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# Electron Binding Energy Of Polar Molecules Using Fermi Löwdin Orbital Self Interaction Corrected Density Functional Scheme

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ELECTRON BINDING ENERGY OF POLAR MOLECULES USING FERMI LÖWDIN  
ORBITAL SELF INTERACTION CORRECTED DENSITY FUNCTIONAL SCHEME

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Dean of the Graduate School

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## **DEDICATION**

*To my lovely wife Vivian Ufondu and my lovely son Zois Ufondu.*

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ORBITAL SELF INTERACTION CORRECTED DENSITY FUNCTIONAL SCHEME

by

PETER OBINNA UFONDU, B.Tech.

THESIS

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The University of Texas at El Paso  
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of the Requirements  
for the Degree of

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Department of Physics  
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## ABSTRACT

Density functional theory (DFT) has become a standard method for electronic structure calculations in physics. The standard approximate density functionals usually do not bind this class of anions, due to self-interaction error (SIE). We apply the recently developed Fermi Löwdin orbitals based self-interaction correction method (FLOSIC) with long-range diffuse gaussian functions to study dipole bound anions ( $VC^-$ ,  $EC^-$ ) and negatively charged water clusters  $(H_2O)_n^-$   $n=2-6$ . These calculations are carried out using Perdew-Wang (1992) local spin density PW91-LDA, Perdew-Burke-Ernzerhof PBE-GGA, and the recently developed Strongly Constrained and Appropriately Normed SCAN-meta-GGA functional which satisfies all the known constraints for exchange-correlation functional. Plot from FLOSIC density difference shows that the excess electron is weakly bound to the molecule and mostly occupies a very diffuse orbital away from the molecular framework. In the water cluster anions  $(H_2O)_n^-$   $n=2-6$ , the extra electron is not bound to any of the water molecules but rather occupies a diffuse orbital. We find that applying FLOSIC brings the LDA, GGA, and SCAN results closer to experimental values for the carbonate molecules. The calculated binding energy give an absolute deviation of 0.41meV for EC at PBE-GGA and 1.95meV for VC at PW91-LDA which agrees with experimental values. LDA functional show slightly larger binding energy in all cases. The water cluster anions  $(H_2O)_n^-$   $n=2-6$ , binds in all level with the FLOSIC GGA with the least mean absolute deviation MAD of 60.1meV relative to CCSD(T).

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## CHAPTER 1.0: INTRODUCTION

Dipole bound molecular anion, is a class of anion produced by a polar molecule with the extra electron been bounded to a large extent by the long-range electrostatics-potential rather than by short range valance potential. In such anions, the excess electron does not reside in a conventional valence orbital but in an orbital whose size, shape, and binding energy is governed by the long-range electrostatics-potential of the polar molecule. This feature is different in the case valence bound anions where the extra electron is located on the lowest unoccupied molecular orbital of the neutral molecule located within the molecular framework. As a conclusive finding followed that molecules with dipole moment of more than 2.5Debye should produce dipole bound anion [1]. Experimentally, In Rydberg electron transfer (RET), dipole-bound anions can readily be formed by colliding polar molecules (with a dipole moment exceeding the critical value mentioned before) with a Rydberg alkali atom (such as Rubidium) excited to various levels [8]. The dipole bound anions are important in certain chemical processes for example charge transfer, interstellar absorption bands, electron capture in biological molecules, and as a pathway for forming valence bound anions [2]. The dipole bound anions have been studied with highly accurate quantum chemical methods that are limited to smaller molecules due to their computational expenses. Jordan and coworkers [3] study shows that even though the extra electron is located away from the molecular framework, electron-electron correlation is needed to accurately describe the weakly bound anion. Density functional theory (DFT) can be applied to relatively larger molecules with hundreds of atoms, but the density functional approximations are known to incorrectly bind atomic anions [4]. Inspection of the orbital energies show that the highest occupied molecular orbital (HOMO) of the anion is usually positive. This implies that, in principle, the calculation is unconverted. This is due the density functional approximations suffer from self-interaction errors due to the fact the self-Coulomb energy is not exactly canceled by the self-approximate exchange-correlation energy. This error is especially large for anions, because of their additional electron. Self-interaction error produces an exchange-correlation potential that incorrectly decays

exponentially in the asymptotic region, instead of decaying as  $-1/r$ . For atomic anions, a large positive barrier appears in the Kohn-Sham potential resulting in positive HOMO resonances, the potential decays as  $(N - Z)/r$  instead of  $(N - 1 - Z)/r$  and self-interaction correction is needed to obtain correct electron affinities. Using Koopman's theorem, one may estimate electron affinity from the HOMO energy of anion, but both relaxation and correlation effects are so large that Koopman's theorem is unhelpful here [5]. Using large basis set, Herbert and Head-Gordon have investigated the effect of basis sets and concluded that using the standard default basis sets without adding supplementary functionals while calculating the electron binding energy will result in an error of the order 0.2 eV [6] also Jensen showed that density functional approximations (DFA) bind only fractional electron where size of the fraction is dependent on the magnitude of the electron affinity and the DFA employed [7].

DFT, allows to compute the electron affinity from the total energy difference between the neutral and anionic system, positive electron affinities result for stable anions. The dipole bound anions present a special challenge for density functional approximations. First, the electron is very weakly bound compared to stable atomic and molecular anions at the geometry of the neutral. Lastly, long-range basis gaussian basis functions are needed to describe the extra electron is located away from molecular framework. Self-interaction corrected density functional theory was employed by Johnson and coworker to study the extra electron binding to CH<sub>3</sub>CN [8]. The results show that the HOMO eigenvalue correctly reproduces the electron binding energy. In this work we apply Gaussian basis functions in conjunction with Fermi Lowdin orbital self-interaction corrected density functionals to study the anions of Ethylene carbonate EC, Vinylene carbonate VC and water cluster anions  $(H_2O)_n^-$   $n=2-6$ . The both EC<sup>-</sup> and VC<sup>-</sup> are interesting that they do not form valence bound anionic states but rather undergo dissociative electron attachment when exposed to low energy electron beam of energy higher than 0.5 eV. Hammer et al. have shown that these VC<sup>-</sup> and EC<sup>-</sup> form true dipole-bound anion systems where they could form anions through Rydberg electron transfer method [6]. Anion photoelectron spectroscopy established the electron binding energies of these molecules at 49 meV and 24 meV respectively for ethylene and

vinylene carbonates. These molecules have relatively large dipole moments of 5.35D and 4.55D for ethylene carbonate and vinylene carbonates, respectively. Results of earlier couple cluster calculations that include single, double and triple excitation CCSD(T) with a large Gaussian basis set showed good agreement with experimental binding energies. Kiyoshi and coworker[9] used DFT with the one parameter progressive (OP) correlation functional to study water cluster anions  $(H_2O)_n^-$   $n=2-6$ , the method show a mean absolute deviation of 13.8 meV from the couple cluster calculations that include single, double and triple excitation CCSD(T).

The existence of highly accurate experimental as well as theoretical data makes these anions suitable for study on the effect of self-interaction for DFAs for these systems. The self-interaction correction is applied through recently developed FLOSIC method which we use to study weakly bound anions as in the dipole bound anions with long range diffuse function which tend to overbind the electron in the anions with the standard DFAs. The next three chapters are as follows: Firstly, chapter two, I will give a theoretical background of the density functional theory and the essential ideas of self-interaction correction SIC and the Fermi Löwdin orbital self-interaction correction FLOSIC approach to DFT. Secondly, in chapter three I will detail the general concepts used to perform this calculation. Finally, in chapter four, I will discuss the results obtained and elaborate on the effect that self-interaction correction.

## CHAPTER 2.0: THEORETICAL BACKGROUND

### 2.1 Density Functional Theory

#### 2.1.1 Electronic Structure Theory

From the non-relativistic quantum theory, the state of any given system is represented by a time-dependent vector in Hilbert space,  $|\psi\rangle$ . This vector obeys the famous Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(\mathbf{x}, t)\rangle = \hat{H} |\psi(\mathbf{x}, t)\rangle, \quad 2.1$$

wherein  $i$  denotes the imaginary unit,  $\hbar$  denotes the reduced Planck constant,  $\frac{\partial}{\partial t}$  denotes the partial time derivation and  $\hat{H}$  denotes the Hamiltonian operator. If the Hamiltonian is time-independent, the separation ansatz of

$$\hat{H} |\psi(\mathbf{x}, t)\rangle = e^{-i\frac{E_t}{\hbar}} |\psi(\mathbf{x})\rangle. \quad 2.2$$

For the so-called stationary state Schrödinger equation gives:

$$\hat{H} |\psi\rangle = E |\psi\rangle. \quad 2.3$$

Herein,  $E$  denotes the total energy of the system in the stationary state  $|\psi\rangle$ . For a many-body system of  $N$  electrons and  $M$  nuclei interacting through a Coulomb potential, the Hamiltonian has the form [10]

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i^N \Delta_i - \sum_{i,l}^{N,M} \frac{Z_l e^2}{4\pi\epsilon_0 |\vec{x}_i - \vec{X}_l|} + \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{4\pi\epsilon_0 |\vec{x}_i - \vec{x}_j|} - \sum_l^M \frac{\hbar^2}{2M_l} \Delta_l + \frac{1}{2} \sum_{l \neq j}^{N,M} \frac{Z_l Z_j e^2}{4\pi\epsilon_0 |\vec{X}_l - \vec{X}_j|}. \quad 2.4$$

Herein,  $\vec{x}_i$  denotes the position of an  $i^{\text{th}}$  electron with the mass  $m_e$  and the negative elemental charge  $-e$ ,  $\vec{X}_l$  denotes the position of a  $l^{\text{th}}$  nucleus with the mass  $M_l$  and the atomic number  $Z_l$ ,  $\Delta$  denotes the Laplacian operator and  $\epsilon_0$  denotes the dielectric constant.

