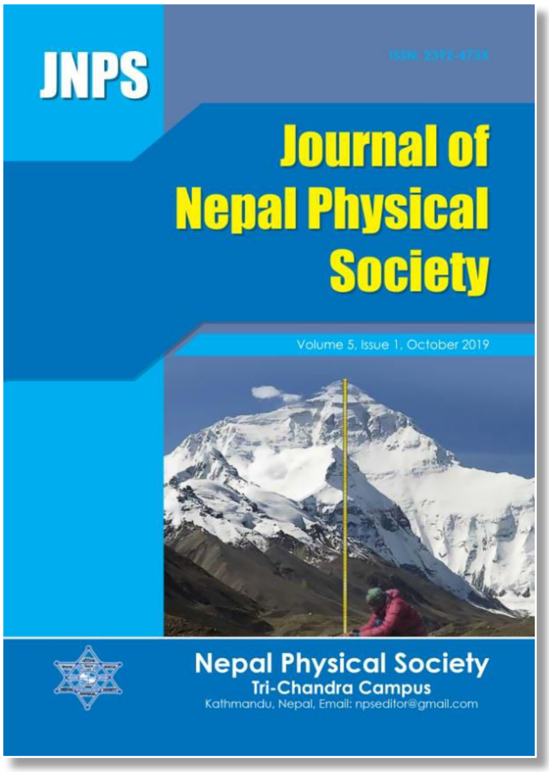
FIRST-PRINCIPLES STUDY OF VAN DER WAALS INTERACTIONS BETWEEN HALOGEN MOLECULES (CL_2 AND I_2)

S. Neopane and N. Pantha

Journal of Nepal Physical Society
Volume 5, Issue 1, October 2019
ISSN: 2392-473X



Editors:
Dr. Vinaya Kumar Jha
Dr. Binod Adhikari
Dr. Kapil Adhikari

JNPS, **5** (1), 19-23 (2019)

Published by:
Nepal Physical Society
P.O. Box: 2934
Tri-Chandra Campus
Kathmandu, Nepal
Email: npseditor@gmail.com

JNPS **5** *(1), 19-23 (2019)*
ISSN: 2392-473X

© Nepal Physical Society

Research Article

FIRST-PRINCIPLES STUDY OF VAN DER WAALS INTERACTIONS BETWEEN HALOGEN MOLECULES (CL_2 AND I_2)

S. Neopane[1] and N. Pantha[2,*]
[1]*St. Xavier's College, Maitighar, Kathmandu, Nepal*
[2]*Tribhuvan University, Kirtipur, Kathmandu, Nepal*
**Corresponding Email: mrnurapati@gmail.com*

ABSTRACT

Density Functional Theory (DFT) based first-principles calculations have been performed to investigate van der Waals (vdW) interactions in between halogen atoms/molecules —Cl-Cl, I-I, Cl_2-Cl_2, Cl_2-I_2, I_2-I_2—via with and without a non-local exchange-correlation (XC) functional (vdW-DF) using Quantum ESPRESSO codes. The non-polar covalent bond length between atomic halogens (Cl-Cl and I-I) is not observed to be affected by vdW interactions and agrees well with experimental values. The binding energy between the atomic halogens, on the other hand, is slightly corrected by vdW interactions. However, the role of vdW interactions is observed to be crucial to bind molecular halogens. The molecules are weakly bound in the presence of vdW interactions, and not correlated (bound) in the absence of them.

Keywords: Density Functional Theory (DFT), halogen molecules, van der Waals interactions

INTRODUCTION

Density Functional Theory (DFT) is one of the most successful and promising quantum mechanical theories of many body systems [1, 2]. The publication of Hohenberg-Kohn theorem in 1964 placed DFT in a firm footing and Kohn-Sham Scheme in 1965 made DFT practical [3][4]. After the development of Kohn-Sham algorithm, many exchange-correlation functionals were developed and DFT became more and more popular among theoretical physicist, biologist, and chemist [2]. Despite of DFT's success, it has struggled to describe long-range electron correlations. Standard DFT-XC functionals such as PBE fails to describe the binding energies in the long-range interactions like in inert molecules and stacked configuration of DNA base pairs. Grimme's DFT-D methods have been one of the popular methods to describe vdW interactions [5]. Numerous works have been performed to study the nature of van der Waals interactions using different functionals in complex systems using DFT. Some of these works include study of 18 DFT functionals in 2006 [6], Rudenko *et al.* study on adsorption of halogen molecules on graphene in 2010 [7], and Lamichhane *et al.* study of graphene-MoS_2 bilayer hetero-system with halogen molecules [8]. Dhakal and Pantha in 2018, have also performed first-principles study to calculate vdW interactions between Br_2 molecules using vdW-DF functional [9]. It is thus interesting to see similar work for other halogen molecules.

