First Principles Study Of Tribopolymerization On Conductive Material Surfaces

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Abstract
While tribopolymer, usually formed due to organic-molecule polymerization under contact surfaces frictions, is used to lubricate and to protect the surfaces of mechanical gears, it is considered as a major source of contamination to Micro-electro-mechanical system and Nano-electro-mechanical system (MEMS and NEMS) transistors. MEMS and NEMS, analogous to atomic force microscopy (AFM) devices, design with mechanical switching motions to reduce the power consumption caused by maintaining the open-circuit voltage in traditional field-effect transistors, can be considered as promising potential candidates to replace current generation transistors. However, the devices failure occurs usually due to adsorption of ambient molecules onto device contact surfaces following stress confined surface catalytic reactions to form tribopolymers, which are usually insulating and sticky. Experimental results only justify those tribopolymers to be hydrocarbon chains, but detailed composition and formation mechanism remain unclear. Here, we perform theoretical and computational studies using density functional theory methods to systematically and comprehensively investigate both the initial conditions of MEMS and NEMS devices contact surfaces with and without exposing the contamination gas molecules particularly benzene and model the mechanical switching cycles among many conducting materials such as metal oxides (RuO2) and metal sillsides (PtxSi). We found that the tribopolymerization mechanism lies on to surface catalytic effect enhanced by local confined stress, and a general trend follows for those materials as we investigated is: (i) chemisorption; (ii) dehydrogenation; (iii) polymerization. In particular, the applied normal stress lowers both the adsorption barrier and the reaction barriers lead to tribopolymerization. In addition, the weaker the initial binding strength of adsorbates the less the polymerization. With the knowledge acquired in our study, we are able to provide criteria for screening and designing tribopolymer-suppressing materials and stimulate the development of MEMS and NEMS to eventually reach practical manufacturing and make them widespread.

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FIRST PRINCIPLES STUDY OF TRIBOPOLYMERIZATION ON CONDUCTIVE MATERIAL SURFACES

Jing Yang

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in

Chemistry

Presented to the Faculties of the University of Pennsylvania

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To my parents,

for their love and support
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ABSTRACT

FIRST PRINCIPLES STUDY OF TRIBOPOLYMERIZATION ON CONDUCTIVE MATERIAL SURFACES

Jing Yang
Andrew M. Rappe

While tribopolymer, usually formed due to organic-molecule polymerization under contact surfaces frictions, is used to lubricate and to protect the surfaces of mechanical gears, it is considered as a major source of contamination to Micro-electro-mechanical system and Nano-electro-mechanical system (MEMS and NEMS) transistors. MEMS and NEMS, analogous to atomic force microscopy (AFM) devices, design with mechanical switching motions to reduce the power consumption caused by maintaining the open-circuit voltage in traditional field-effect transistors, can be considered as promising potential candidates to replace current generation transistors. However, the devices failure occurs usually due to adsorption of ambient molecules onto device contact surfaces following stress confined surface catalytic reactions to form tribopolymers, which are usually insulating and sticky. Experimental results only justify those tribopolymers to be hydrocarbon chains, but detailed composition and formation mechanism remain unclear. Here, we perform theoretical and computational studies using density functional theory methods to systematically and comprehensively investigate both the initial conditions of MEMS and NEMS devices contact surfaces with and without exposing the contamination gas molecules particularly benzene and model the mechanical switching cycles among many conducting materials such as metal oxides (RuO2) and metal sillisides (PtxSi). We found that the tribopolymerization mechanism lies on to surface catalytic effect enhanced by local confined stress, and a general trend follows for those materials as we investigated is: (i) chemisorption; (ii) dehydrogenation; (iii) polymerization. In particular, the applied normal stress lowers both
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Chapter 1

Introduction
Tribopolymer is created by the friction motion when two surfaces are in contact with each other by any kind of external force. Very commonly, the tribopolymer formed by long-chain organic molecules is used to lubricate the surface and prevent surface wear and corrosion. The black squishy substance usually found on bicycle chains are majorly tribopolymers, which look unclean but are benefit to bicycles for longer lifetime. However, once the tribopolymer forms on electronic devices, the sticky black chemical substance might break the circuit and cause damages to the devices.

In particular, micro- or nano-electromechanical system (MEMS/NEMS) devices are design to overcome the deficiencies of current silicon-based microelectronics field-effect transistors (FETs), which usually make use of p-n junction to perform on/off switching to control the electrical behavior of the circuit (see Fig. 1.1).

In particular, FETs are facing the problem of down-scaling limitation due to increasing of wasting power generation [2]. As shown in Fig. 1.2, the wasting power scales up with decreasing of device size. With 20 nm device, the wasting power is over twice of the amount compare to the device regular functioning power requirement.
Figure 1.1: Schematic picture of comparison between NEMS and FET devices.
The schematic picture for NEMS and FET comparison is shown in Fig. 1.1 [3]. In stead of using p-n junction, NEMS connects source and drain by an conductive actuator and the gate, before is to control the hole carriers in the p-type material when applying voltage between the gate and the body, now is to control the actuator for closing and opening the physical air cap. By doing so, the mechanical switch is able to maintain a clean open-circuit stage rather than FETs require an open-circuit voltage to keep the circuit at off state. Furthermore, the mechanical switch devices could significantly reduce the gate voltage required for compensating the drain current leakage, or subthreshold swing, during the process of the circuit turning from a stable “off” state to a stable “on” state (see Fig. 1.3). Therefore, MEMS/NEMS devices are able to reach smaller scale compare to FETs, lower power consumption and boost up the efficiency and can be considered as the next generation high performance computing electronic devices [4, 5, 6, 7, 8].
Figure 1.2: Power consumption with respect to scale of the microelectronic devices [2]. The dynamic power is the power required by regular functioning of device shown in blue-ish grey. The leakage power is in blue.
However, one of the tough problems blocks MEMS/NEMS devices from pragmatic manufacturing and massive production is the contact resistance control, and tribopolymer formation closely relates to this issue. Experimentally, tribopolymer can be observed under scan tunnelling microscopy and can be described as a type of sticky linkage substance. When exposing with benzene contaminated environment, MEMS devices show increment of electrical contact resistance (ECR) and degradation of device life time with increasing concentration of benzene [9, 10]. Previous studies only provide a hypothesis that the tribopolymer on MEMS/NEMS could be some heavy weighted hydrocarbons [10], but the exact polymer structure and correct formation mechanism still remain unclear. The difficulty for the experimentalists to measure the tribopolymer composition on MEMS/NEMS devices lie to lack of sampling strategies from such small devices. Therefore, the theoretical and computational investigations and predications become essential to figure out the tribopolymer composition and formation, which could further provide fruitful insights and criteria for MEMS/NEMS material screening and search, and hence assist MEMS/NEMS devices for further development.