Neglecting spin for the moment, the stationary state  $|\psi\rangle$  can be reformulated as the many-body wave function  $\psi = \psi(\vec{x}_1, \dots, \vec{x}_N, \vec{X}_1, \dots, \vec{X}_M)$ . The mass of the nuclei is so enormous in comparison to the electron mass  $m_e$  that, the nuclei stand still from the electronic point of view, while the electrons themselves appear to be moving instantaneously from the perspective of the nuclei. This is called the Born-Oppenheimer or adiabatic approximation, and it leads to a separation of electron dynamics from nuclear dynamics, introducing the electronic Hamiltonian  $\hat{H}_e$ . This electronic Hamiltonian is written as [10]

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ext} + \hat{V}_{int} + \hat{V}_{II}. \quad 2.5$$

Using Hartree atomic units ( $\hbar = 4\pi\epsilon_0 = m_e = e = 1$ ) from now on, the electronic kinetic energy operator  $\hat{T}_e$  is given as [10]

$$\hat{T}_e = -\frac{1}{2} \sum_i^N \Delta_i, \quad 2.6$$

the attractive Coulomb potential  $\hat{V}_{ext}$  between the electrons and nuclei can be written as [10]

$$\hat{V}_{ext} = - \sum_{i,I}^{N,M} \frac{Z_I}{|\vec{x}_i - \vec{X}_I|}, \quad 2.7$$

and the repulsive Coulomb potential  $\hat{V}_{int}$  between the electrons is formulated as [10]



$$\hat{V}_{int} = \sum_{i \neq j}^N \frac{1}{|\vec{x}_i - \vec{x}_j|} . \quad 2.8$$

Finally, the repulsive Coulomb potential  $\hat{V}_{II}$  between the nuclei is given as [10]

$$\hat{V}_{II} = \frac{1}{2} \sum_{I \neq J}^{N,M} \frac{Z_I Z_J}{|\vec{X}_I - \vec{X}_J|} . \quad 2.9$$

This last term is solely dependent on the positions of the nuclei, which are treated as parameters in the electronic Hamiltonian. For a given set of nuclear positions,  $\hat{V}_{II}$  is an approximation because the nuclei are treated as classical particles. Anyway, the matter of finding the most energetically favorable nuclear positions is only addressed after the electronic Hamiltonian has been solved. The solution to the stationary Schrödinger equation involving  $\hat{H}_e$  is a wave function of the form  $\emptyset = \emptyset(\vec{x}_1, \dots, \vec{x}_N)$ . The nuclear 3M degrees of freedom have been successfully eliminated in order to tackle a problem which depends only on the electron positions as basic variables. There are several approaches to solve the electronic stationary Schrödinger equation, but this thesis will concentrate on the method called density functional theory (DFT), including both the fundamental concepts and the practical proceedings. The rest of this section will be fully dedicated to DFT, starting with its basis, i.e. the theorems of Hohenberg and Kohn [14].

### 2.1.2 The Theorems of Hohenberg and Kohn

Even with the simplifications made above, the number of spatial variables to be calculated in order to obtain the correct solution corresponding to the electronic Hamiltonian is still 3 N. As no computer available today is powerful enough to make these calculations in a finite amount of time, it is logical that this obstacle was even more insurmountable back in the 1960s, when Pierre Hohenberg and Walter Kohn took on the challenge. Their first Hohenberg-Kohn theorem

proclaims that, for any system of interacting particles moving in an external potential  $\hat{V}_{ext}(\vec{x})$ , said potential is determined uniquely by the ground state particle density  $n_0(\vec{x})$  of the system - except for a constant [10, 14]. However, determining the external potential equals determining the Hamiltonian, which in turn determines all the wave functions of the ground state and the excited states. As the wave functions contain the complete information of the system, any property of the system can be interpreted as a functional of this density  $n_0(\vec{x})$  [10, 14].

This function depends on merely three spatial coordinates. Thus, the introduction of the ground state density as a new basic variable has led to the establishment of the term "density functional theory" for the Hohenberg-Kohn theorems and the ideas they spawned.

Unfortunately, as enlightening as this theorem is in this respect, it does not provide any actual solution to the stationary Schrödinger equation of electronic structure theory [10]. The second Hohenberg-Kohn theorem, however, states that a universal functional for the total energy  $E[n]$ , which depends on the particle density  $n(\vec{x})$ , can be defined and that this functional is valid for any external potential  $\hat{V}_{ext}(\vec{x})$ , [10, 14]. For any given  $\hat{V}_{ext}(\vec{x})$ , the global minimum value of this energy functional is the ground state total energy of the system  $E_0$ , and the density minimizing the functional equals the ground state particle density  $n_0(\vec{x})$  [10, 14]. The universal energy functional of Hohenberg and Kohn  $E_{HK}[n]$  is written as [10]

$$E_{HK}[n] = T_e[n] + E_{int}[n] + \int d^3x \hat{V}_{ext}(\vec{x})n(\vec{x}) + \hat{E}_H. \quad 2.10$$

The electronic kinetic energy  $T_e[n]$  is formulated as [10]

$$T_e[n] = \langle \emptyset | T_e | \emptyset \rangle, \quad 2.11$$

the internal potential energy  $E_{int}[n]$  is written as [10]

$$E_{int}[n] = \frac{1}{2} \iint \frac{n(\vec{x})n(\vec{x}')}{|\vec{x} - \vec{x}'|} d^3x d^3x' + E_{xc}(n), \quad 2.12$$

the external potential  $\hat{V}_{ext}(\vec{x})$  is given as [10]

$$\hat{V}_{ext}(\vec{x}) = - \sum_{i,I}^{N,M} \frac{Z_I}{|\vec{x}_i - \vec{X}_I|}, \quad 2.13$$

and the electron density  $n(\vec{x})$  is defined as [10, 17]

$$n(\vec{x}) = N \int d^3 x_2, \dots \int d^3 x_N |\Phi(\vec{x}, \vec{x}_2, \dots, \vec{x}_N)|^2. \quad 2.14$$

Again, it is important to mention that this total energy functional  $E_{HK}[n]$  is only useful for finding the ground state total energy and the corresponding electron density, not for obtaining any properties of excited states. But even for the ground state, the second Hohenberg-Kohn theorem does not yield any explicit expressions for the kinetic energy functional  $T_e[n]$  and the internal potential energy functional  $E_{int}[n]$ . This seems to make the search for a minimum value of  $E_{HK}[n]$  by varying  $n(\vec{x})$  impossible [10]. Fortunately, Walter Kohn and Lu Jeu Sham found an ansatz to make up for this deficit in the original Hohenberg-Kohn theorems in 1965, a year after the latter were published [13]. This Kohn-Sham ansatz will be the topic of the next section.

### 2.1.3 The Kohn-Sham Ansatz

Basically, this ansatz of Kohn and Sham consists of substituting the many-body system of the Hohenberg-Kohn theorems with an auxiliary system of non-interacting electrons [10, 12, 13, 17, 18]. As such, the state of this auxiliary system is represented by a single-electron wave function  $\psi(\vec{x})$  the so-called Kohn-Sham orbital, which is delocalized in nature [12]. The Kohn-Sham (KS) orbital is consequently determined by a single-electron auxiliary Hamiltonian  $\hat{H}_{aux}$ , defined as [10]

$$\hat{H}_{aux} = -\frac{1}{2}\Delta + \hat{V}_{aux}(\vec{x}). \quad 2.15$$

This Hamiltonian incorporates a yet undefined, mean-field potential term  $\hat{V}_{aux}$ . This auxiliary system is created in such a way as to possess a ground state electron density identical to the one of the original systems [10, 12]. Introducing spin, the wave function describing the state of the Kohn-Sham system  $\psi(\vec{x})$  can be reformulated as  $\psi^\sigma(\vec{x})$ . In the ground state, the  $N^{\sigma=\uparrow}$  majority spin electrons present in the system occupy the  $N^{\sigma=\uparrow}$  majority spin orbitals  $\psi_i^{\sigma=\uparrow}(\vec{x})$  corresponding to the  $N^{\sigma=\uparrow}$  lowest energy eigenvalues  $\epsilon_i^{\sigma=\uparrow}$  for the majority spin, and the same is valid for the minority spin [10]. Accordingly, the ground state electron density  $n(\vec{x})$  of the auxiliary system can be constructed from the orbitals as [10, 12, 13, 17]

$$n(\vec{x}) = \sum_{\sigma} \sum_i^{N^{\sigma}} |\psi_i^{\sigma}(\vec{x})|^2, \quad 2.16$$

Furthermore, the total energy functional of Hohenberg and Kohn  $E_{HK}[n]$ , is rewritten as the Kohn-Sham functional  $E_{ks}[n]$ , which is of the form [10]

$$E_{ks}[n] = T_{ks}[n] + \int d^3x \hat{V}_{ext}(\vec{x})n(\vec{x}) + E_H[n] + E_{xc}[n] \quad 2.17$$

Herein, the kinetic energy of the non-interacting electrons  $T_{ks}[n]$  is given as [10]

$$T_{ks}[n] = -\frac{1}{2} \sum_{\sigma} \sum_i^{N^{\sigma}} \langle \psi_i^{\sigma}(\vec{x}) | \Delta | \psi_i^{\sigma}(\vec{x}) \rangle, \quad 2.18$$

and the Hartree energy  $E_H[n]$ , a term constructed as an analogon of the classic Coulomb self-interaction energy of the density  $n(\vec{x})$ , is defined as [10, 12, 13, 17]

$$E_H[n] = \frac{1}{2} \iint d^3x d^3x' \frac{n(\vec{x})n(\vec{x}')}{|\vec{x} - \vec{x}'|}. \quad 2.19$$

Lastly, the exchange-correlation energy  $E_{XC}[n]$  includes all the non-classical many-body effects needed in the functional to justify the equivalence of  $E_H[n]$ .

The mathematical expressions of  $E_{XC}[n]$ , the exchange-correlation energy can be expressed as [10]

$$E_{XC}[n] = T_e[n] - T_{KS}[n] + E_{int}[n] - E_H[n]. \quad 2.20$$

Thus, it can be viewed as the difference between the kinetic and internal potential energies in the original many-body system of Hohenberg and Kohn and in the auxiliary non-interacting electron system of Kohn and Sham [10]. In order to find the global minimum value of the Kohn-Sham functional  $E_{KS}[n]$ , which means finding the correct ground state total energy and ground state electron density, the functional is varied with respect to the spin-dependent Kohn-Sham orbitals  $\psi_i^\sigma(\vec{x})$ . This leads to variational equations of the type [10]

$$\frac{\delta E_{KS}[n]}{\delta \psi_i^{\sigma,*}(\vec{x})} = \frac{\delta T_{KS}[n]}{\delta \psi_i^{\sigma,*}(\vec{x})} + \left[ \frac{\delta \int d^3x \hat{V}_{ext}(\vec{x})n(\vec{x})}{\delta n^\sigma(\vec{x})} + \frac{\delta \hat{E}_H[n]}{\delta n^\sigma(\vec{x})} + \frac{\delta \hat{E}_{XC}[n]}{\delta n^\sigma(\vec{x})} \right] \frac{\delta n^\sigma(\vec{x})}{\delta \psi_i^{\sigma,*}(\vec{x})} = 0 \quad 2.21$$

Calculating the functional derivatives [10],

$$\frac{\delta T_{KS}[n]}{\delta \psi_i^{\sigma,*}(\vec{x})} = -\frac{1}{2} \Delta \psi_i^\sigma(\vec{x}), \quad 2.22$$

$$\frac{\delta \int d^3x \hat{V}_{ext}(\vec{x})n(\vec{x})}{\delta n^\sigma(\vec{x})} = \hat{V}_{ext}(\vec{x}), \quad 2.23$$

$$\frac{\delta \hat{E}_H[n]}{\delta n^\sigma(\vec{x})} = \int d^3x' \frac{n(\vec{x}')}{|\vec{x} - \vec{x}'|} = \hat{V}_H(\vec{x})[n], \quad 2.24$$

$$\frac{\delta \hat{E}_{XC}[n]}{\delta n^\sigma(\vec{x})} = V_{XC}^\sigma(\vec{x})[n], \quad 2.25$$

and

$$\frac{\delta n^\sigma(\vec{x})}{\delta \psi_i^\sigma(\vec{x})} = \psi_i^\sigma(\vec{x}), \quad 2.26$$

allows to develop an effective Kohn-Sham Hamiltonian  $\hat{H}_{KS}^\sigma$ . This Hamiltonian acts on the spin-dependent orbitals  $\psi_i^\sigma(\vec{x})$ , yielding the so-called Kohn-Sham equations [10]

$$(\hat{H}_{KS}^\sigma - \varepsilon_i^\sigma) \psi_i^\sigma(\vec{x}) = (-\frac{1}{2} \Delta + V_{KS}^\sigma(\vec{x}) - \varepsilon_i^\sigma) \psi_i^\sigma(\vec{x}) \quad 2.27$$

$$V_{KS}^\sigma(\vec{x}) = \hat{V}_{ext}(\vec{x}) + \hat{V}_H(\vec{x})[n] + V_{XC}^\sigma(\vec{x})[n]. \quad 2.28$$

Hence, the ground state density  $n(\vec{x})$  is constructed from spin-dependent Kohn-Sham orbitals stemming from a Hamiltonian. The potential terms of this Hamiltonian are, except for  $\hat{V}_{ext}(\vec{x})$ , functionals of this very same density. The Kohn-Sham equations must be solved self-consistently for  $n(\vec{x})$ ,  $\hat{V}_H(\vec{x})[n]$  and  $V_{XC}^\sigma(\vec{x})[n]$  [10].