Van der Waals interactions are relatively weaker interactions in nature. These occur between either induced dipoles, between induced dipole and polar molecule, or between polar molecules [10]. In the case of halogen molecules, van der Waals interaction occurs between induced dipoles and is known as London dispersion force. Due to instantaneous distortion of electrical symmetry around a halogen molecule, an electric dipole is formed. This dipole may in turn produce a displacement of the electron distribution in an adjacent molecule, inducing second one to become a dipole that is weakly attracted or bonded to the first by London dispersion force [11].

The elements of the group VIIA of the modern periodic table are known as halogens. The group consists of five elements: fluorine, chlorine, bromine, iodine and astatine. Chlorine occurs exclusively as halide ion, whereas iodine can also be traced in organic compounds. Differences in the properties of halogens are due to their differences in atomic sizes. Each halogen atom interacts with the same type of another atom forming halogen molecule [12].

In the present work, we consider the nature of interactions between the atomic and molecular halogens by assuming chlorine and iodine as a model system. After this introduction, we first discuss about computational method in short, followed by results and discussion. Finally, we conclude our main results before acknowledgements and references.

COMPUTATIONAL DETAILS

Quantum ESPRESSO (QE) [13] has been used to carry out density functional theory based first-principles calculations [3][4] both with and without using vdW-DF[14][15], a non-local exchange correlation functional with modification proposed by Roman-Perez and Soler. To simulate the interaction between ion cores and valence electrons, Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) model of ultrasoft pseudopotential with electronic exchange-correlation effects using generalized gradient approximation (GGA) formalism as described by Perdew–Burke–Ernzerhof (PBE) [16] has been used. All pseudopotentials were downloaded from official QE site and the calculations were based on self-consistent field (SCF) method [17].

We consider the interactions between: Cl-Cl, I-I, Cl_2-Cl_2, Cl_2-I_2, and I_2-I_2—to study both intra-molecular interaction in a halogen molecule and inter-molecular interaction between halogen molecules. For such purpose, a box of optimal size, which isolates the interaction from neighboring boxes, is determined with appropriate values of cut off energy for wavefunction and k-point sampling. Then, in the case of intra-molecular interaction, the separation between two halogen atoms is varied and equilibrium is determined both with and without vdW-DF. Using thus obtained value of equilibrium separation, binding energy is calculated. In the case of inter-molecular interaction, the separation between two halogen molecules inside optimal box size is varied and both equilibrium separation and binding energy of the systems are calculated using vdW-DF. However, the halogen molecules are found to be not correlated (not bound) in the absence of vdW interactions.

The formula used to calculate binding energy of halogen molecule is:

$$\Delta E = 2E_X - E_{X_2} \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

Where, E_X and E_{X_2} are the ground state energies of halogen atom X and molecule X_2 respectively.

The formula used to calculate binding energy of molecular halogen system is:

$$\Delta E = E_{X_1} + E_{X_2} - E_{X_1-X_2} \cdots\cdots\cdots (2)$$

Where, E_{X_1}, E_{X_2} and $E_{X_1-X_2}$ are the ground state energy of the molecules X_1, X_2 and halogen system X_1-X_2 respectively.

RESULTS AND DISCUSSION

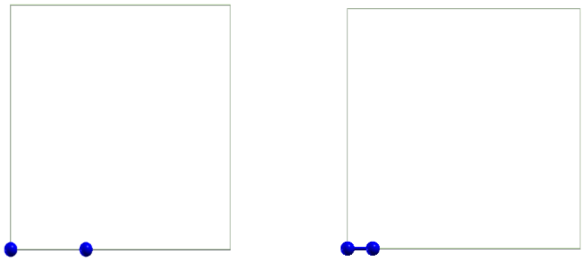
Here we describe the main results of the present work which includes the nature of interaction between atomic and molecular halogens.