Previously, many theoretical works have focused on study how molecules react under high pressure. Wen and his coworkers found that benzene undergoes multiple phase transition to form molecular crystals and eventually turns to amorphous carbon beyond 80 GPa [11]. Others find radicals within the hydrocarbon chains assist longer chain structure formation under high pressure [12]. In terms of tribochemical simulations, \textit{ab initio} molecular dynamics on mechanical shear induced polymerization for allyl alcohol [13], hydrocarbon with 10 carbon atoms (\(\alpha\)-pinene, pinane, and \(n\)-decane) [14], and alkylsilane [15] has shown similar mechanism on polymer formation, which is, in short, physisorbed molecules follow sliding direction to anchor (chemisorb) on the surface and lead to further complex long chain formation. These researches follow the direction of tribopolymer being lubricant but not contaminant. On the opposite side, our goal is to study the tribopolymer
Figure 1.3: I-V curve of microelectronic devices. The red line indicates performance of FET devices, whereas the green dashed line shows the behavior of NEMS devices. The current is in logarithm scale. The figure is taken from Ref. [3].
composition and formation and takes advantage of such analysis to discover and design tribopolymer resistant materials for MEMS/NEMS devices.

In order to explain the reaction mechanisms theoretically and computationally, we employ density functional theory (DFT) [16] method with a plane-wave basis set throughout the entire work of this thesis. Non-local pseudopotentials of atoms are used to describe interactions between nuclear and electrons surrounded. The fundamental knowledge for DFT along with the theory of pseudopotential is documented in Chapter 2.

To further improve the accuracy of the pseudopotential, we also work generating hybrid pseudopotentials. The consistency between the exchange-correlation functional used in pseudopotential construction and in the actual density functional theory calculation is essential for the accurate prediction of fundamental properties of materials. However, routine hybrid density functional calculations at present still rely on generalized gradient approximation (GGA) pseudopotentials due to the lack of hybrid functional pseudopotentials. In Chapter 3, we present a scheme for generating hybrid functional pseudopotentials, and we analyze the importance of pseudopotential density functional consistency for hybrid functionals. By including 0.25 of exact exchange in the hybrid-functional, or PBE0 functional, we benchmark our pseudopotentials for structural parameters and fundamental electronic gaps of the Gaussian-2 (G2) molecular dataset and some simple solids. Our results show that using our new PBE0 pseudopotentials in PBE0 calculations improves agreement with respect to all-electron calculations.

Van der Waals interaction between molecules and surfaces is essential to our study of tribopolymerization mechanism. In Chapter 4, we describe a post-DFT method to correct the total energy and lattice constants of molecular solids and perform the calculation of sublimation energies and lattice constants for series of fullerene crystals.

Once the methodology is well developed, we then start the investigation of tribopolymer formation mechanism on variety of contact surfaces. Previously, we have computationally
observed benzene form tribopolymer on pure metal surface such as Pt and Au surfaces [17] and figured out chemisorption of benzene is the key to start the tribopolymer accumulation. In Chapter 5, we turn our focus to conductive metal oxides due to low electric effect of surface oxidation. We study the initial surface condition of RuO$_2$ surface and its adsorption behavior with benzene. We find that adsorption of benzene on O-poor RuO$_2$(110) via C-Ru bonds is stronger than adsorption on the O-rich RuO$_2$(110) via H-O bonds. For an in-depth study of the adsorption behavior, we include the van der Waals interaction for a holistic investigation. By incorporating the thermodynamic chemical potentials into the adsorption simulations, we describe a model that can provide guidance for realistic situations.

In Chapter 6, we investigate benzene adsorption on Bi$_2$Te$_3$ (111) surface, a topological insulator material. We compare electronic structure characteristics of three different kinds of benzene-adsorbed (111) surfaces: that of Bi$_2$Te$_3$, that of Au, a prototypical inert metal, and that of Pt, a prototypical catalytic metal. Using first-principles calculations based on dispersion-corrected density functional theory, we show that benzene is chemisorbed on Pt, but physisorbed on Au and Bi$_2$Te$_3$. The adsorption on Bi$_2$Te$_3$ is particularly weak, consistent with a minimal perturbation of the electronic structure at the surface of the topological insulator, revealed by a detailed analysis of the interaction of the molecular orbitals with the topological surface states. The evidence of this study shows that Bi$_2$Te$_3$ (111) as a topological insulator material can be considered as a potential MEMS/NEMS material.

The initial adsorption behavior is indeed an important factor for tribopolymerization. The other factor is the stress-induced catalytic effect of the surface. In Chapter 7, we demonstrate a compression model to mimic MEMS/NEMS working principle to study the normal stress effect on benzene tribopolymerization on RuO$_2$ (110) surface. First, mechanical force during compression changes the benzene molecules from slightly physisorbed to strongly chemisorbed. Further compression causes deformation and chemical linkage of the benzene molecules. Finally, the two contacts detach, with one having a complex or-
ganic molecule attached and the other with a more reactive surface. The complex organic molecule, which has an oxabicyclic segment, can be viewed as the rudiment of tribopolymer, and the more reactive surface can trigger the next adsorption–reaction–tribopolymer formation cycle. Based on these results, we also predict tribopolymer formation rates by using transition–state theory and the second–order rate law. This study deepens our understanding of tribopolymer formation (especially on metal oxides) and provides strategies for suppressing tribopolymerization.

In Chapter 8, we perform a comprehensive study for Pt$_3$Si(001) surface to justify such material is promising to MEMS/NEMS devices. Experimentalists have found that a class of conductive silicides, platinum silicides (Pt$_x$Si), could be synthesized simply by using solid-state diffusion [18]. Pt$_3$Si possesses the best conductivity out of this class [19]. However, the basic physical and chemical properties for such a material is very limited from either experimental or theoretical aspect. In this chapter, we focus on Pt$_3$Si surface material and determined thermodynamically stable surface to be Pt$_3$Si(001) with Pt$_2$Si$_2$ as terminating structure. Similar to experimental observation, the study of binding strength of oxygen shows that the material is inert to surface oxidation. Furthermore, the density functional theory calculation on surface reaction with applied normal stress demonstrates that partially oxidized Pt$_3$Si surface presents low tendency of tribobopolymer formation with benzene. Our study has further proved that the Pt$_3$Si could be a promising material for MEMS/NEMS devices.
Chapter 2