In the following, a short look at three of the most common exchange-correlation approximations, LDA, GGA and Meta-GGA will be given. These are also the functionals employed for the calculations later in this thesis.

## 2.2 FUNCTIONALS FOR EXCHANGE AND CORRELATION

### 2.2.1 Local Density Approximation LDA

The local spin density approximation LDA was developed by Kohn and Sham and it tells that, for system where the electron density varies over space the exchange and correlation are primarily local phenomena. for spin- unpolarized homogenous system the exchange energy is analytically as a functional of the density in the LDA approximation

$$E_{xc}[n] = \int d^3x \varepsilon_{xc}^{LDA}(n(x)). \quad 2.29$$

Where  $\varepsilon_{xc} = \varepsilon_x + \varepsilon_c$ .  $\varepsilon_{xc}^{LDA}(n(r))$  is the exchange energy density that depend on  $n(x)$  and is defined as:

$$\varepsilon_x^{LDA}(n) = -\frac{3^{\frac{4}{3}}}{4\pi^{\frac{1}{3}}} n^{\frac{4}{3}} = -C_x^{LDA} n^{\frac{4}{3}} \quad 2.30$$

For spin polarized homogenous system the exchange energy is analytically as a functional of the density in the LDA approximation:

$$E_{xc}[n^\uparrow, n^\downarrow] = \frac{1}{2} (E_{xc}[2n^\uparrow] + E_{xc}[2n^\downarrow]). \quad 2.31$$

LDA gives close to correct exchange correlation energy to system that have similar property to homogenous system like the close shell system, metal and electron gas.

### 2.2.2 Generalized Gradient Approximation GGA

The generalized gradient approximation exchange correlation energy is a functional of both the local spin densities and the local spin density gradients. It uses the dimensionless enhancement factor  $F(s)$  as

$$E_{xc}^{GGA}[n, \nabla n] = \int d^3x \varepsilon_{xc}^{LDA}(n(x)) F_{xc}(s(x)), \quad 2.32$$

where

$$S = |\nabla n| / [2(3\pi^2)^{\frac{1}{3}} n^{\frac{4}{3}}]. \quad 2.33$$

### 2.2.3 Strongly Constrained and Appropriately Normed SCAN

The SCAN exchange correlation energy is a functional of both the local spin densities, the local spin density gradients and the kinetics energy density defined as

$$E_{xc}[n] = \int d^3x \varepsilon_{xc}^{unif}(n) F_{xc}(s, \alpha). \quad 2.34$$

Here,

$$S = |\nabla n| / [2(3\pi^2)^{\frac{1}{3}} n^{\frac{4}{3}}], \quad 2.36$$

is the dimensionless density gradient.

$$\alpha = (\tau - \tau^w) / \tau^{unif} \quad 2.37$$

Where  $\tau = \sum_i^{occ} |\psi|^2$ , the positive orbital kinetic energy density,

$\tau^w = |\nabla n|^2 / 8n$  is the single-orbital limit of  $\tau$  and  $\tau^{unif} = (\frac{3}{10})(3\pi^2)^{2/3}$  known as the uniform density limit.

Obviously, the three functionals possess their characteristic strengths and weaknesses, and their usefulness is heavily dependent on the system at hand. The development of new and better functionals remains one of the main challenges for advancing density functional theory within the Kohn-Sham ansatz. However, instead of creating an entirely original functional, it is often more practical to add a term to those already existing, in order to correct some of their more apparent shortcomings. Many of the corrections currently in use aim to eliminate the so-called self-interaction error (SIE) [10, 18, 19, 20]. The nature of this error and the different approaches to tackle it will be the topic of the following section.



## 2.3 SELF-INTERACTION CORRECTIONS TO DENSITY FUNCTIONAL THEORY

The self-interaction error SIE is responsible for several weaknesses DFT calculations often exhibit. For solids, the SIE has been identified as the source for the systematic underestimation of the semiconductor band gaps [18, 27, 28]. These gaps are calculated as differences of orbital energy eigenvalues - specifically, as the differences between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) energies [18, 27, 28]. In general, uncorrected DFT does not fulfill Koopman's theorem, which identifies the HOMO energy as the negative of the ionization potential and the LUMO energy as the negative of the electron affinity [10, 18, 28]. In Koopman's theorem, orbital relaxation processes are neglected [1, 32]. The disagreement with Koopman's theorem stems partly from the tendency of DFT to increase the orbital energies in a non-systematic way [30, 31].

Furthermore, in localized, electrically neutral systems, the effective Kohn-Sham potential  $V_{KS}^{\sigma}(\vec{x})$  fails to reproduce the expected, asymptotically correct long-range behavior of  $-1/r$  [22, 28, 29]. A third disadvantageous consequence of the SIE is that several experimentally stable negative ions, e.g. ethylene carbonate, are calculated to possess positive HOMO energies by DFT, does not give a good descriptor of the EA. In the following, the terms formally describing the SIE will be introduced. As a matter of fact, both the Hartree energy functional, expressed as [10, 12, 13]

$$E_H[n] = \frac{1}{2} \iint d^3x d^3x' \frac{n(\vec{x})n(\vec{x}')}{|\vec{x} - \vec{x}'|} \quad 2.37$$

and the exchange-correlation energy functional  $E_{XC}[n]$  contain terms which describe the unphysical interaction of an orbital with itself. In the former functional, the Coulomb self-repulsion of an electron is included, the latter incorporates the effect of an electron exchanging with and being correlated to itself. It is worth noting that the validity of these statements does not depend on the concrete exchange-correlation functional in use but is of a general nature. If the exact

exchange-correlation functional  $E_{XC,\text{exact}}[n]$  were known, this would not pose a problem, as the self-interacting terms would perfectly compensate each other for each orbital. This phenomenon can be written as

$$E_{XC,\text{exact}}[n_i^\sigma, 0] + E_H[n_i^\sigma] = 0 \quad 2.38$$

In this equation,  $n_i^\sigma$  represents the spin-dependent orbital electron density defined as  $n_i^\sigma = |\psi_i^{\sigma=\uparrow}(\vec{x})|^2$ . However, as only approximate exchange-correlation functionals  $E_{XC,\text{appr}}[n]$  are applied in practice, this equation is sadly not fulfilled for any of the orbitals, resulting in the presence of the self-interaction error energy  $E_{SIE}$  in the functional. It is defined as

$$\sum_{\sigma} \sum_i^{N^\sigma} E_{XC,\text{appr}}[n_i^\sigma, 0] + E_H[n_i^\sigma] = E_{SIE}[n_1, n_2, \dots]. \quad 2.39$$

Eliminating  $E_{SIE}$  is thus the aim of self-interaction corrections (SIC) to density functional theory. The SIC methods, proposed by Perdew and Zunger and the approach used by Mark Pederson et al will be presented in the following subsections [20, 22, 29].

### 2.3.1 Perdew-Zunger Self Interaction Correction

The problem of self-interaction error which occur in density functional theory such as Rydberg state missing, mis-ordering of states of some systems, incorrect description of stretch bonds, problems with unstable anions due to the fact that the sum of the Hartree interaction energy and the approximated exchange correlation energy does not properly vanish for all one-electron system. This led to the introduction of self-interaction correction SIC proposed by Perdew and Zunger.

In their approach, they introduce orbital -dependent corrections to the exchange correlation energy functional:

$$E_{xc}^{pZ}[n^\uparrow, n^\downarrow] = E_{xc}[n, n^\downarrow] - \sum_\sigma \sum_i^{N_\sigma} \{U[n_{i\sigma}] + E_{xc}[n_{i\sigma}, 0]\}. \quad 2.40$$

For the correct exchange-correlation functional, the correction should vanish. Where  $n_{i\sigma}$  is the number of occupied orbitals of spin  $\sigma$ ; is the orbital density for the KS orbital  $\varphi_{i\sigma}$

$$n_{i\sigma} = |\varphi_{i\sigma}|^2 \quad 2.41$$

the total energy of an N-electron system is

$$E^{pZ} = E^{DFT}[n] + \sum_i U^{SIC}[n_i] \quad 2.42$$

The Schrodinger-like equations like that of the Kohn-sham equations for N-electron system is got by varying the  $E^{pZ}$  with respect to spin-orbital  $\varphi_i^\sigma$

$$\{H_{0\sigma} + V_{i\sigma}^{SIC}\}\varphi_{i\sigma} = \sum_j^N \lambda_{ij}^\sigma \varphi_{j\sigma} \quad 2.43$$

The PZ-SIC leads to an energy expression that is not unitarily invariant. The PZ-SIC scheme is effective with small systems such as atoms using Kohn-Sham orbitals but for larger systems use of KS orbitals can lead to size extensivity problem which means that the SI corrections for the total system is not equal to the sum of the corrections for the parts. The size-extensivity problem can be avoided by employing localized orbitals. Pederson et al. have shown that the localized orbitals need to satisfy the localization equations to ensure that the SI corrected total energy is minimized. The localization equations are:

$$\langle \varphi_{i\sigma} | V_{i\sigma}^{SIC} - V_{j\sigma}^{SIC} | \varphi_{j\sigma} \rangle = 0 \quad 2.44$$

However solving the localization equations on top of the KS equations makes it computationally expensive to apply SI corrections and therefore SIC calculations have been limited to small molecules only.

### 2.3.2 Fermi Löwdin Self-Interaction Correction (FLOSIC)

Within the FLOSIC approach, the necessity of the solving the computationally demanding localization equations vanishes. Using the FLOSIC approach the localized orbitals are constructed based on the fermi orbitals. For a spin system of  $N$  number of electrons, the starting point is to have the Kohn-Sham occupied orbitals  $\varphi_{i\sigma}$  transformed into Fermi orbitals  $F_{i\sigma}$  which is defined by [40,41,42,43,44]

$$F_{i\sigma} = \frac{\sum_i^{N\sigma} \varphi_{i\sigma}^* a_{i\sigma} \varphi_{i\sigma}(r)}{\sqrt{\sum_i^{N\sigma} |a_{i\sigma} \varphi_{i\sigma}|^2}} = \sum_i^{N\sigma} F_{ij} \varphi_{i\sigma}(r) \quad 2.45$$

In the above equation,  $a_{i\sigma}$  is the Fermi orbital descriptor FOD that describes the classical electronic position. Furthermore, the FODS are the variational parameters for minimizing the orbital dependent part of the energy and the  $F_{ij}$  is the fermi orbital transformation matrix.

