxygen. The van der Waals density functional (vdW-DF)[13, 14, 15] is one of the
promising methods for the weak interaction, and is able to describe the dispersion interaction and covalent bonding seamlessly within the framework of DFT. The vdW-DF has succeeded to reproduce energetics and structural properties of a wide range of materials[13, 16, 17]. Unfortunately, vdW-DF is developed only for non-spin-polarized systems, and as a practical extension of vdW-DF to spin-polarized systems, we propose vdW-DF with spin-polarization dependent gradient correction (vdW-DF-SGC)[18, 19]. Our method has been applied to the oxygen molecular dimer and solid oxygen at ambient pressure (α phase), and shown to improve the description of the oxygen systems over the original vdW-DF. However, the error in the structural properties of solid oxygen obtained with vdW-DF-SGC is still considerably large and there is room for further improvement.

In the previous study[19], we have found that one of the reasons for the deviation from the experiment is an overestimation of the antiferromagnetic interaction between molecules, because the wave functions for the antiferromagnetic state are more delocalized than those for the ferromagnetic ones, and more accurate description of the electron correlation[20] is necessary to describe the solid oxygen. Our final goal is to develop a density functional, which can be practically used for spin-polarized systems in the framework of vdW-DF, and at the current stage, we are aiming at further improving the vdW-DF-SGC. Unfortunately, our tests are limited to a series of oxygen molecules, but systems, in which ferromagnetic moment is localized on single molecule, are suitable for investigation. In this paper, we analyze the impact of the spin-dependent gradient correction in vdW-DF-SGC, by introducing the scaling parameter in the spin-polarization gradient correction to local correlation energy, to gain insight into the magnetic and molecular interactions in the solid oxygen. We show that by using a set of optimal parameters, antiferromagnetic interaction can be reduced, and the calculated structural parameters and energetics of solid oxygen are improved.

2 Methods and Systems

We briefly review the vdW-DF-SGC method and explain the way of improving the correlation functional. In the method, the exchange correlation energy functional is composed of exchange, local correlation, nonlocal correlation, and spin-polarization-dependent gradient correction energy functionals:

\[ E_{xc}[n_{\uparrow},n_{\downarrow}] = E_{xc}^{GGA}[n_{\uparrow},n_{\downarrow}] + E_{c}^{LSDA}[n,\zeta] + E_{c}^{nl}[n] + \alpha_{GC}(E_{c}^{GGA}[n,\zeta] - E_{c}^{GGA}[n,\zeta = 0]). \]  

The last term in parentheses is estimated as follows:

\[ E_{c}^{GGA}[n,\zeta] - E_{c}^{GGA}[n,\zeta = 0] = \int d\mathbf{r} \mathbf{n}(\mathbf{r}) \{ H(r_{s},\zeta,t) - H(r_{s},0,t) \}. \]  

where \( H, r_{s}, \zeta, \) and \( t \) are the gradient contribution, Seitz radius \((n = 3/4\pi r_{s}^{3})\), the relative spin polarization, and the dimensionless density gradient proportional to \( |\nabla n|\), respectively [21]. In this work, the scaling parameter \( \alpha_{GC} \) has been introduced, which was set to unity in the previous works[18, 19]. The vdW-DF-SGC reduces the overestimation of antiferromagnetic interaction compared to the original vdW-DF, indicating that spin-polarization-dependent gradient correction (SGC) term [the last term in Eq.(1)] has an effect of destabilizing antiferromagnetic coupling[18, 19]. Indeed, in an H-type molecular pair the electron density at the intermediate region between molecules was found to be much reduced from the antiferromagnetic pair to the ferromagnetic one. This behavior can be justified by the Pauli’s exclusion principle. As a consequence, there appeared no energy change of SGC term at the displacement of molecular distance in the ferromagnetic pair, whereas for the antiferromagnetic pair the repulsive
behavior appeared from the SGC term, as discussed below. Thus, we propose to introduce \( \alpha_{GC} \) to optimize SGC term to reduce the difference between ferromagnetic and antiferromagnetic states, as one of improving methods. Note that the present functional is reduced to the original vdW-DF in the absence of spin polarization.