Interaction in Cl-Cl and I-I systems

For Cl-Cl interaction, we consider two chlorine atoms separated by a distance of 5 Bohr inside a box of size 35 Bohr (Fig. 1) with cut off energy for wavefunction 40 Ry and with Γ (Gamma) k-point sampling. Then the separation between the two atoms is varied. The calculated bond length of chlorine molecule with and without vdW (Fig. 2) is 3.83 Bohr (2.03 Å) and 3.79 Bohr (2.00 Å) respectively, which agrees well with the experimental value 1.99 Å [18].

Similarly, In the case of I-I interaction, two iodine atoms are kept at 5 Bohr distance. These atoms are placed inside a box of size 35 Bohr with cut off energy for wavefunction 45 Ry and with Γ (Gamma) k-point sampling. Then the separation between the two atoms is varied. The calculated bond length of iodine molecule with and without vdW is 5.18 Bohr (2.74 Å) and 5.09 Bohr (2.69 Å) respectively. These calculated bond lengths also agree well with the experimental value 2.70 Å [18].

As seen from Fig. 2, when the two chlorine atoms are brought closer, the total energy of the system decreases gradually until it becomes minimum at a certain distance. This distance is called equilibrium separation, where the system is stable. If the atoms are brought further closer, the total energy of the system gradually starts to increase and thus the system starts to become unstable. It’s because, when the halogen atoms are brought closer than equilibrium separation, their electronic shells start to overlap. The overlapping of electronic shells repels halogen atoms with respect to each other, which is described by Pauli Exclusion Principle [11].



(a) **(b)**

Fig. 1*: (a) Two chlorine atoms interacting inside a box (b) Formation of a covalent bond between two chlorine atoms at equilibrium distance.*

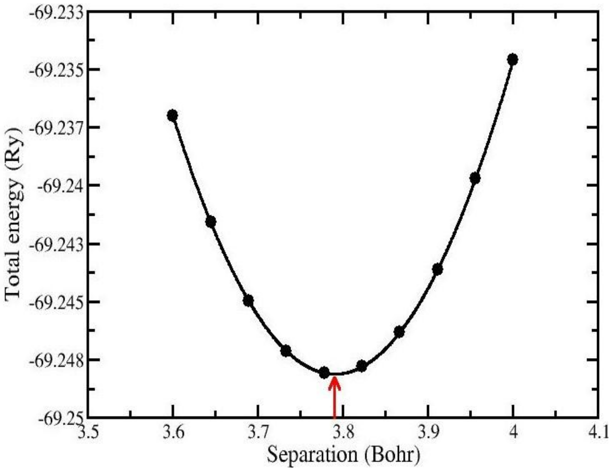


Fig. 2: *Total energy versus separation in chlorine atoms in the proximity of minimum total energgy without vdW-DF.*

Table 1: The table shows the calculated bond lengths between halogen atoms with and without vdW interactions. We also tabulate the experimental values for comparision.

Halogen Molecule	Bond Length with vdW-DF (Å)	Bond Length without vdW-DF (Å)	Experi-mental value (Å) [18]
Cl_2	2.03	2.00	1.99
I_2	2.74	2.69	2.70

From above table, in both the halogen molecules, the calculted bond length without considering vdW interactions is almost equal to the one calculted considering vdW interactions. This is due to the presence of covalent bonding bewteen atoms [19].

Binding Energy of halogen molecules

Binding Energy (B.E.) is the minimum energy required to break a system of particles into its constituent particles. In the case of halogen molecule, B.E. is defined as the minimum energy required dissociating the halogen molecule into its constituent atoms.

The B.E. is calculated by calculating the ground state energy of an isolated atom and of an isolated molecule and by using formula (1).