The density of the Fermi orbitals is equal to the spin density of the KS-orbital and it is normalized since the Kohn-Sham orbital are orthonormal.

$$|F_j^\sigma(a_j)|^2 = n^\sigma(a_j) \quad 2.46$$

The Löwdin's method of symmetric orthonormalization is applied to the FOs which yields a set of orthonormal local orbitals that are used for SI correction.

The total minimum energy associated with the set of FODs is derived by varying the initial FODs positions until the forces  $\vec{F}_{FOD}$  on the FOD are less than  $10^{-3} a.u.$

The force on FODs is given by:

$$\vec{F}_{FOD} = \sum_{\sigma} \sum_j^{N^{\sigma}} -\nabla_{\sigma a_j} E_{PZ}[n_1, n_2, \dots]. \quad 2.47$$

However, the self-consistence solution to the total minimum energy must be determined for each set of FODs which is calculated during optimization process.

This chapter end the derivation of the Fermi Löwdin self-Interaction correction theory and then, the next chapter gives details about the computational application to this theory to polar molecules: vinylene carbonate and ethylene carbonate and water cluster anions.

### CHAPTER 3.0: METHODOLOGY

The calculations on Vinylene carbonate  $VC^-$ , Ethylene carbonate  $EC^-$  and water cluster anions  $(H_2O)_n^-$   $n=2-6$  in this thesis are done using 0.2 version of FLOSIC on Naval Research Laboratory Molecular Orbital Library (NRLMOL) code[40-47], it is a massively parallel code for electronic structure calculations mostly on large molecules and clusters[43].

This code uses very large Gaussian-orbital basis sets and variational integration mesh to perform numerically precise calculations on molecules.  $VC^-$ ,  $EC^-$  and water cluster anions  $(H_2O)_n^-$   $n=2-6$  in this thesis have been evaluated using PW91-LDA, PBE-GGA and SCAN density functional<sup>2</sup>. For these calculations, the structures of neutral molecules are optimized to equilibrium with self-consistent Kohn Sham-DFT to obtain structures with maximum gradient of  $10^{-3}$  atomic units as the convergence criterion using PBE-GGA with Gaussian-orbital basis sets with long-range diffuse functions. The dipole moment of the molecules studied here have the negative end on the oxygen tip and the extra electron therefore binds on the positive side of the dipole located towards the base of the molecule. For VC and EC, we find that adding extra functions to the terminal hydrogens and carbons has more effect on the binding energy. The extra long-range Gaussians were chosen such that the  $(N+1)$  the exponent is  $1/3$  of the  $N$ th Gaussian. The functions were added till the anion total energies converged at the level of generalized gradient approximation of Perdew, Burke, and Ernzerhof [11].

The additions of the extra s and p type single Gaussian functions are shown as  $C_{ks}l p H_{msnp}$ , where  $k, l$  and  $m, n$  are the numbers of s and p type functions on C and H atoms, respectively. As more and more functions are added the binding energy converges. The rest of the calculations were done with the largest basis set shown in Table.4.1. This was done in order to evaluate the molecular properties at the density functional theory DFT level. Furthermore, self-consistent FLOSIC

calculations have been made using the PW91-LDA, PBE-GGA and SCAN meta-GGA. Regarding the FLOSIC calculations, the molecular geometry and the wave-function was adopted from the previous DFT calculations because of efficiency reasons. The classical electronic positions were optimized to obtain structures with forces below  $10^{-3}$  Ha/Bohr for the FODs. For all molecules and using the three functionals, further calculations (anion) were performed with one electron added to the optimized neutral molecule without relaxing the molecular geometry. This was done in order to obtain the vertical binding energy ( $E_{\text{VBE}}$ ) values, which are defined as difference between the total energies of the neutral and the anion molecule at the neutral geometry.

$$E_{\text{VBE}} = E_{\text{N}} - E_{\text{N}+1} \quad 3.1$$

Herein,  $E_{\text{N}}$  represents the total energy of the Neutral molecule and  $E_{\text{N}+1}$  the total energy of the anion. The values of the excess electron binding energies for both  $VC^-$  and  $EC^-$  as well as the dipole moment for the neutral molecules are obtained and compared with the already published experimental values.

In addition, The vertical electron detached energy was also computed for both PBE-GGA, PW91-LDA and SCAN functional using the optimized MP2 anion geometry for  $(H_2O)_n^-$   $n=2-6$  again calculations (neutral) were performed by removing one electron from the optimized anion of  $(H_2O)_n^-$   $n=2-6$  without relaxing the molecular geometry.

$$E_{\text{VDE}} = E_{\text{N}} - E_{\text{N}+1} \quad 3.2$$

Lastly, the classical electronic positions, that is, the FODs, were obtained from the finished FLOSIC calculations, and they will be evaluated with respect to their chemical meaning. Furthermore, the average distances between the bonding were measured, and they will be analyzed as well.

To visualize the electronic geometries of the molecules, figures were created using the program Jmol. In these figures, the structures were constructed using the atoms of the respective molecules, applying the optimized molecular geometries which were obtained at the DFT calculations. Moreover, the FODs were assumed to occupy the positions of the electron orbitals, which were taken from the converged FLOSIC GGA calculation. The FODs were represented by cyan atoms and the extra FOD is located at a distance away from the molecule. The FOs of each spin channel were connected to yield approximate tetrahedron structure around the oxygen and carbon atoms.



## CHAPTER 4.0: RESULTS AND CONCLUSION

The vertical electron affinities for vinylene carbonate, ethylene carbonate and the vertical detached energy water cluster  $(H_2O)_n^-$   $n=2-6$  from two to six were computed with FLOSIC method is applied in conjunction with LDA, GGA, and meta-GGA functionals which represent increasing hierarchy and complexity in density functional approximation. We have chosen LDA as parametrized in PW91 functional [1], PBE [11], and SCAN functionals [47] for our calculations. These functional represent different levels of density functional approximation on the "Jacob's ladder" to density functional heaven. The local density approximation is the lowest rung, followed by generalized gradient approximation, and meta-GGA approximations. The last two functionals are semi-local that depend on the gradients of density and on the kinetic energy density. The purpose is to check the performance of the binding energies of the anions with LDA, PBE, and SCAN functionals.

### 4.1: Vinylene Carbonate and Ethylene Carbonate.

The equilibrium geometries for vinylene carbonate and ethylene carbonate in Fig. 4.1.1 and 4.1.2 below are optimized using the PBE-GGA functional in the standard density functional theory. The bond lengths and angles are measured to be 0.12nm for O=C, 0.139nm for C-O and 126.1 degree and 0.137nm for O-C-O in VC and 124.7 degree for O-C-O in EC also 117.5 degree and 108.5 degree are the angles of O-C-H for VC and EC respectively. The bond lengths are 0.108nm and 0.11nm for C-H in VC and EC and the H-C-H angle is 109.5 degree for EC. Also, the C-C for EC with bond length of 0.154nm. which are in coherence with the experimental bond length and angles. The arrangement of the optimal FODs for the atoms of the molecule both Ethylene and Vinylene are characterized by a shell structure corresponding to the principal quantum number of the electrons. Outer shell FODs are arranged on the vertices of a tetrahedron center of the 1s on both carbon and oxygen as seen fig 4.1.3.