As another way, we propose to scale the relative spin polarization in order to optimize the antiferromagnetic interaction as follows:

\[
\zeta \rightarrow \alpha_{\zeta} \zeta.
\]

where \( \alpha_{\zeta} \) is scaling factor of \( \zeta \). This scale may be related with the fact that the averaged sub-lattice magnetic moment in antiferromagnetic systems is reduced from the elemental saturated value [20]. In both the local correlation energy functional and SGC term, \( \zeta \) is used as an argument of spin scaling function (SSF) \( \phi(\zeta) = [(1 - \zeta)^{2/3} + (1 + \zeta)^{2/3}] / 2 \) which was derived within the random-phase-approximation [22]. As a consequence, scaled \( \zeta \) is equivalent to what scales the SSF. Note that \( \alpha_{\zeta} \) does not exceed unity. In both of the parametrizations (\( \alpha_{GC} \) and \( \alpha_{\zeta} \)), we expect a negligible change in the potential energy curve for ferromagnetic pairs since the dependence of correlation energy functional is investigated, but not of exchange energy functional. Indeed, as reported later in the next section, there is no dependence on \( \alpha_{GC} \) and \( \alpha_{\zeta} \) in the potential energy curve.

In this work, we have examined effects of these two scaling parameters in H-type oxygen molecular dimer and solid oxygen at ambient pressure. We used plane wave basis set and ultrasoft pseudopotential [23, 24]. For exchange and local correlation energy functions, \( E_x \) and \( E^LSDA \), we used the versions of revPBE and PW92, respectively [25, 26]. In the pseudopotential construction, we neglected the nonlocal correlation \( (E_{nl}^c) \) and employed the semilocal exchange and correlation functionals. This treatment has been justified, because the nonlocal correlation vanishes in spherical atomic calculation [27]. To compute the nonlocal correlation energy efficiently, we used an order \( N \log N \) method [28, 29]. In the method, we used the cutoff of 8 a.u. for the wave number \( q_0 \) and 31 \( q_0 \) values \( (q_0) \), which were constructed by a logarithmic mesh except near \( q_0 = 0 \) [19]. We have already confirmed a reliability of these parameters in the previous study [19]. The kinetic energy cutoffs of 40 Ry and 350 Ry were used for the wave functions and charge density, respectively, in the H-type cluster calculation. We used large energy cutoffs for the plane wave basis (160 Ry and 960 Ry) in the crystal calculation to achieve the convergence in the pressure tensor, since the potential energy surface is very sluggish in the solid oxygen. We optimized the lattice parameters of solid oxygen to converge within a pressure of 0.05 GPa. The cubic box with a dimension of 10.6 Å was used in the cluster calculation. In the cluster calculations, optimized bond length of the isolated molecule was used (1.232 Å), which is slightly larger than the experimental value (1.207 Å [30]).

### 3 Results and Discussions

First, we have investigated the scaling parameters \( \alpha_{GC} \) and \( \alpha_{\zeta} \) in the H-type oxygen molecular dimer. Figure 1 shows the \( \alpha_{GC} \) dependence of the binding energy as a function of the distance between centers of molecules \( (d) \) for both antiferromagnetic and ferromagnetic states. Using the original vdW-DF-SGC \( (\alpha_{GC} = \alpha_{\zeta} = 1) \), the potential energy curve of antiferromagnetic pair has the equilibrium distance of 3.20 Å and the binding energy of 45 meV. The equilibrium distance agrees well with the accurate data from the quantum chemistry approaches but the binding energy is larger [7, 10]. For ferromagnetic pair, the potential energy curves have a slightly large equilibrium distance with a slightly high binding energy, compared with the quantum
chemistry approaches \cite{7, 10}. As implied in the previous study \cite{19}, the antiferromagnetic state is destabilized and the equilibrium distance becomes larger as $\alpha_{GC}$ is increased, whereas the interaction energy curve for the ferromagnetic state is unchanged. Thus, the $\alpha_{GC}$ plays a role to tune the stability of the antiferromagnetic state only. Figure 1 also shows the magnetization of oxygen atom. By increasing $\alpha_{GC}$, atomic magnetic moment decreases, implying that the wave function extends more to the intermolecular region.