Theory and Methodology
2.1 Many-electron Schrödinger equation

In the very beginning of quantum mechanics development, the many-electron problem has been considered by Hartree in 1928 [20]. For an atomic system with \( N \) electrons, the time-independent Schrödinger equation in the Born-Oppenheimer approximation [21] is given, analogous to one-electron equation, by

\[
\hat{H}\Psi = E\Psi \tag{2.1}
\]

where the Hamiltonian operator \( \hat{H} \) operates on the electronic wavefunction \( \Psi, \Psi = \Psi(x_1, x_2, \ldots, x_n) \), and obtains the electronic energy of \( E \). \( \hat{H} \) is represented as

\[
\hat{H}(R, r) = \sum_{i=1}^{N} \left( -\frac{1}{2}\nabla_i^2 \right) + \sum_{i=1}^{N} v(R_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{2.2}
\]

where \( -\frac{1}{2}\nabla_i^2 \) is the kinetic operator of an electron, \( v(R_i) \) describes the attraction between nucleus with charge \( Z \) and \( i \)-th electron along distance of \( R_i \), or external potential, which takes the form of

\[
v(R_i) = -\frac{Z}{R_i} \tag{2.3}
\]

The last term of Eq. 2.2 is the interaction between two electrons separated by distance of \( r_{ij} \) if considering pair-interaction only. \( x_i \) are the coordinates of \( i \)-th electron consist of spacial coordinates \( r_i \) and spin coordinates \( s_i \). More compactly, Eq. 2.2 can be rewritten into an operator form as

\[
\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee} \tag{2.4}
\]

Variationally solving Eq. 2.1, by taking a full minimization of \( E[\Psi] \) with all possible many-electron wavefunctions, allows us to obtain the true ground state energy, \( E_0 \). We use
functional derivative of $E[\Psi]$ with respect to $\Psi$ gives

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.5)$$

$$\langle \Psi | \hat{H} | \Psi \rangle = \int \Psi^* \hat{H} \Psi \, dx \quad (2.6)$$

$$\delta[\langle \Psi | \hat{H} | \Psi \rangle - E \langle \Psi | \Psi \rangle] = 0 \quad (2.7)$$

where $E$ is the Lagrange multiplier, but $E[\Psi]$ is the functional form of the electronic energy.

## 2.2 Hartree-Fock approximation

It is obvious that a better initial choice of the wavefunction with more accurate description to the system could benefit the convergence to the true ground state in variational method. The Hartree-Fock approximation considered the Pauli’s principle treats the electronic wavefunction as a Slater determinant, which consists of a product of antisymmetrized orthogonal orbital wavefunctions $\psi_i(x)$ [22].

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(x_1) & \psi_2(x_1) & \ldots & \psi_N(x_1) \\
\psi_1(x_2) & \psi_2(x_2) & \ldots & \psi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(x_N) & \psi_2(x_N) & \ldots & \psi_N(x_N)
\end{vmatrix} \quad (2.8)$$

$$= \frac{1}{\sqrt{N!}} \det[\psi_1(x_1) \psi_2(x_2) \ldots \psi_N(x_N)] \quad (2.9)$$

Now, the expectation value of the total energy $E_{HF}$ can be written as,

$$E_{HF} = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij}) \quad (2.10)$$
where $H_i$ combines the integrals of kinetic energy and external potential forms

$$
H_i = \int \psi_i^*(x) \left[ -\frac{1}{2} \nabla^2 + v(x) \right] \psi_i(x) dx
$$

(2.11)

$J_{ij}$ are hartree integrals and $K_{ij}$ are exchange integrals. Taking $i$- and $j$-th wavefunction at coordinates $x_1$ and $x_2$, the two integrals can be represented as

$$
J_{ij} = \int \int \psi_i(x_1) \psi_j^*(x_1) \frac{1}{r_{12}} \psi_j^*(x_2) \psi_j(x_2) dx_1 dx_2
$$

(2.12)

and

$$
K_{ij} = \int \int \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{12}} \psi_i(x_2) \psi_j^*(x_2) dx_1 dx_2
$$

(2.13)

and the wavefunctions follow

$$
\int \psi_i^*(x) \psi_j(x) dx = \delta_{ij}
$$

(2.14)

With Hartree-Fock approximation, the exact exchange of the electrons in the system has been well defined and close to 99% of the total energy can be accounted for by Hartree-Fock wavefunctions [20]. The correlation energy under this scope of knowledge is defined as

$$
E_c = E_{\text{total}} - E_{HF}.
$$

(2.15)

### 2.3 Density Functional Theory

To simplify the approach of solving many-electron wavefunction dependent Schrödinger equation, the electronic density with its differential equation forms are initially derived by Thomas and Fermi [23, 24, 25, 26]. They approximate electrons in the system as uniform electron gas and the only the relation between total kinetic energy and electronic density
is established. The modern density functional theory (DFT) has been raised by Hohenberg and Kohn in 1964 [27]. The density functional theory is built on two theorems according to Hohenberg and Kohn. One states: \textit{the electronic density, }\textit{n}(r), \textit{uniquely determines the external potential }v_{\text{ext}}(r) \textit{ with a trivial additive constant.} Since \textit{n}(r) \textit{integrates to the total number of electrons in the system and unique to the external potential, all the information about the system including the ground-state wavefunctions from solving the actual Schrödinger equation should also be determined by }\textit{n}(r). \textit{The second states that the energy functional with respect to the electronic density (}n(r)\textit{) finds a global minimum equal to the ground-state energy given a valid trial density.} This implies a variational principle to find the ground-state energy.

Even DFT have replaced solving the many-body Schrödinger equation, the method is not ready for practical use yet. The reason is that the kinetic operator is a non-local operator. Kohn and Sham provide a functional formalism to reduce the many-electron problem to a one-electron problem by deriving the Kohn-Sham (KS) equation [28]. In particular, KS functional for total energy \(E[n]\) is written as

\[
E_{\text{KS}}[n] = T[n] + \int n(r)v_{\text{ext}}(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|}drr' + E_{\text{xc}}[n]
\]  

(2.16)

where \(T[n]\) as the kinetic energy density functional of non-interacting ground state electrons and \(E_{\text{xc}}[n]\) as the exchange-correlation energy. Second and third terms describe the electron-nucleus interaction and electron-electron interaction respectively. Minimize \(E[n]\) by taking the functional derivative of \(E[n]\) with respect to \(n(r)\) and apply the constraint of

\[
\int n(r)dr = N,
\]

(2.17)
we obtain

$$\frac{\delta}{\delta n(r)}(E_{KS}[n] - \mu \int n(r)dr) = 0,$$

(2.18)

where $\mu$ is a Lagrange multiplier for the constraint of Eq. 2.17. We then define the hartree potential to be

$$v_H(r) = \int \frac{n(r)}{|r - r'|}dr',$$

(2.19)

the exchange-correlation potential to be

$$v_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)},$$

(2.20)

Note that all of these potentials are in local form. We substitute these forms in Eq. 2.18 and obtain

$$\frac{\delta T[n]}{\delta n(r)} + v_{\text{ext}}(r) + v_H(r) + v_{xc}(r) = \mu.$$  

(2.21)

The obtained density is written as

$$n(r) = \sum_i N |\psi_{KS}^i(r)|^2,$$

(2.22)

where $\psi_{KS}^i(r)$ is defined as KS wavefunctions, or KS orbitals which behave like one-electron orbitals. Combine all the potential terms together as

$$v_{\text{eff}}(r) = v_{\text{ext}}(r) + v_H(r) + v_{xc}(r),$$

(2.23)

we finally obtain the KS equation for each electron in the system as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r)\right] \psi_{KS}^i(r) = e_{KS}^i \psi_{KS}^i(r).$$

(2.24)
The total energy of the system is represented as

\[ E = \sum_i^N \epsilon_i - \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + E_{xc}[n] - \int v_{xc}(r)n(r)dr \] (2.25)

Note that each electron in the N-electron atomic system does not interact with one other but feels the exchange-correlation potential with a many-body feature built-in. Such approach finally makes DFT computation practical and is able to solve fairly large systems.