In chlorine molecule, the binding energy with and without vdW is calculated as 2.985 eV and 3.395 eV respectively. Similarly, the binding energy in iodine with and without vdW is calculated as 2.104 eV and 2.367 eV respectively. In both the cases, the use of vdW-DF resulted in a much better value for binding energy when compared with experimental value: 2.514 eV for chlorine and 1.566 eV for iodine molecule [18]. This can be attributed to the use of revPBE functional for the calculation of exchange energy in the case of vdW-DF [14]. The revPBE functional is known to provide better results for binding energy than PBE functional [20].

Table 2: The table shows the calculated binding energies of halogen atoms with and without vdW interactions. We also tabulate the experimental values for comparision.

Halogen Molecule	B.E. with vdW-DF (eV)	B.E. with PBE (eV)	Experi-mental value (eV) [18]
Cl_2	2.985	3.395	2.514
I_2	2.104	2.367	1.566

Interaction in molecular halogen systems

To study the interaction between two halogen molecules, optimized box size is determined. For that purpose, the size of the box is varied. The cut off energy for wavefunction is set equal to 55 Ry and a mesh of 3×3×3 k-points is used. The separation at which the curve of total energy versus box size gets saturated is taken as optimum box size. For I_2-I_2 system, the optimum box size is 25 Bohr (13.23 Å) (Fig. 3).

After the determination of box size, the separation between the two-halogen molecules is varied. When the molecules are far from each other, no interaction is seen. However, when they are brought closer and closer, an attractive interaction is observed. Further, when they are brought closer than a certain distance, due to overlap of electronic shells a repulsive interaction is observed. The separation at which the total energy of the system is minimum is taken as the equilibrium separation. The variation of total energy with separation in the vicinity of minimum total energy for I_2-I_2 system is shown in Fig. 4. The observed value of equilibrium separation at which the system is most stable under van der Waals interaction as calculated using the vdW-DF functional is 8.46 Bohr (4.48 Å).

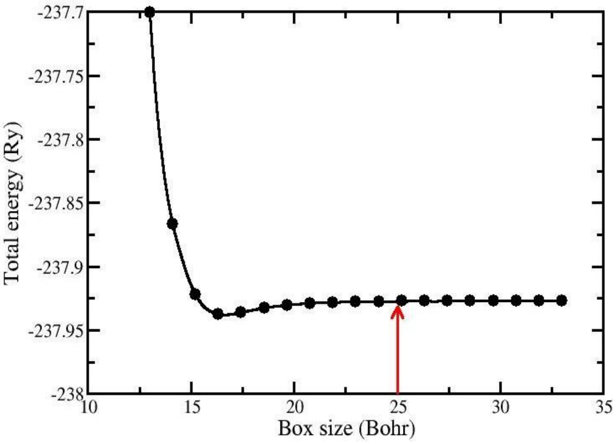


Fig. 3: *Total energy versus box size for I_2-I_2 system.*

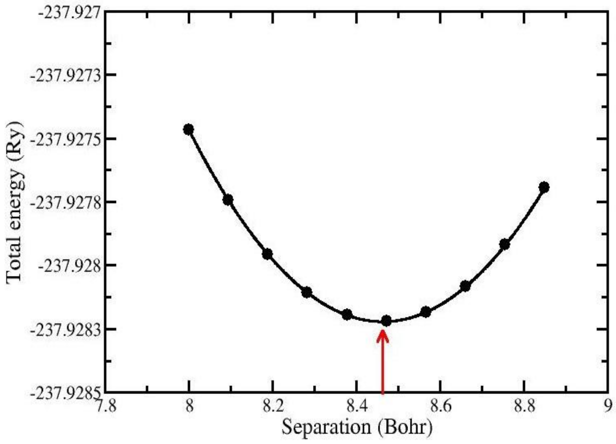


Fig. 4: *Total energy versus separation in the vicinity of minimum total energy for I_2-I_2 system.*

Similarly, for Cl_2-Cl_2 and Cl_2-I_2 systems, calculation of saturation separation was 23 Bohr (12.17 Å) and 25 Bohr (13.23 Å) respectively. Also, the equilibrium separation for Cl_2-Cl_2 system was 7.83 Bohr (4.14 Å) and for Cl_2-I_2 system was 8.51 Bohr (4.50 Å).

Table 3: The table shows the calculated equilibrium separation of molecular halogen systems.