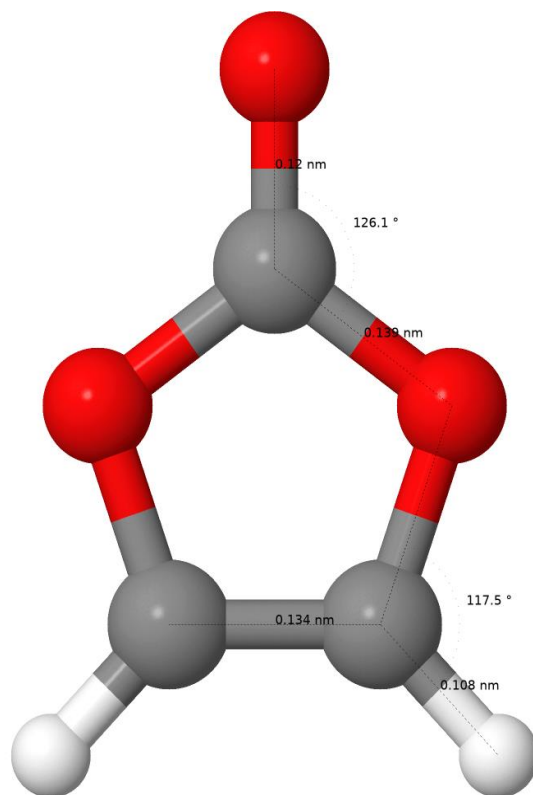


Figure 4.1.1 Optimized geometry for Vinylene carbonate

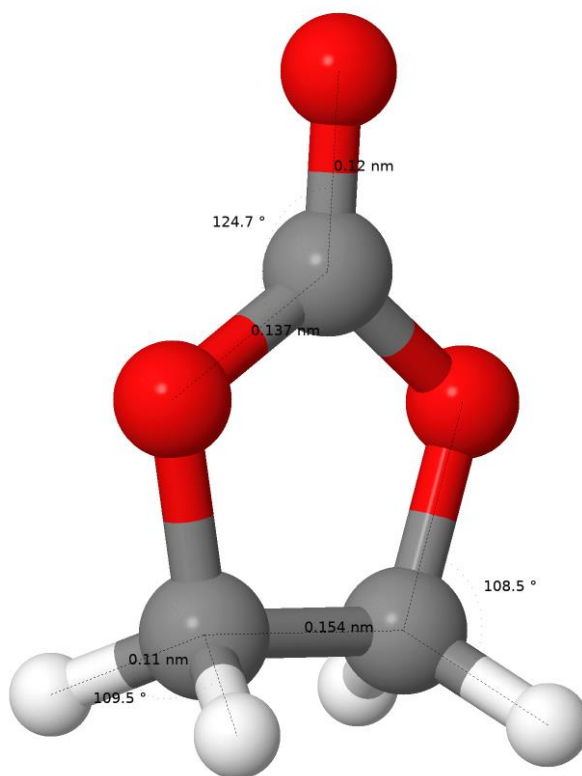


Figure 4.1.2: Optimized geometry for Ethylene carbonate

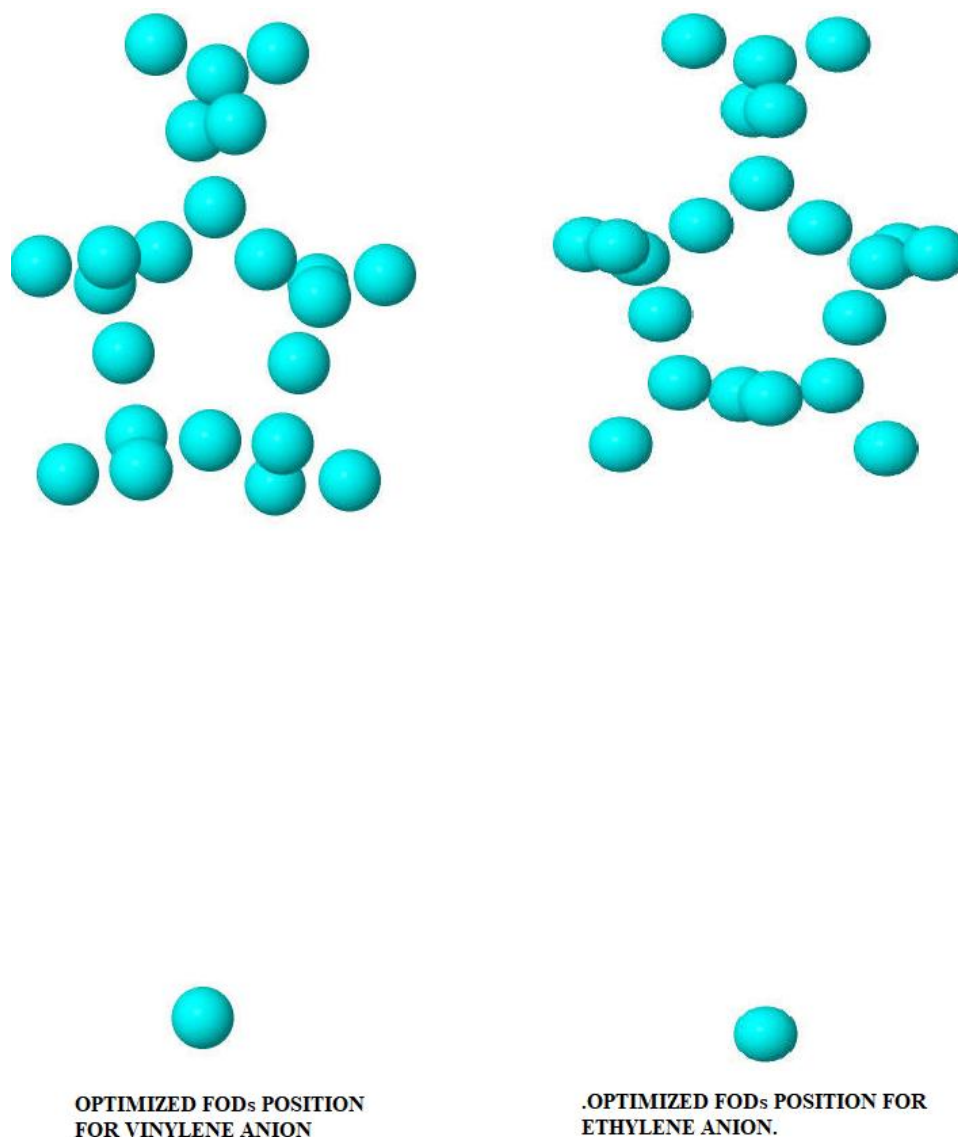


Figure 4.1.3: Optimized Fermi orbital descriptors

Vinylene carbonate and ethylene carbonate both have negative binding energy meaning not binding when using the default Gaussian basis sets. The inclusion of extra long-range diffused functions to the defaults basis sets shows binding of the excess electron and was used to obtain the basis sets criterion for convergence as seen in Table 4.1.1 and illustration 4.1.1. The horizontal axis shows the extra Gaussians added to the carbon and hydrogen. Here the left most entry shows

the electron binding energy with default basis functions used in NRLMOL [41-47] for carbon and hydrogen (C0H0).

The additions of the extra s and p type single Gaussian functions are shown as  $C_{ks}l_pH_{msnp}$ , where k,l and m,n are the numbers of s and p type functions on C and H atoms, respectively. The stars on the s and p indicate that these functions have the same exponents. The binding energy does not change significantly after the inclusion of the 3s and 1p diffuse function to the hydrogen atom. The exponent added are  $2.4E-02a.u.$ ,  $8.2E-3a.u.$  and  $2.7E-3a.u.$  for hydrogen atom at (7s6p2d) and  $2.5E-2a.u.$  and  $8.5E-3a.u.$  for Carbon atom (6s5p4d).

Table 4.1.1: Basis sets convergent criterion

Basis Sets	Binding Energy (a.u)
0C0H0	-0.03594
0C0H1	-0.00978
1CsH0	-0.01334
1CsH1	-0.0083
1CpH1	-0.00919
1Cs/pH0	-0.00972
1Cs/pH1	-0.00617
2CspH0	-0.00405
2CspH1	-0.00394
2CspH2s	-0.00133
2CspH3s1p	0.00231
2CspH2s1p	0.00234
2CspH3s2p"	0.00237
2CspH2(sp)	0.00239

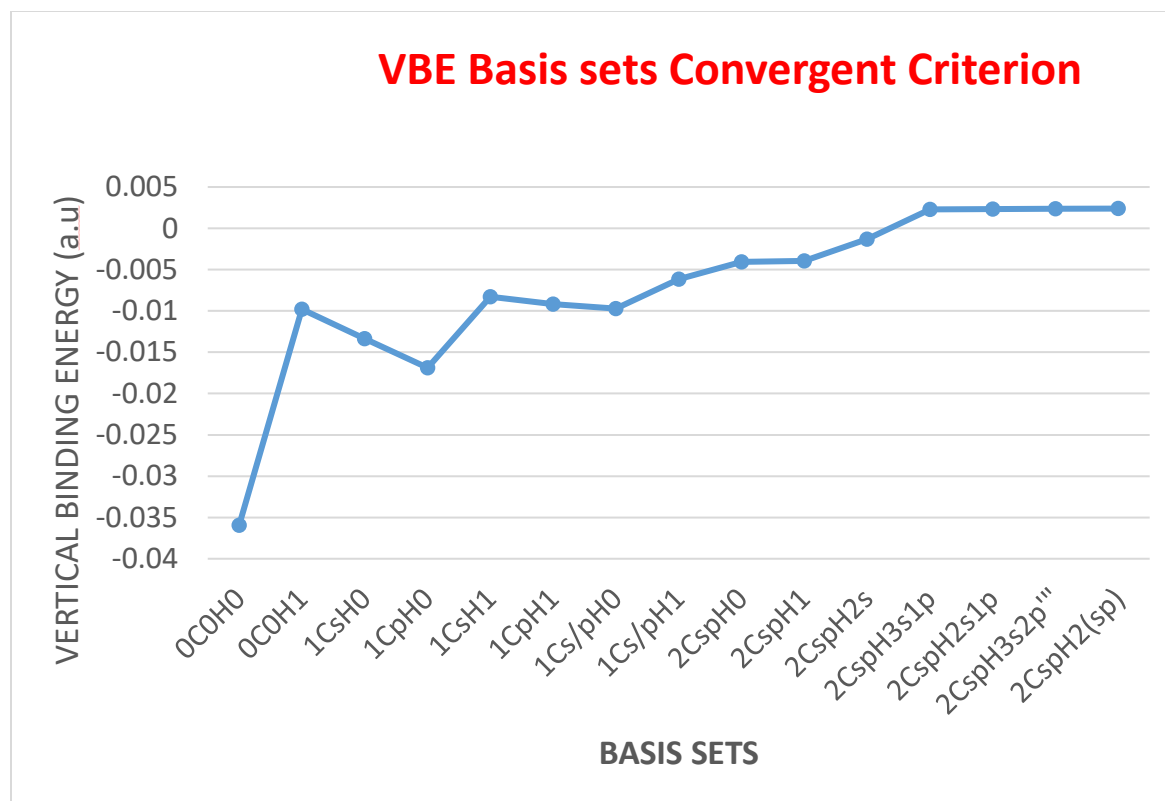


Illustration 4.1.1: Basis sets convergent criterion

Table 4.1.2: Calculated electron binding energy in meV.

FUNCTIONAL	MOLECULE	DIPOLE(D)	VBE (meV)	DEVIATION EXP.(meV)	ANION-HOMO-EVALUES(meV)
LDA	Vinylene	4.46	71.20	47.20	3.66E+02
GGA		4.35	64.79	40.79	3.22E+02
SCAN		4.51	-30.50	-54.50	4.08E+02
LDA	Ethylene	5.38	160.25	111.25	5.79E+02
GGA		5.25	105.35	56.35	3.93E+02
SCAN		5.44	-52.23	-101.23	3.26E+02
FLO-LDA	Vinylene	4.66	25.95	1.95	-4.41E-04
FLO-GGA		4.49	8.39	-15.61	3.56E-04
FLO-SCAN		4.67	-3.97	-27.97	3.48E+00
FLO-LDA	Ethylene	5.59	79.66	30.66	-2.30E-03
FLO-GGA		5.38	48.59	-0.41	-7.75E-04
FLO-SCAN		5.59	13.47	-35.53	-3.64E+01

Table 4.1.2 also reports the dipole moment of the neutral molecule for Vinylene and Ethylene carbonate calculated with standard density functional and Fermi Lowdin self-interaction corrected

density functional theory. This calculation has been carried out with the inclusion of long-range Gaussian diffused functions. The dipole moment in Table 4.1.2. show a dispersion of 0.14D to 0.20D for all three functional between the standard DFT and DFT-SIC at all case the DFT-SIC have higher neutral dipole moment both for the case VC and EC. The electron binding energy have shown great improvement with the inclusion of the self-interaction correction to DFT and at all functional it approximates the energy closer to the experimental value as shown in illustration 4.1.2.