2.3.1 Local density approximation

In Eq. 2.23, the external potential and Hartree potential are well known and easy to solve, but the exchange-correlation potential is still unknown and hence can only be approximated to a certain accuracy. After more than two decades of functional development, all different kinds of density functionals with level of accuracy can be summarized in Perdew’s Jacob’s ladder [29] as shown in Fig. reffig:jacob. Basically, higher rung of the ladder provide higher accuracy but requires larger amount of computing time. The full review of density functional will not be discussed in this thesis but only the major functionals being used in the works presented in the thesis. The local density approximation is the earliest and simplest form to account for exchange-correlation energy [28]. Such an approximation consider the inhomogeneous electronic system is in slowly varying limit, and the electron gas within a small volume from every point has \( r \) distance from the origin is considered to be homogeneous. Now, we introduce the local density approximation (LDA) exchange-correlation energy form as

\[ E_{xc}^{LDA}[n] = \int n(r)\epsilon_{xc}^{LDA}(r)dr \] (2.26)
Figure 2.1: Jacob’s ladder summarizing the density functional approximation to the exchange-correlation energy
where $\epsilon_{xc}^{\text{LDA}}[n]$ is the average exchange-correlation energy of $N$ electrons, and Eq. 2.20 becomes

$$\psi_{xc}^{\text{LDA}}(r) = \epsilon_{xc}(n(r)) + n(r) \frac{\partial \epsilon_{xc}(n(r))}{\partial n(r)}$$

(2.27)

where $\epsilon_{xc}(n)$ can be divided as

$$\epsilon_{xc}(n) = \epsilon_x(n) + \epsilon_c(n)$$

(2.28)

and $\epsilon_x(n)$ takes the form of Thomas-Fermi is

$$\epsilon_x(n) = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} n(r)^{1/3}$$

(2.29)

LDA exchange-correlation functionals are suitable for stable systems. The accuracy of calculating structure parameters for lattices achieves 1-2% compare with experiments.

### 2.3.2 Generalized gradient approximation

The limitation of LDA majorly lies in to three aspects: (i) lack of consideration of system inhomogeneities, (ii) self-interaction is not canceled completely, (iii) non-local exchange-correlation is not included, so that calculated systems usually show over-binding. One natural route to improve the exchange-correlation energy approximation is to expand the density in terms of the gradient and higher order terms [30]. In general, the density gradient expanded exchange-correlation energy functional is in the following form,

$$E_{xc}[n] = \int n(r) \epsilon_{xc}[n(r)] F_{xc}[n(r), \nabla n(r), \nabla^2 n(r), \ldots] \, dr$$

(2.30)

where $F_{xc}$ is the enhancement factor that modifies the performance of $\epsilon_{xc}^{\text{LDA}}$. Perdew, Burke, and Ernzerhof (PBE) presented a generalized gradient approximated exchange-correlation
functional [31] is considered to be improve the accuracy of energetics and structural parameters of inhomogeneous system. In such functional, the exchange of the enhancement factor $F_x(n, \xi, s)$ involves the local density $n$, magnetization density $\xi$, and the dimensionless density gradient $s = |\nabla n(r)|/(2k_Fn)$, and the Fermi wavevector $k_F = (3\pi n)^{1/3}$. The expression is shown as

$$F_x = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}$$

(2.31)

where $\mu$ is from the second order density gradient expansion. The correlation term from PBE is similar to that proposed by Perdew and Wang [32]. It takes the form

$$E_{xc}^{\text{PBE}} = \int n(r)\left[\epsilon_{xc}^{\text{LDA}}(n, \xi) + H[n, \xi, t]\right] dr,$$

(2.32)

where $t$ is a dimensionless density gradient and $H$ is a mathematical form derived based on multiple density gradient constraints.

### 2.3.3 Hybrid density functionals

Both LDA and GGA density functionals cannot have resolve the self-interaction error issue completely. The demand for including exact exchange is hight demanded. The hybrid density functionals have been proposed to get rid of the self-interaction errors [33, 34, 35]. PBE0 exchange-correlation energy density functional form is

$$E_{xc}^{\text{PBE0}} = E_{xc}^{\text{GGA}} + \frac{1}{4}(E_x - E_x^{\text{GGA}}),$$

(2.33)

where $\frac{1}{4}$ of the Hartree-Fock exchange is mixed in the exchange-correlation energy of PBE-GGA form.

The range-separated hybrid functional [36, 35] divides PBE function into short-range
and long-range pieces and only mixes in the Hartree-Fock exchange to short-range portion. The functional form becomes

\[
E_{xc}^{\text{HSE06}} = a E_{xc}^{\text{HFSR}}(\omega) + (1 - a) E_{xc}^{\text{PBE,SR}}(\omega) + E_{xc}^{\text{PBE,LR}}(\omega) + E_{xc}^{\text{PBE}},
\]

(2.34)

where \(\omega\) is an adjustable parameter to tune the short-range (SR) interactions.

### 2.4 Plane-wave basis sets

For solids with periodic boundary conditions, plane-wave basis sets are simple and efficient to use. According to Bloch’s theorem, the wavefunction of a periodic system is the same for every period but with a phase factor change corresponding the lattice vector, which is listed as below

\[
\Psi_{i,k}(r + R_n) = e^{i k \cdot R_n} \Psi_{i,k}(r),
\]

(2.35)

where \(R_n\) is any lattice vector described as

\[
R_n = n_1 a_1 + n_2 a_2 + n_3 a_3
\]

(2.36)

with \(a_i\) the bravais lattice vector basis and any integer number \(n_i\). The vector \(k\) describes the coordinates under reciprocal space of lattice as

\[
K_m = m_1 b_1 + m_2 b_2 + m_3 b_3,
\]

(2.37)

where \(m_i\) are integer numbers and \(b_i\) are reciprocal lattice basis vectors holding the relation of

\[
b_i \cdot a_j = 2\pi \delta_{ij}
\]

(2.38)
where \( \delta_{ij} \) is the Kronecker delta:

\[
\delta_{ij} = 0, \quad i \neq j; \tag{2.39}
\]
\[
\delta_{ij} = 1, \quad i = j. \tag{2.40}
\]

The relationship between real space and reciprocal space of lattice vectors follows,

\[
R_n \cdot K_m = 2\pi \cdot \text{integer} \tag{2.41}
\]

Analogous to real space condition \( r \to r + R_n \), \( k \) in Eq. 2.35 holds \( k \to k + K_m \). This tells that all the information of a periodic system can be transformed back to first Brillouin zone (BZ) represent with \( k \) vectors.