Molecular halogen system	Optimized Box size (Å)	Equilibrium separation (Å)
Cl_2-Cl_2	12.17	4.12
I_2-I_2	13.23	4.48
Cl_2-I_2	13.23	4.50

Binding Energy of molecular halogen systems.

The binding energy of the molecular halogen system is calculated by calculating the ground state energy of the system and the ground state energy of the molecules in the system using formula (2).

The calculated values of binding energies for Cl_2-Cl_2, I_2-I_2, and Cl_2-I_2 are 0.087 eV, 0.160 eV, and 0.092 eV respectively.

Table 4: The table shows the calculated binding energy of molecular halogen systems.

Molecular halogen system	Binding Energy (eV)
Cl_2-Cl_2	0.087
I_2-I_2	0.160
Cl_2-I_2	0.092

From the table, it is clear that all the three interactions are in the range of van der Waals interactions. Since the binding energy of chlorine molecule is high, it is less reactive in intermolecular interaction and thus, both equilibrium separation and binding energy of Cl_2-Cl_2 system is minimum. Further, despite the larger size of iodine molecule, the equilibrium separation for I_2-I_2 system is not the greatest. It is due to the high binding energy of I_2-I_2 system as compared to Cl_2-I_2 system.

CONCLUSIONS

Our density functional theory based first-principles calculations show that the influence of vdW interaction in the case of bond length for halogen molecule is almost non-existent. However, vdW interaction plays a significant role in the binding energy of the system. Use of vdW-DF functional made the value of binding energy agree better with the experimental value. Also, only in the presence of vdW-DF functional, there is a bounded molecular halogen system with binding energy in the range of vdW interactions.

ACKNOWLEDGEMENTS

Authors would like to acknowledge St. Xavier's College, Kathmandu, Nepal for providing research platform and computational facilities. S. Neopane likes to extend his gratitude to N. Dulal and D. Bhattarai for useful discussion.

REFERENCES

[1] W. Koch and M. C. Holthausen, *A Chemist Guide to Density Functional Theory*, Wiley-VCH, Weinheim, 2 ed. (2001).

[2] R. G. Parr and W. Yang, *Density Functional Theory of atoms and molecules*, Oxford University Press, New York (1989).

[3] P. Hohenberg, W. Kohn, Phys. Rev. **136**, B864 (1964).

[4] W. Kohn, L. J. Sham, Phys. Rev. **140**, 1133 (1965).

[5] J. Klimes and A. Michaelides, J. Chem. Phys. **137**, 120901 (2012).

[6] Y. Zhao and D. G. Truhlar, J. Phys. Chem. A **110**, 13126 (2006).

[7] A. N. Rudenko, F. J. Keil, M. I. Katsnelson, and A. I. Lichtenenstein, Phys. Rev. B **82**, 035427 (2010).

[8] S. Lamichhane, P. Lage, G.B. Khatri, N. Pantha, N. P. Adhikari and B. Sanyal, J. Phys. **765**, 012011 (2016).

[9] B. Dhakal and N. Pantha, JPPC 1(1), 59(2018).

[10] V.A. Parsegian, *van der Waals Forces*, Cambridge University Press, New York (2006).

[11] W.D. Callister, Jr and D.G. Rethwisch, *MATERIAL SCIENCE AND ENGINEERING: AN INTRODUCTION*, John Wiley & Sons, Inc., New York, 8 ed. (2010).

[12] M. Halka and B. Nordstorm, *Halogens and Nobel gases*, Facts on File, Inc., New York (2010).

[13] P. Giannozzi et al., J. Phys. Condens. Matter **21**, 395502 (2009).

[14] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **96**, 246401 (2004).

[15] G. R. Perez and J. M. Soler, Phys. Rev. Lett. **103**, 096102 (2009).

[16] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. **77**, 3865 (1996).

[17] S.M. Blinder, Am. J. Phys. **33**, 431 (1965).

[18] N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Elseiver Ltd., Oxford, 2 ed. (1998).

[19] I. Hamada and S. Yanagisawa, Phys. Rev. B **84**, 153104 (2011).

[20] Y. Zhang and W. Yang, Phys. Rev. Lett. **80**, 890 (1998).