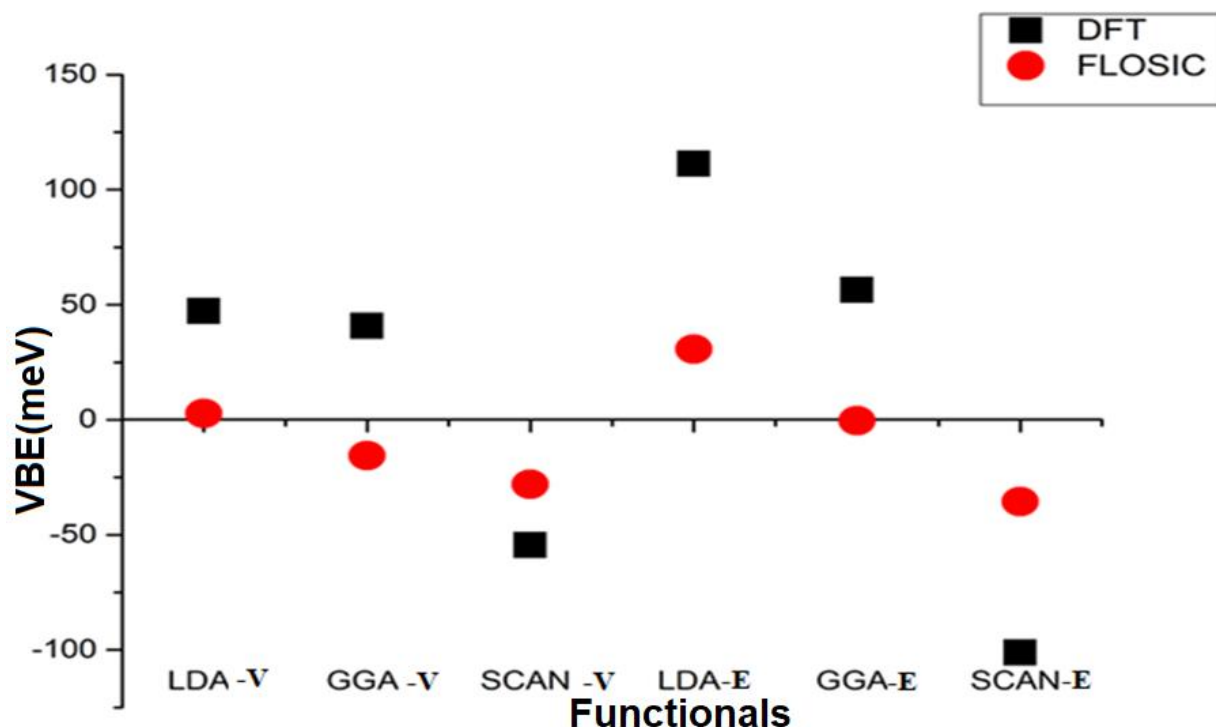
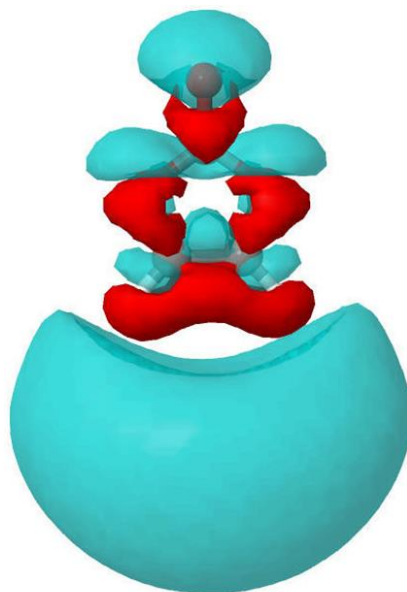


Illustration 4.1.2: Deviation energy plot FLOSIC/DFT energy vs Experiment energy V-Vinylene carbonate and E-Ethylene carbonate.

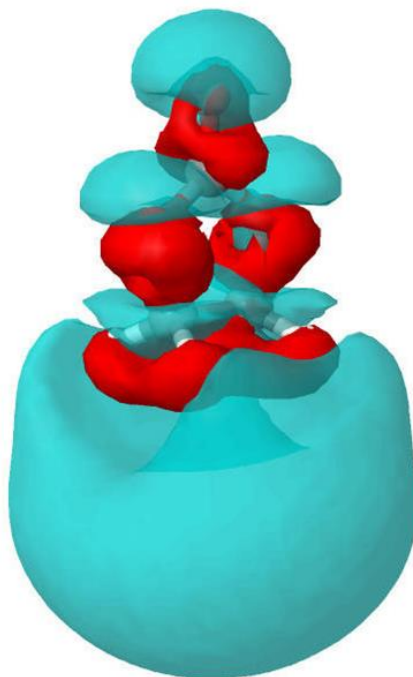
. The eigenvalues of the highest occupied molecular orbitals (HOMO) of the anions should mimic the electron detachment energies according to Koopman's theorem. The DFT eigenvalues are positive in all cases showing the incorrect asymptotic nature of the DFA potentials. For the case of FLOSIC, the HOMO eigenvalue of vinylene carbonate with FLOSIC-LDA is negative but vanishingly small. The eigenvalues with FLOSIC-GGA and FLOSIC-SCAN re positive. In case of ethylene carbonate, FLOSIC with all the three functionals result in negative eigenvalues.

However, the eigenvalues with FLOSIC-LDA and FLOSIC-GGA are smaller compared to the experimental binding energies. On the other hand, FLOSIC-SCAN shows a larger negative eigenvalue. The overall, gives the impact of SIC to the density functional approximation.



#### VINYLENE CARBONATE

Figure 4.1.4: Electron density difference for Vinylene.



#### ETHYLENE CARBONATE

Figure 4.1.5: Electron density difference for Ethylene.

Table 4.1.3: Electron binding energy compared with other methods in eV.

FUNCTIONAL	MOLECULE	DIPOLE(D)	VBE (meV)	DEVIATION EXP. (meV)	ANION-HOMO- EVALUES(meV)
FLO-LDA	Vinylene	4.66	25.95	1.95	-4.41E-04
FLO-GGA		4.49	8.39	-15.61	3.56E-04
FLO-SCAN		4.67	-3.97	-27.97	3.48E+00
KT			11.97	-12.03	
HF			12.94	-11.06	
MP2		4.59	15.58	-8.42	
CCSD			20.43	-3.57	
CCSD(T)			20.11	-3.89	
EXP		4.55	24	0	
FLO-LDA	Ethylene	5.59	79.66	30.66	-2.30E-03
FLO-GGA		5.38	48.59	-0.41	-7.75E-04
FLO-SCAN		5.59	13.47	-35.53	-3.64E+01
KT			23.95	-25.05	
HF			26.36	-22.64	
MP2		5.39	31.7	-17.3	
CCSD			40.43	-8.57	
CCSD(T)			40.88	-8.12	
EXP			49	0	

The Table 4.1.3, the FLOSIC results are compared with that from Hammer and co-authors [3]. For the vinylene molecule, the FLO-SCAN functional does not bind the excess electron and with deviation of 27.97meV followed by FLO-GGA which bind the excess electron but underestimate by 15.61meV while FLO-LDA functional is in good agreement with just 1.95meV above the experimental value. For the ethylene carbonate molecule, the FLO-LDA (30.66meV) over bind the excess electron while FLO-SCAN binds the excess electron but underestimates the binding energy by 35.53meV. The deviations of other methods are by KT-HF (25.05meV), HF (22.64meV), MP2 (17.3meV), CCSD (8.57meV), CCSD(T) (8.12meV). The FLO-GGA binding energy is in good agreement with just 0.41meV compared to Rydberg electron transfer experimental value [3].

The computed electron binding energies for the FLO-GGA calculation get better as the number of carbon-hydrogen C-H increases. Illustration 4.3. show the mean absolute deviation of the three functionals for both molecules. The SCAN results are the most deviant with mean absolute deviation of 31.75meV followed by the Koopman's Theorem (KT-HF) with 18.54meV, Hartree-Fock (HF) with 16.85meV, FLO-LDA with 16.73meV, second order Moller Plesset(MP2) with



12.86meV. The FLO-GGA show good mean deviation with 8.01meV which is not computationally as expensive as the couple cluster single, double and triple excitation (CCSD(T) with 6meV.

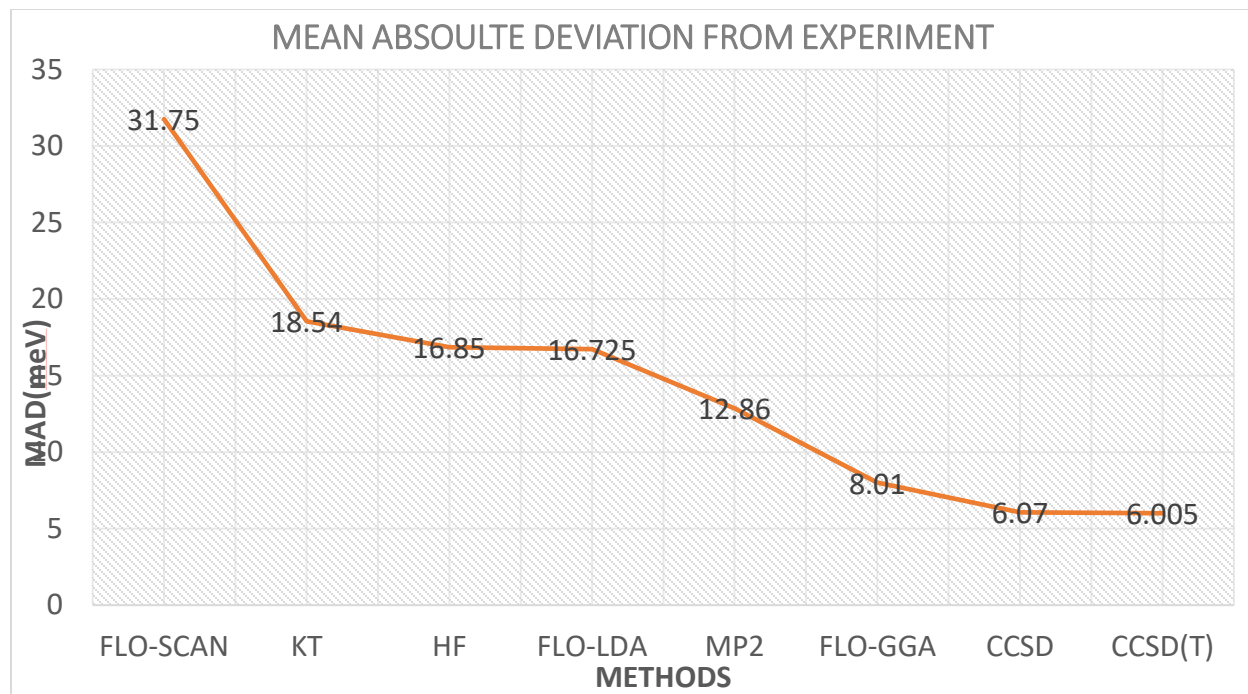


Illustration 4.1.3: VBE Mean absolute deviation from experiment.

In FIG. 4.1.4 and FIG. 4.1.5 show the electron density difference between the anion and neutral. This plot is done with an iso-surface of 0.000014. From this plot, it is shown that most of the excess charge is located outside of the molecule showing the location of the extra electron. The diffuse electron cloud is compact for the Ethylene carbonate molecule in FIG 4.1.5 with a higher dipole moment of 5.38Debye compare with Vinylene 4.49Debye. Furthermore, there is charge redistribution around the molecules due to the direction of the dipole moment. The red lobe is the negative density different while the cyan color lobe is the positive density different.

This conclude that the binding of the excess electron by both vinylene carbonate anion and ethylene carbonate anion is a true dipole bound also the generalized gradient approximation with Perdew-Wang correlation functional is a success to predicting the positive electron binding energy.

The close agreement of the calculated electron binding energy with experiment shows that the FLOSIC method has good approximation for the potential at the asymptotic region.

#### 4.2: Water Cluster Anions

The water cluster anions  $(H_2O)_n^-$   $n=2-6$  were studied for 20 isomers. These twenty isomers include one dimer, five trimers, four tetramers, five pentamer, and five hexamers which are grouped based on the orientation of the hydrogen bonds and the excess electron captured. The label are as follows: I-Internally trapped electron, AA double acceptors clusters describe base on the number of double acceptor water molecules with their hydrogen atoms do not involve in any hydrogen bonding, D- are cyclic clusters with all water molecules involve in hydrogen bonding, L-linear clusters with twisted line bound by successive hydrogen bonds. The double acceptors clusters have water molecules which are acceptors of hydrogen bonding from two separate water molecules. These isomers are shown in FIG.4.2.1 to 4.2.6

The 2L is shown in FIG 4.2.1 one with the optimized FODs in cyan and the other with the electron positive density difference in blue. The FODs corresponding to the valence electrons orbitals form a tetrahedron around the oxygen and the extra FOD for the anion it located at the optimal distance describe by the long-range potential at  $4.4\text{\AA}$  from the acceptor molecule for the case of water dimer.