The wavefunction in Eq. 2.35 can be represented as

\[
\Psi_{i,k}(r) = e^{ik \cdot r} u_{i,k}(r), \tag{2.42}
\]

where \( u_{i,k}(r) \) follows

\[
u_{i,k}(r + R_n) = u_{i,k}(r). \tag{2.43}\]

Expend the above function use Fourier series

\[
u_{i,k}(r) = \sum_m c_{i,m} e^{iK_m \cdot r}. \tag{2.44}\]

We substitute Eq. 2.44 into Eq. 2.42 to obtain the wavefunction in representation of a linear combination of plane waves as

\[
\psi_{i,k}(r) = \sum_m c_{i,k+K_m} e^{i(k+K_m) \cdot r}. \tag{2.45}\]
Replacing $q$ with $k + K_m$, the wavefunction above can be rewritten as

$$\psi_{i, k}(r) = \sum_j c_{i, q_j} e^{i q \cdot r}$$  \hspace{1cm} (2.46)

With the plane-wave basis represented wavefunction in hand, the KS equation (Eq. 2.24) can be rewritten as

$$\sum_{m'} \left[ \frac{\hbar^2}{2m} |k + K_m|^2 \delta_{m, m'} + v_{\text{eff}}(K_m - K_{m'}) \right] c_{i, K_{m'}} = \epsilon_i c_{i, K_m}$$  \hspace{1cm} (2.47)

The equation shows that potential energy is independent with reciprocal lattice vector $k$, but the accuracy of the total energy lies to sampling $k$-points of BZ within a certain cutoff energy to obtain the relative accurate kinetic energy. This cutoff energy holds

$$\frac{\hbar^2}{2m} |k + K_m|^2 < E_{\text{cut}}.$$  \hspace{1cm} (2.48)

### 2.5 Atomic pseudopotentials

The use of pseudopotential could reduce the basis set size in solving the Schrödinger-like equation, such as KS equation. The heavy computational efforts usually attribute to capturing the core region rapid oscillation of the electronic wavefunctions in an atomic system whose contribution to the chemical bonding is fairly less compare to the valence electron behavior. The pseudopotential, based on frozen core approximation, eliminates the core electron contribution to act on the system and retains the valence shell information. Fig. 2.2 portrays the relationship between the pseudopotential and true coulombic potential. Within a chosen cutoff value of $r$, the pseudopotential is a finite shallow potential instead of infinitely decreasing behavior. The corresponding wavefunction obtained by pseudopotential, or pseudo-wavefunction, is smooth and nodeless within $r_c$. Beyond the cutoff radius,
the pseudo- and all electron potential present the same feature.

2.5.1 Optimized pseudopotential construction

Norm-conserving pseudo-wavefunctions [37] should obey the following criteria:

1. \( \phi_{nl}^{PS}(r) = \phi_{nl}^{AE}(r) \), \( \frac{d\phi_{nl}^{PS}(r)}{dr} = \frac{d\phi_{nl}^{AE}(r)}{dr} \), \( \frac{d^2\phi_{nl}^{PS}(r)}{dr^2} = \frac{d^2\phi_{nl}^{AE}(r)}{dr^2} \) for \( r \geq r_c \). (2.49)

2. \( \epsilon_{nl}^{PS} = \epsilon_{nl}^{AE} \) (2.50)

3. \( \langle \phi_{nl}^{PS} | \phi_{nl}^{PS} \rangle = \langle \phi_{nl}^{AE} | \phi_{nl}^{AE} \rangle = 1 \) (2.51)

4. \( \left. \frac{d}{d\epsilon} \left( \frac{d \ln \phi_{nl}^{PS}(r)}{dr} \right) \right|_{R,\epsilon_{nl}} = \left. \frac{d}{d\epsilon} \left( \frac{d \ln \phi_{nl}^{AE}(r)}{dr} \right) \right|_{R,\epsilon_{nl}} \), \( R \geq r_c \) (2.52)

Together, they guarantee wavefunction smoothness and continuity, that the solutions of the pseudo-system are accurate representations of the corresponding all-electron system, and that the error of eigenenergy shifts caused by chemical bonding is small for gentle changes to the wavefunctions and density [37], hence improving the transferability, or applicability of the pseudopotential in different chemical environments.

In the RRKJ method [38], the pseudo-wavefunction is constructed as a sum of \( N_b \) spherical Bessel functions \( j_l(q_k r) \):

\[
\phi_{nl}^{PS}(r) = \begin{cases} 
\sum_{k=1}^{N_b} c_{nk} r j_l(q_k r), & r < r_c \\
\phi_{nl}^{AE}(r), & r \geq r_c 
\end{cases}
\] (2.53)

where the coefficients, \( c_{nk} \), are chosen to normalize the wavefunction and satisfy continuity constraints at \( r_c \). Additional \( c_{nk} \) coefficients improve plane-wave convergence. Once the pseudo-wavefunction is constructed, the pseudopotential is obtained by inverting the pseudo-KS equation above (see Eq.(3.4)). In applications of the pseudopotential in solid-
Figure 2.2: The schematic picture portraying the comparison between all electron and pseudization behavior of both wavefunction and coulombic potential. $V_{AE}$ the all electron coulombic potential, $V_{PS}$ the pseudopotential, $\Psi_{AE}$ the all electron wavefunction, and $\Psi_{PS}$ the pseudo-wavefunction.
state or molecular calculations, the screening effect of the valence electrons will generally be different from that in the atomic calculation. Therefore, the valence electron screening is removed to obtain a descreened pseudopotential, $V_{ion,l}^{PS}(r)$ for each angular momentum $l$, by subtracting Hartree and exchange-correlation potentials from the screened pseudopotential

$$V_{ion,l}^{PS}(r) = V_{l}^{PS}(r) - V[H][\rho_{val}](r) - V[xc][\rho_{val}](r),$$

(2.54)

where $V[H][\rho_{val}](r)$ and $V[xc][\rho_{val}](r)$ are calculated only from the valence charge density. The full pseudopotential, written in semilocal form, is then

$$V_{ion}^{PS} = \sum_{lm} V_{ion,l}^{PS}(r) |Y_{lm}\rangle \langle Y_{lm}|$$

$$= V_{loc}(r) + \sum_{l} \Delta \hat{V}_{l}^{SL}$$

(2.55)