Figure 2 shows the magnetic coupling constant $J$, defined by the energy difference between ferromagnetic and antiferromagnetic states: $J = E_F - E_{AF}$. The figure indicates a stability of antiferromagnetic state in a wide range of $\alpha_{GC}$’s and $d$’s. The strength of $J$ decreases as increasing $\alpha_{GC}$ or $d$ and becomes comparable to those estimated in the methods of quantum chemistry (CASSCF, RCCSD(T))\cite{7, 10} when $\alpha_{GC} = 8$ and $d = 3.3$ Å. Unlike the quantum chemistry approaches, there is a region where the ferromagnetic state is more stable (negative $J$) at the larger $\alpha_{GC}$’s ($\alpha_{GC} = 8, 12$) and larger $d$'s in the present frame work of vdW-DF-SGC. Such ferromagnetic stability can come from a direct exchange interaction between the orbitals on the molecules. However, these interactions should be very small at $d \sim 4$ Å.

Figure 3 shows the dependence of the binding energy curve on $\alpha_{\zeta}$ for antiferromagnetic and ferromagnetic states. As $\alpha_{\zeta}$ decreases, energy difference between antiferromagnetic and ferromagnetic states decreases. In this case the equilibrium distance does not change, but the repulsive nature of potential curves becomes strong. As shown in Fig. 3, the magnetic moment slightly increases when the antiferromagnetic state is destabilized. This is an opposite trend, compared with the case of $\alpha_{GC}$.

Since magnetic energy of the electron correlation is estimated as a local relative spin polarization in Eq.(1), it is unable to distinguish stability between antiferromagnetic and ferromagnetic states by the local spin density. Nevertheless once the difference of spin densities in magnetic states is generated through self-consistent field calculations, the system can converge to the respective magnetic state.

Next, we have applied vdW-DF-SGC with $\alpha_{GC}$ and $\alpha_{\zeta}$ to the solid oxygen at ambient pressure. The crystal structure belongs to a $C2/m$ (monoclinic) space group and its magnetic unit cell contains two molecules with an antiferromagnetic coupling \cite{1}. The molecular axis has been known to tilt from the $z$-direction perpendicular to $ab$ plane by a few degrees within the $ac$-plane. This effect is tiny and is negligible for the present work. In Table 1, we report optimized structural parameters, crystal binding energy, and magnetic energy for typical sets of scaling parameters $\alpha_{GC}$ and $\alpha_{\zeta}$. We have found that by applying $\alpha_{GC}$, the lattice parameters are improved as compared with the previous theoretical result\cite{19}. For example, by setting $\alpha_{GC} = 4$ and $\alpha_{\zeta} = 1$, we obtain the nearest neighbor distance between molecules of 3.14 Å, which is larger than that of 3.05 Å with $\alpha_{GC} = 1$ and $\alpha_{\zeta} = 1$. The effects on $\alpha_{\zeta}$ appeared also in the lattice parameter $a$, but the detail trend depends largely on $\alpha_{GC}$; when $\alpha_{GC} = 2$ ($\alpha_{GC} = 4$), $a$ increased (decreased). However, the overall effect of $\alpha_{\zeta}$ is not as large as that of $\alpha_{GC}$.