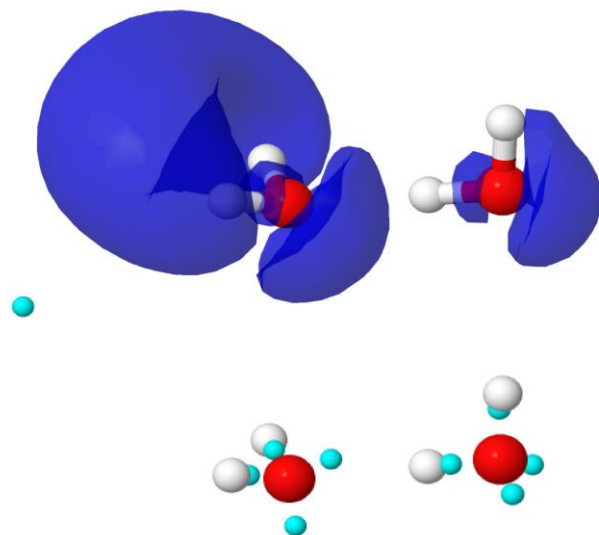


Figure 4.2.1 Water dimer (2L) and FODs

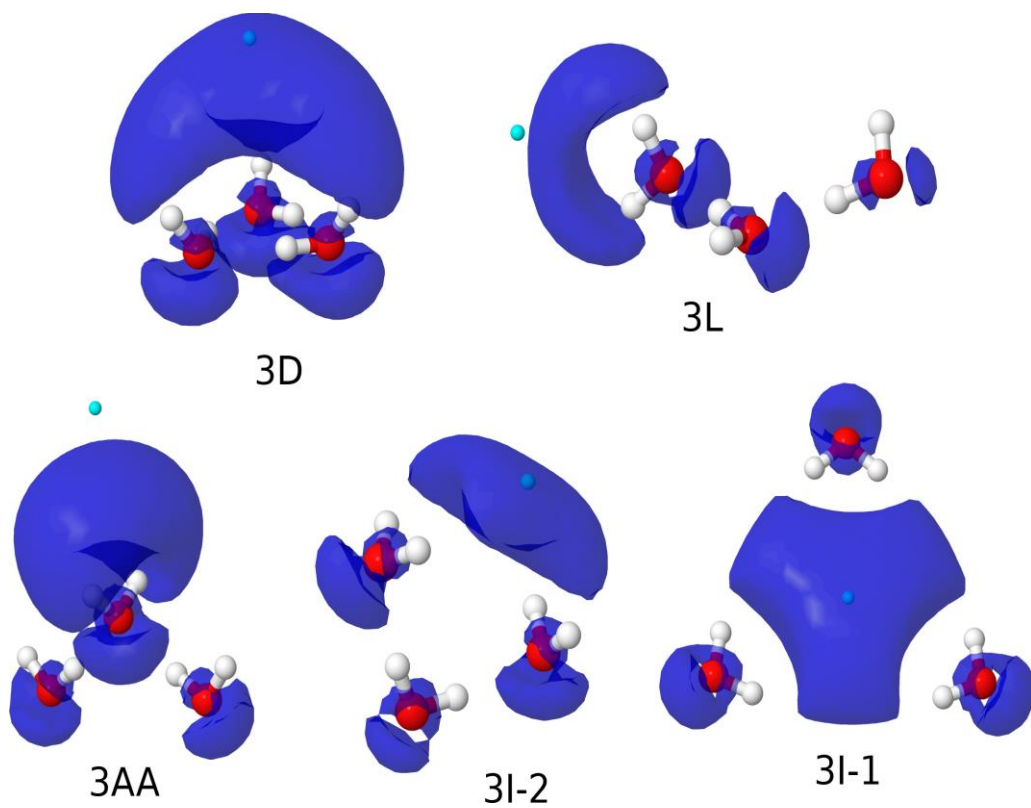


Figure 4.2.2 Water trimers with extra FOD

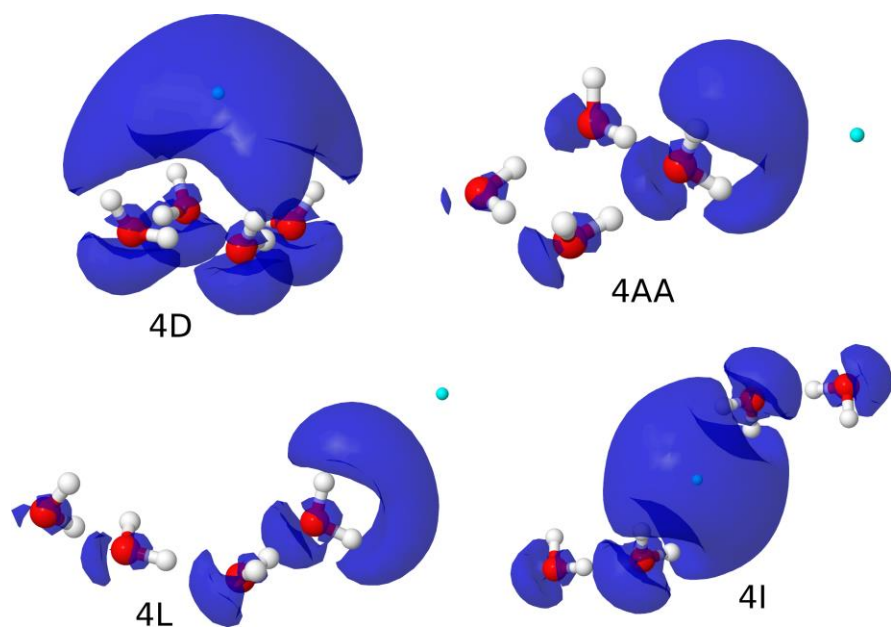


Figure 4.2.3 Water tetramers with extra FOD

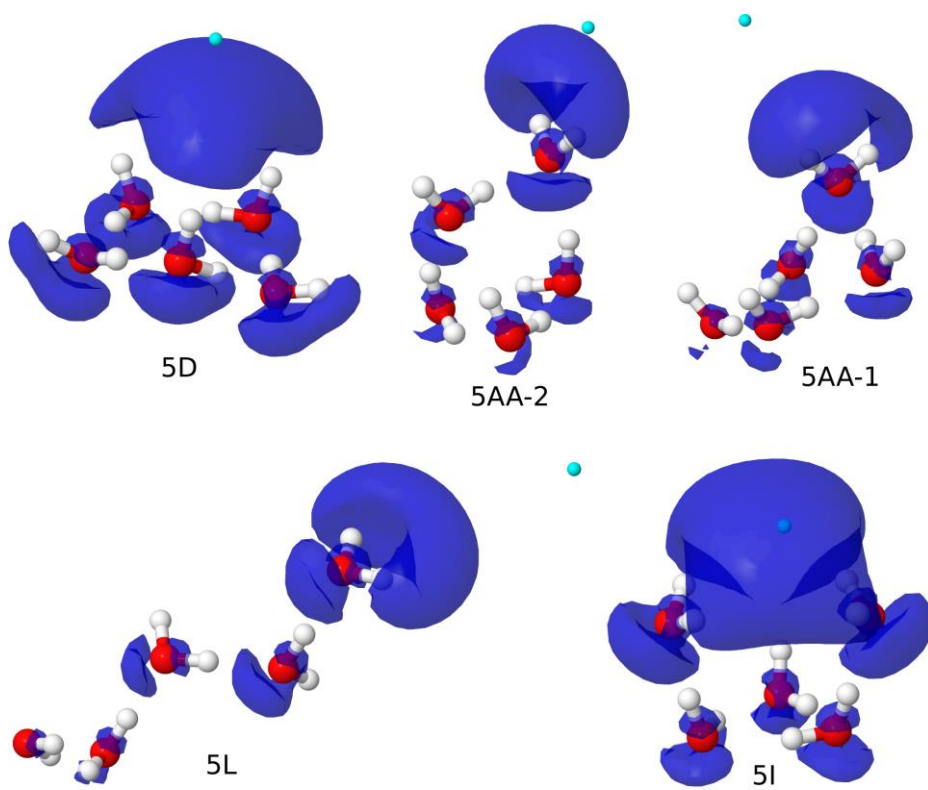


Figure 4.2.4 Water pentamers with extra FOD

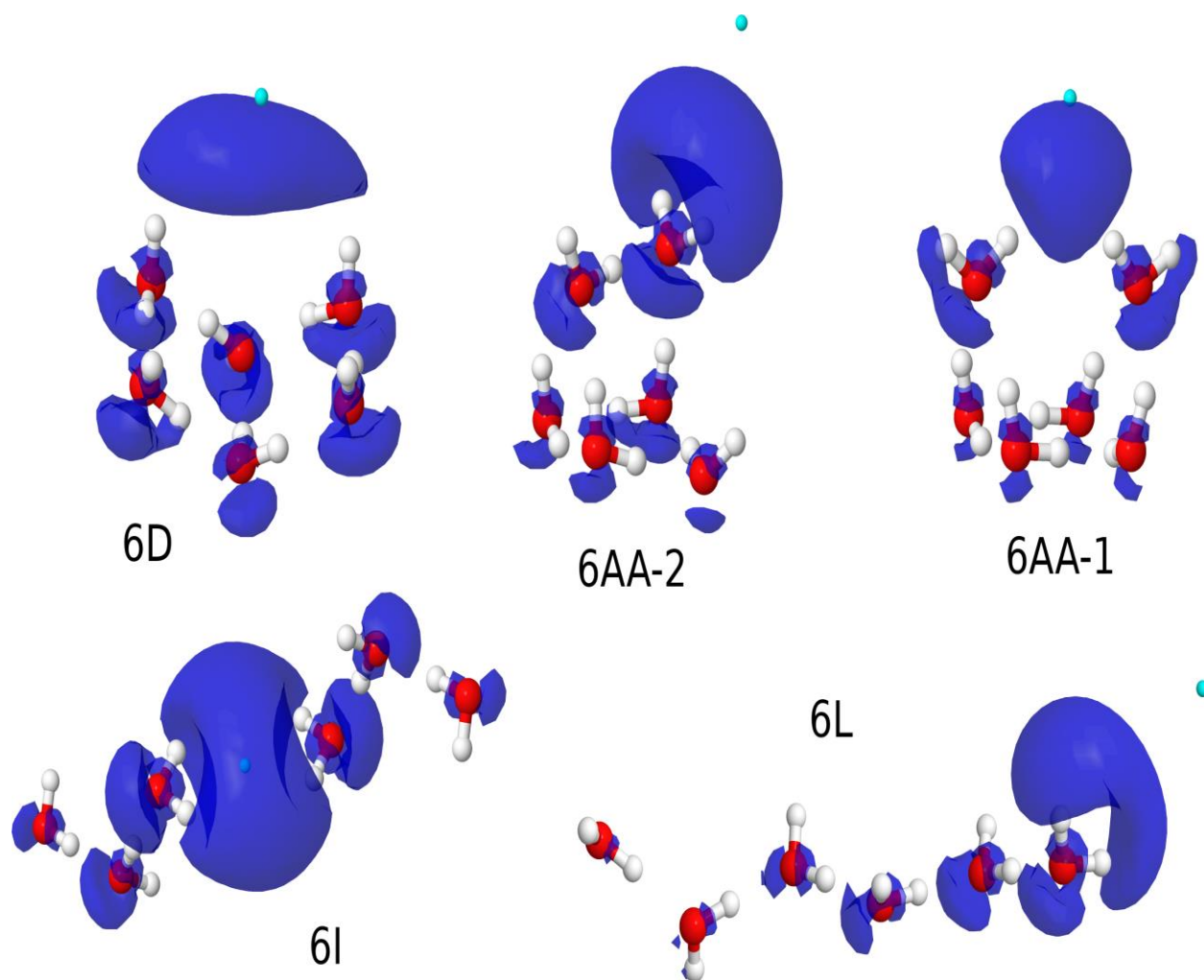


Figure 4.2.5 Water hexamers with extra FOD

The very interesting part is that the 4I and 6I are made of two dimers(2L) and two trimers(3L) respectively with the extra electron trapped in between the direction of dipole moment. Also, AA-2 for both pentamer and hexamer both have dimer(2L) on the top as hydrogen bond acceptor to both trimer and tetramer.