In the second line, the potential is expressed as the sum of a local potential $V_{loc}(r)$ and semilocal corrections $\Delta \hat{V}_{l}^{SL}$, which are projections in the angular coordinates yet local in the radial coordinate. In order to reduce the memory cost of computation, we write the semilocal pseudopotential in a fully-separable nonlocal Kleinman-Bylander [39] form

$$\hat{V}_{ion}^{PS} = \hat{V}_{loc} + \sum_{l} \Delta \hat{V}_{l}^{NL}$$

(2.56)

$$\Delta \hat{V}_{l}^{NL} = \Delta \hat{V}_{l}^{SL} |\phi_{nl}^{ps}\rangle \langle \phi_{nl}^{ps}| \Delta \hat{V}_{l}^{SL}$$

Writing the pseudopotential in this form ensures that semilocal and nonlocal pseudoatoms have the same eigenvalues and wavefunctions for the reference configuration. The transferability of such a nonlocal pseudopotential, to configurations other than the reference, can be improved by applying the designed nonlocal strategy, which involves modifying the projectors of Eq. 2.56 [40]. In particular, the augmentation correction as a box potential is added to $\hat{V}_{loc}$ and subtracted from the non-local correction corresponding to each orbital,
the equation is written as

\[ \hat{V}^{PS} = (\hat{V}^{loc} + \hat{A}) + \sum_l \left( \langle \phi_{nl} | (\Delta \hat{V}_l^{SL} - \hat{A}) | \phi_{nl} \rangle \right) \frac{\langle \phi_{nl} | (\Delta \hat{V}_l^{SL} - \hat{A}) | \phi_{nl} \rangle}{\langle \phi_{nl} | (\Delta \hat{V}_l^{SL} - \hat{A}) | \phi_{nl} \rangle} \] (2.57)

Note that based on the KB non-local transformation,

\[ \hat{V}^{SL} | \phi_{nl}^{PS} \rangle \equiv \hat{V}^{NL} | \phi_{nl}^{PS} \rangle \] (2.58)

does not imply that

\[ \hat{V}^{SL} = \hat{V}^{NL}, \]

in which basis-set dimension of the two operators are different. In OPIUM, the non-local pseudopotential is iteratively built into the solver using numerov method. In hybrid pseudopotential generation, we make used of semi-local pseudopotential in the solver that

\[ V^{SL}(r) = \frac{\langle r | \hat{V}^{NL} | \phi_{nl}^{PS} \rangle}{\phi_{nl}^{PS}(r)}. \] (2.59)

We implement pseudopotential construction on a radial grid, with accuracy depending on the radial grid size. The use of a logarithmic grid ensures enough grid points near the core to describe oscillations of the all-electron wavefunctions in that region, while capturing the tail of the wavefunctions at large distances from the core to sufficient accuracy. The logarithmic grid is defined as

\[ r_i = aZ^{-1/3} e^{(i-1)b}, i = 1, ..., N \] (2.60)

where \( N \) is the number of grid points, spanning a sufficiently large real space range \( (r_{max}) \), \( Z \) is the core charge, and \( a \) controls the position of the first grid point, and \( b \) determines the grid spacing. We use values of \( a = 0.0001 \) and \( b = 0.013 \). The number of grid points \( N \) is
obtained by setting $r_{\text{max}}=80$ Bohr.

### 2.6 Van der Waals interactions

The van der Waals (vdW) interaction is a representation of intermolecular forces describing the attraction and repulsion among molecules [41]. vdW interactions are caused by the charge density fluctuation among any interacting particles. The interaction is considered to be long-range interaction as opposed to short-range interactions, which involves direct exchange and correlation of the electrons between particles. From the perspective of pair-interaction of the particles, vdW interaction can be considered as dipole-dipole interaction between two charged particles, London dispersion when two particles are neutral, or dipole-induced dipole interaction between a charged and uncharge particle. Theoretical studies of vdW attractions have been a long history. Here, we focus on the recent work incorporating with DFT development. The non-retarded vdW interaction between two spherical symmetric systems A and B can written as Equation (2.61).

\[
E_{\text{vdW}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots ,
\]

(2.61)

In particular, the coefficient $C_6$ represents the instantaneous dipole-dipole interaction, $C_8$ represents the dipole-quadrupole interaction, and $C_{10}$ represents the quadrupole-quadrupole and the dipole-octupole interactions [42]. $R$ is the distance between A and B. To implement the van der Waals interaction into DFT, a major trend is to correct the internal energy of the system after the self-consistent DFT computation. One of the methods is DFT-D [43, 44, 45, 46, 47]. The method is to obtain long-range coefficients ($C_i$) of single atoms
empirically and correct the internal energy of the system by using formula below,

$$E_{\text{vdW}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij} f_{\text{dmp}}(R_{ij})}{R_{ij}^6}, \quad (2.62)$$

where $s_6$ is a global scaling factor, $N_{\text{at}}$ is the number of atoms, $C_6$ is the dispersion coefficient, $R_{ij}$ is the interatomic distance and $f_{\text{dmp}}(R_{ij})$ is some damping function to take care of the singularity when $R_{ij}$ is infinitesimal small. For layered systems, Tkatchenko-Scheffler’s method DFT-TS [48, 49] is more accurate than previous ones due to the long-range coefficients are calculated from high level quantum mechanics methods, such as MP2 method, and many-body interaction is included besides pair-wised interactions. The van der Waals density functional (vdW-DF) was developed in 2010 [50, 51], the performance is good for lattice constants of molecular solids but not for their cohesive energies [49]. Tao and his coworkers start from building simple physics model for calculating the atomic multipole polarizability, and obtain the long-range coefficients from it [52, 42, 53], has shown many improvements in calculating molecular and solids physical properties [54, 55].
Chapter 3

Hybrid functional pseudopotentials
3.1 Introduction

Density functional theory (DFT) methods have proven to be successful for understanding and predicting the physical and chemical properties of materials. With approximations such as the local density approximation (LDA) [28] and generalized-gradient approximation (GGA) [31], DFT can reproduce many fundamental properties of solids, such as lattice constants and atomization energies [56]. However, LDA and GGA usually underestimate the fundamental band gaps of semiconductors and insulators [57]. The use of hybrid functionals in DFT, which combine part of the exact Hartree-Fock (HF) exchange with local or semilocal approximations (PBE0, HSE, B3LYP) [34, 58, 59], has become a popular option for addressing this problem.

The pseudopotential approximation is often used to reduce the complexity of DFT calculations. By replacing the nucleus and core electrons with a finite shallow potential, the solution of the Kohn-Sham equation is simplified because of the reduced number of electrons in the system. Accuracy is preserved because the core electrons are not involved in chemical bonding [38, 40].