The lattice parameter $a$ is in excellent agreement with the experiment, when $\alpha_{GC} = 8$ and $\alpha_{\zeta} = 1$. However, other lattice parameters deviate from the experimental values. In our optimization about $\alpha_{GC}$ and $\alpha_{\zeta}$, the potential curves of ferromagnetic molecular pair do not change. This may limit a region of searching space for exchange and correlation energy functionals. In the previous works \cite{31}, the weak repulsive nature was realized by optimizing the exchange functional, whereas the original functional shows a stronger repulsive nature at short distances \cite{13}. The potential energy of ferromagnetic dimer is also important in determining the structural parameters in solid oxygen as well as those of antiferromagnetic dimer. Because there are ferromagnetic molecular pairs at the next nearest neighbors within $ab$ plane, the structural
Figure 1: Binding energy ($\Delta E$) curves for the oxygen molecular dimer in the H-Type configuration as a function of the distance connecting the center of molecules ($d$) for several $\alpha_{GC}$’s and $\alpha_\zeta = 1$. The left and right panels show antiferromagnetic and ferromagnetic cases, respectively. The atomic magnetic moments ($M_O$) are shown on the upper parts.

Figure 2: Magnetic interaction $J (= E_F - E_{AF})$ for the oxygen molecular dimer in the H-type configuration as a function of the distance between molecules for several $\alpha_{GC}$’s and $\alpha_\zeta = 1$.

details might depend on the ferromagnetic potentials of molecular pairs. Another importance in ferromagnetic potential of molecular pair may be related with the phase transition to $\delta$ phase at the high pressure, at which the nearest neighbor magnetic coupling between molecules of neighboring $ab$ planes is changed from antiferromagnetic to ferromagnetic one [3].

The binding and magnetic energies, as expected from the results of H-type molecular dimer, were reduced as $\alpha_{GC}$ increases. In particular, the magnetic energy at $\alpha_{GC} = 8$ and $\alpha_\zeta = 1$ becomes about one-fourth (21 meV) of that at $\alpha_{GC} = \alpha_\zeta = 1$. This energy is consistent with the magnetic interaction energy of oxygen molecule ($2 \mu_B$) under the large experimental magnetic field ($\sim 200$ T)[5]; 23 meV. Structural properties at high magnetic fields are under consideration by taking into account a giant magneto-volume effect in solid oxygen [32].
Figure 3: Binding energy (ΔE) curves for the oxygen molecular dimer in the H-Type configuration and atomic magnetic moment (MO) as a function of distance of molecules for several αζ’s and αGC = 1. The left and right panels show antiferromagnetic and ferromagnetic cases, respectively.

Table 1: Optimized lattice parameters (a, b, c, and β), equilibrium volume (V₀), binding energy of molecule (ΔE), and magnetic energy per molecule (ΔE\text{mag}) for solid oxygen at ambient pressure. Experimental values are also shown for comparison.

<table>
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<tr>
<th>αGC</th>
<th>αζ</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (deg)</th>
<th>V₀ (Å³)</th>
<th>ΔE (meV)</th>
<th>ΔE\text{mag} (meV)</th>
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<td>177</td>
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|     |     | 5.403 | 3.429 | 5.086 | 132.3   | 34.85   |          |                |     |

4 Summary

We have introduced the scaling parameters αGC and αζ for the local correlation energy functional in vdW-DF-SGC, to improve the description of the magnetic interaction in spin-polarized systems. In the H-type oxygen molecular dimer, the antiferromagnetic state is destabilized as αGC increases or αζ decreases. The structural parameters of solid oxygen are improved by choosing the optimum αGC’s. It was also found that our treatment reduces both the binding and magnetic energies in the solid oxygen, indicating that the energy functional improves the description of the energetics of spin-polarized vdW systems. The new approach developed in this work has adjustable parameters, and further investigation on the correlation energy functional may reveal applicability and limitation for an application range on real material.

It is well recognized that the density functional approach can construct one of starting
points for analyzing and designing materials. This is true regardless of spin-polarized and non-polarized systems. For non-polarized systems, the number of research works related with non-empirical vdW force increases abruptly and abundantly. This is because there was a large area of materials hidden by a poor description on vdW interaction before the development of non-empirical vdW. As similar to non-spin polarized cases, we expect the new area of magnetic materials, in which vdW force plays an important role in structural, magnetic, and energetic properties.

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