It is obvious that the Ds are the most stable and have the lowest VDE which is related to the number of hydrogen bonding involve in the formation of the structure. The AA are the next more stable isomers than the linear or the internal isomers using the three functionals.

Table 4.2.1: Vertical detached energies of the water cluster anions in meV.

ISOMER	FLOSIC GGA	FLOSIC LDA	SCAN	CCSD(T)	MP2	B3LY
2L	76.9	121.3	96.2	28.6	8.7	193.9
3L	211.2	289.8	258.3	146.2	114.6	345.6
4L	307.1	408.1	362.1	254.9	213.5	478.0
5L	353.6	435.3	406.9	294.0	249.6	527.2
6L	444.7	552.3	205.5	380.6	331.0	642.6
3AA	245.2	347.9	300.4	186.7	146.1	399.2
4AA	385.5	511.3	468.7	336.1	283.4	561.1
5AA-1	436.4	573.5	510.1	369.5	312.7	600.4
5AA-2	417.4	560.7	510.9	376.3	318.1	592.3
6AA-1	600.2	814.4	745.8	553.3	481.8	846.6
6AA-2	520.1	684.3	621.3	477.1	413.7	705.6
3I-1	310.4	438.8	353.4	190.4	155.2	526.0
3I-2	250.6	348.2	292.9	174.6	138.0	426.6
4I	493.7	687.7	610.3	438.5	394.1	713
5I	538.5	729.7	637.3	468.9	405.9	757.4
6I	870.4	1131.0	1046.8	838.9	793.4	1119.9
3D	58.0	96.2	67.3	5.7	-13.8	184.1
4D	105.3	158.1	123.0	48.5	22.4	239.4
5D	130.2	184.3	146.3	61.1	30.7	285.0
6D	181.6	255.3	135.1	104.2	62.7	346.7

The Vertical detached energies of for the twenty water isomers are tabulated in Table 4.2.1. for MP2, B3LYP, SCAN, FLOSIC-LDA, FLOSIC-GGA and CCSD(T) and are plotted in illustrated

in 4.2.1. The deviations are estimated from reference CCSD(T) values, the B3LYP gives over-binding energy in all cases with the MAD values 238.3meV because the B3LYP mixes only

Table 4.2.2: Deviation of VDE relative to CCSD(T) in meV

ISOMERS	FLOSIC GGA	FLOSIC LDA	SCAN	MP2	B3LYP
2L	48.3	92.7	67.6	-19.9	165.3
3L	65.0	143.6	112.1	-31.6	199.4
4L	52.2	153.2	107.2	-41.4	223.1
5L	59.6	141.3	112.9	-44.4	233.2
6L	64.1	171.7	124.7	-49.6	262.0
3AA	58.5	161.2	113.7	-40.6	212.5
4AA	49.4	175.2	132.6	-52.7	225.0
5AA-1	66.9	204.0	140.6	-56.8	230.9
5AA-2	41.1	184.4	245.0	-58.2	216.0
6AA-1	46.9	261.1	192.5	-71.5	293.3
6AA-2	43.0	207.2	144.2	-63.4	228.5
3I-1	120.0	248.4	163.0	-35.2	335.6
3I-2	76.0	173.6	118.3	-36.6	252.0
4I	55.2	249.2	171.8	-44.4	274.5
5I	69.6	260.8	168.4	-63.0	288.5
6I	31.5	292.1	207.9	-45.5	281.0
3D	52.3	90.5	61.6	-19.5	178.4
4D	56.8	109.6	74.5	-26.1	190.9
5D	69.1	123.2	85.2	-30.4	223.9
6D	77.4	151.1	101.2	-41.5	242.5
ABS TOTAL	1203.8	3594.8	2645.9	872.3	4756.5
MAD	60.1	179.7	132.2	43.6	237.8

a constant fraction of the HF exchange irrespective of the electron-electron distance and underestimates the exchange repulsions in the long-range region which result to excess electron bounding. The FLOSIC-GGA lead substantial improvement over other methods in calculating the

vertical detached energies for the 20 isomers. The FLOSIC-GGA functional gives agreeable result with the CCSD(T) with an MAD values of 60.1meV, this agreement is due to the self-interaction correct properly estimate the long-range potential at the asymptotic region for anionic system. The accurate prediction for FLOSIC GGA functional is highly satisfactory in view of the low computational cost.

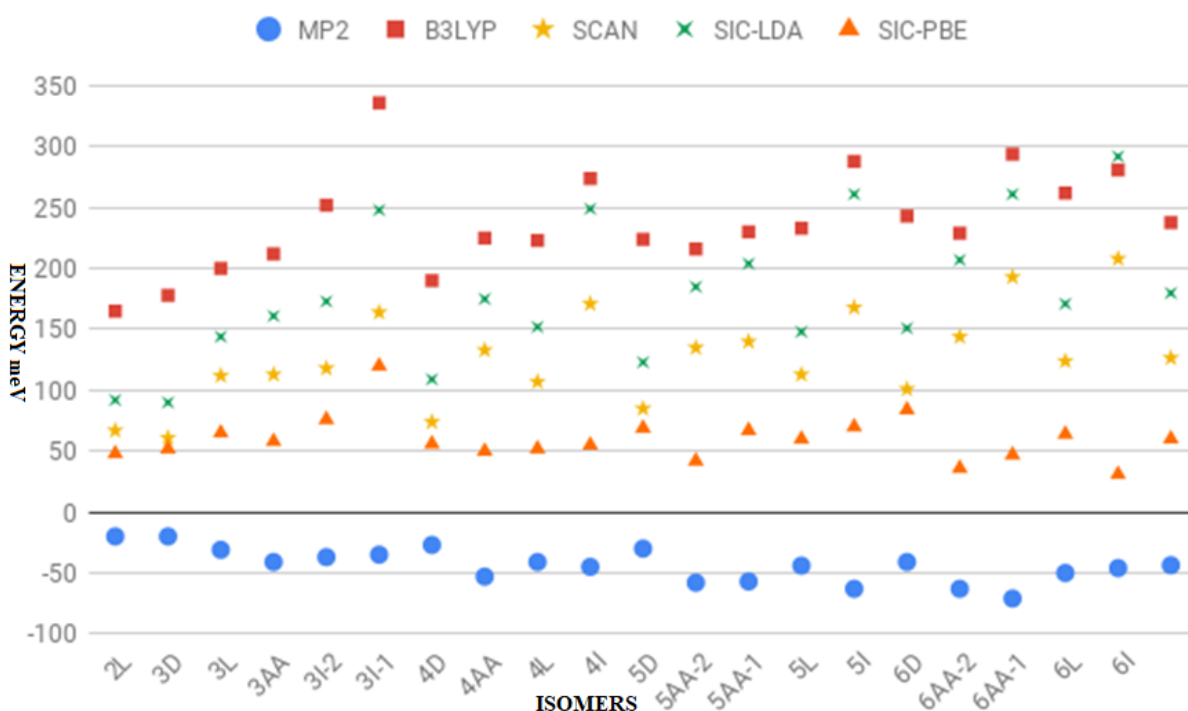


Illustration 4.2.1: Vertical detached energy obtained by the CCSD(T) methods vs deviation in meV.

This calculation shows that the three functional FLOSIC-GGA, FLOSIC-LDA and SCAN compute the detached energies differently. In all functionals the D-isomers of the water molecule anion deviation increases as the number of water molecules increases. Furthermore, the D's have the least mean absolute deviations MAD in all functional for GGA (51.0 meV), LDA (118.6meV) and SCAN (80.6meV). The I's have the 3I-1 as the most deviated for GGA (120.0meV) and the 6I for LDA and SCAN functional (292.1meV) and 108.8meV respectively. The MAD for the I's are GGA (70.4meV), LDA (244.8) and SCAN (165.9meV).



On the other hand, the L's and AA's do not follow a particle trend instead it has the 5AA-1 and the 3L as the most deviated for GGA (66.98meV) and (65.0meV), the 6AA-2 and 4L for LDA (207.2meV) and (153.2meV) and SCAN functional have the most deviated at 5AA-2 and 6L (245.0meV) and (124.7meV) respectively.

It is interesting that the FLOSIC GGA and MP2 gives the error in an opposite direction. This feature has been previously investigated by Harbert and Head-Gordon [6] that this sign inverse for MP2 is due the change in the Hartree-Fock exchange integrals of the B3LYP functional which leads to the decrease in the vertical detached energy for the fact that the MP2 is based on the HF and DFT.

### 4.3: Conclusion

The Fermi Lowdin Orbital Self-interaction correction (FLOSIC) scheme have been used to calculate electron binding energy for Vinylene carbonate  $VC^-$ , Ethylene carbonate  $EC^-$  and water cluster anions  $(H_2O)_n^-$   $n=2-6$  using long range Gaussian diffusions. The purpose of this research is to obtain the effect of self-interaction correction behavior with polar molecules since the standard density functional is not able to correctly compute the binding energy due to self-interaction error from the density functional approximation. Inspection of the orbital energies show that the DFT HOMO of the anion for  $VC^-$  and  $EC^-$  is usually positive in all functional. The FLOSIC lower orbital energies and yield negative HOMO energies for the anion. Results from all functional have shown the importance of including long-range diffuse function when computing the binding energy, also density difference shows that the excess electrons are not localized but are diffused over the molecule.

For both VC and EC also water cluster anion the FLOSIC PBE have shown good approximation for the electron binding energies.

### **Future Direction**

More anionic systems need to be studied with FLOSIC to understand the effects of the calculated electron binding energy for highly spin system like  $HCN^-$ ,  $CN^-$  and  $HNC^-$ , where the Hartree-Fork density is too inaccurate due to spin contamination.

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