Even though hybrid density functional calculations using pseudopotentials are currently very popular, these calculations solve the Kohn-Sham equation using pseudopotentials constructed at a lower rung of Jacob’s ladder [60], such as GGA. This is due to a lack of hybrid functional pseudopotentials available to the community. The mismatch of the level of density functional approximation between pseudopotential construction and target calculation is theoretically unjustified, and could lead to reduced accuracy [61]. In this work, we have developed hybrid density functional pseudopotentials to restore pseudopotential consistency in hybrid functional DFT calculations.

Prior to this work, Hartree-Fock pseudopotentials developed over the last decade [62, 63] have proven to be useful in calculations with correlated electrons. The inclusion of HF
exchange leads to stronger electron binding and mitigates the underbinding errors of GGA. It has been suggested that HF pseudopotentials may be useful in a variety of contexts, such as modeling systems with negatively-charged reference states [63] and in diffusion Monte Carlo simulations [64, 65]. The successful development of HF pseudopotentials [63] has opened the possibility of constructing hybrid pseudopotentials by including an exact exchange component into GGA potentials. Previous work demonstrated PBE0 pseudopotentials for gallium, indium and nitrogen atoms [66]. However, such pseudopotentials were simple linear combinations of the HF pseudopotential and the GGA pseudopotential without self-consistently solving hybrid PBE0 all-electron calculations.

In this paper, we construct consistent pseudopotentials (Sec. 3.2) for the PBE0 hybrid density functional, following the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) method [38]. This work extends Ref. [63], which was solely concerned with HF pseudopotentials, by considering self-consistent solutions of a pseudoatom under PBE0, thus moving beyond the non-self-consistent scheme of Ref. [66]. We benchmark the hybrid functional pseudopotential accuracy for diatomic molecules in the G2 dataset and for simple solids, focusing on geometric parameters and band gaps (Sec. 3.3). We find that the use of consistent PBE0 pseudopotentials improves the accuracy of PBE0 calculations of molecules and solids. Using these pseudopotentials, the mean absolute relative error (MARE) of HOMO-LUMO gaps of molecules is reduced to 4.5% from the MARE of 7.96% obtained by inconsistently using PBE pseudopotentials in PBE0 calculations. Likewise, the MARE of band gaps of simple solids is reduced to 6.56% from 7.90%. The use of consistent PBE0 pseudopotentials was found to have a relatively small effect on bond lengths (MARE reduced to 0.53% from 0.71%) and lattice parameters (MARE reduced to 0.57% from 0.66%). The mean absolute errors (MAEs), which illustrates the absolute deviation of using pseudopotentials from all-electron PBE0 calculations, indicates the same performance. Furthermore, the PBE0 pseudopotential generator is implemented in the OPIUM software package [67].
3.2 Theoretical Methods

In this section, we provide an overview of the standard theory behind pseudopotential construction, before discussing the special considerations that must be taken into account for hybrid functional pseudopotentials.

3.2.1 Pseudopotential construction

The all-electron (AE) wavefunctions and eigenvalues of an atom are the foundation for the construction of all pseudopotentials. The AE Kohn-Sham (KS) equation is

\[
\left[-\frac{1}{2} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_{\text{H}}[\rho(\mathbf{r})] + V_{\text{xc}}[\rho(\mathbf{r})]\right] \psi^{\text{AE}}_i(\mathbf{r}) = \epsilon^{\text{AE}}_i \psi^{\text{AE}}_i(\mathbf{r}),
\]  

(3.1)

where \(-\frac{1}{2} \nabla^2\) is the single-particle kinetic-energy operator, \(V_{\text{ion}}(\mathbf{r})\) is the ionic potential that electrons feel from the nucleus, \(V_{\text{H}}[\rho(\mathbf{r})]\) is the Hartree potential, and \(V_{\text{xc}}[\rho(\mathbf{r})]\) is the exchange-correlation potential, which are functionals of the charge density \(\rho(\mathbf{r})\). The all-electron wavefunction is denoted by \(\psi^{\text{AE}}_i(\mathbf{r})\), and the all-electron energy eigenvalues by \(\epsilon^{\text{AE}}_i\).

For an atom, \(V_{\text{ion}}(\mathbf{r}) = -\frac{Z}{r}\), where \(Z\) is the nuclear charge. Representing the wavefunction in spherical coordinates, \(r = |\mathbf{r}|\) and each \(\psi^{\text{AE}}_i(\mathbf{r})\) can be written as,

\[
\psi^{\text{AE}}_{nm}(\mathbf{r}) = \frac{\phi^{\text{AE}}_{nl}(r)}{r} Y_{lm}(\theta, \phi),
\]  

(3.2)

where \(n, l, m\) are principal, angular, and spin quantum numbers, and \(\theta\) and \(\phi\) are the corresponding angles from spherical coordinates. \(\phi^{\text{AE}}_{nl}\) is the radial wavefunction and \(Y_{lm}(\theta, \phi)\) are the spherical harmonics. Now, Eq. 3.1 can be simplified in terms of \(\phi^{\text{AE}}_{nl}\):

\[
\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{\text{KS}}(r)\right) \phi^{\text{AE}}_{nl}(r) = \epsilon^{\text{AE}}_{nl} \phi^{\text{AE}}_{nl}(r),
\]  

(3.3)
where $V_{\text{KS}}(r) = V_{\text{ion}}(r) + V_{\text{H}}(r) + V_{\text{xc}}(r)$. Instead of solving the full all-electron KS equation as in (Eq. 3.1), it is computationally more efficient to solve the radial equation (Eq. 3.3) self-consistently to obtain the radial wavefunction, $\phi_{nl}^{\text{AE}}(r)$ and corresponding eigenvalue, $\epsilon_{nl}^{\text{AE}}$.

In most molecular or solid systems, the valence electrons of atoms within the system are more crucial than core electrons, because they are more involved in chemical bonding. The core electrons mostly contribute to the electrostatic shielding of the nucleus. The AE wavefunctions of core electrons can contain rapid oscillations, which makes them hard to represent in plane wave basis sets and causes further difficulty in solving Eq. 3.3 numerically. Therefore, it is advantageous to construct pseudopotentials, which capture the valence electron behavior and also eliminate the need to recalculate the core electron wavefunctions.

Replacing the potential by a pseudopotential operator, the KS equation can be written as,

$$
\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + \hat{V}_{\text{PS}} \right] \phi_{nl}^{\text{PS}}(r) = \epsilon_{nl}^{\text{PS}} \phi_{nl}^{\text{PS}}(r),
$$

(3.4)

where $\hat{V}_{\text{PS}}$ is the screened pseudopotential operator. Note that such an operator is usually non-local (is an integral operator on $\phi_{nl}^{\text{PS}}(r)$). Similar to $V_{\text{KS}}$, $\hat{V}_{\text{PS}} = \hat{V}_{\text{ion}}^{\text{PS}} + V_{\text{H}}(r) + V_{\text{xc}}(r)$. $\epsilon_{nl}^{\text{PS}}$ is the pseudo-eigenvalue, and $\phi_{nl}^{\text{PS}}(r)$ is the pseudo-wavefunction.

### 3.2.2 Hartree-Fock pseudopotentials

Pseudopotentials can be constructed by solving the all-electron (AE) and pseudopotential (PSP) equations, Eq. 3.1 and Eq. 3.4, above using different exchange-correlation functionals, such as LDA or GGA. It is crucial that the exchange-correlation functional used for pseudopotential construction is the same as the functional used in the target calculation [61]. When the exchange-correlation functional contains the Fock operator, as is the
case for the hybrid functionals presently in widespread use, there are special considerations that must be taken into account in constructing the pseudopotential. Here, we consider the case of Hartree-Fock (HF) pseudopotentials, where the exchange-correlation functional is just the Fock operator, and will examine the PBE0 hybrid functional in the next subsection, where the Fock operator and PBE exchange-correlation are combined. For the HF pseudopotential, instead of solving the KS equation as in Eq.(3.3), we solve the Hartree-Fock equation,

\[
\left( \hat{T} + V_{\text{ion}}(r) + \hat{V}_{\text{HF}}\left\{ \psi_{n'l'} \right\} \right) \psi_{nl}(r) = \epsilon_{nl} \psi_{nl}(r), \tag{3.5}
\]

where \( \psi_{nl}(r) \) still takes the form in Eq.(3.2) (dropping the AE superscript for simplicity), \( V_{\text{ion}}(r) \) is the ionic potential, and \( \hat{V}_{\text{HF}}\left\{ \psi_{nl} \right\} \) is the HF potential, which depends on the set of wavefunctions \( \{ \psi_{nl} \} \). It is separated into two terms,

\[
\hat{V}_{\text{HF}}\left\{ \psi_{n'l'} \right\} = \hat{V}_{\text{H}}\left\{ \psi_{n'l'} \right\} + \hat{V}_{\text{x}}\left\{ \psi_{n'l'} \right\}. \tag{3.6}
\]

The Hartree potential takes the form

\[
\langle \psi_{nl} | \hat{V}_{\text{H}}\left\{ \psi_{n'l'} \right\} | \psi_{nl} \rangle = \sum_{n'l'} \int d^3r' d^3r \frac{|\psi_{n'l'}(r')|^2 |\psi_{nl}(r)|^2}{|r - r'|}, \tag{3.7}
\]

and the exact exchange operator acts as

\[
\langle \psi_{nl} | \hat{V}_{\text{x}}\left\{ \psi_{n'l'} \right\} | \psi_{nl} \rangle = \sum_{n'l'} \int d^3r' d^3r \frac{\psi_{nl}(r) \psi_{n'l'}^*(r') \psi_{n'l'}(r') \psi_{nl}^*(r')}{|r - r'|}. \tag{3.8}
\]

Direct evaluation of the Fock integral above (Eq. 3.8) requires introduction of angular variables for orbitals with non-zero angular momentum. This would result in non-spherical pseudopotentials, as well as introduce complexity into the pseudopotential generation process, which would then depend on the exact atomic configuration, including magnetic quan-
tum numbers. To circumvent these issues, we make use of a spherical approximation, to construct spherical Hartree-Fock pseudopotentials. Spherical approximations are routinely used to construct spherical LDA and GGA pseudopotentials, which are widely used successfully in electronic and structural calculations.

We use the Hartree-Fock spherical approximation of Froese Fischer [68] based on the concept of the “average energy of configuration” introduced by Slater [69]. Consider all atomic configurations where the $i$-th shell, with principal and total angular quantum numbers $n_i$ and $l_i$, is occupied with weight $w_i$. That is, all permutations of $w_i$ electrons occupying the $(2l_i + 1)$-degenerate shell $(n_i l_i)$.

The average energy of all such atomic configurations, expressed as a sum over pairs of atomic orbitals $(n_i l_i)$ and $(n_j l_j)$, is

$$E_{av}^{HF} = \sum_{i=1}^{m} w_i [I(n_i l_i, n_i l_i) + \left( \frac{w_i - 1}{2} \right) \sum_{k=0}^{2l_i} f_k(l_i, l_i) F^k(n_i l_i, n_i l_i)]$$

$$+ \sum_{i=2}^{m} \left\{ \sum_{j=1}^{i-1} w_i w_j \left[ F^0(n_i l_i, n_j l_j) + \sum_{k=|l_i - l_j|}^{(l_i + l_j)} g_k(l_i, l_j) G^k(n_i l_i, n_j l_j) \right] \right\}, \quad (3.9)$$

Here, the first summation represents the one electron contribution,

$$I(n l, n l) = -\frac{1}{2} \int_0^\infty \phi^*_n(r) \left( \frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l + 1)}{r^2} \right) \phi_n(r) dr. \quad (3.10)$$

The other terms contain the interaction terms between pairs of electrons. $F^k$ and $G^k$ are the Hartree and exchange energy Slater integrals,

$$F^k(n l; n' l') = \int_0^\infty \int_0^\infty \phi_n(r) \phi_{n'}(r') \frac{r^{k <}}{r^{k+1}_{>}} \phi_{n'l'}(r') \phi_{n'l'}(r') dr dr', \quad (3.11)$$

and

$$G^k(n l; n' l') = \int_0^\infty \int_0^\infty \phi_n(r) \phi_{n'}(r') \frac{r^{k <}}{r^{k+1}_{>}} \phi_{n'l'}(r) \phi_{n'l'}(r') dr dr', \quad (3.12)$$
where \( r_\text{<} (r_\text{>}) \) is the lesser (greater) of \( r \) and \( r' \). Details of the derivation are provided in Appendix C, and the numerical coefficients \( f_k \) and \( g_k \) are tabulated in Ref. [69]. We note that the integrals in Eq. 3.10–3.12 for the average energy depend only on the radial coordinate, and hence are a simplification of Eq. 3.8.

Taking functional derivatives of Eq. 3.9 with respect to the radial wavefunctions \( \phi_i(r) \), we arrive at Hartree-Fock equations for the wavefunctions of a Hartree-Fock atom. The set of \( m \) radial wavefunctions \( \phi_i, i = 1, \ldots, m \) obeys the coupled set of equations

\[
\hat{L} \phi_i(r) = \frac{2}{r} \left[ Y_i[\{\phi\}](r) \phi_i(r) + X_i[\{\phi\}](r) \right] + \sum_{j=1}^{m} \varepsilon_{ij} \phi_j(r),
\]

where \( \hat{L} = \frac{d^2}{dr^2} - 2V_{\text{ion}}(r) - \frac{l(l+1)}{r^2} \) is the single-particle part of the Hartree-Fock Hamiltonian, \( (2/r)Y_i[\{\phi\}](r) \) and \( (2/r)X_i[\{\phi\}](r) \) are the Hartree and exchange terms [70], \( \varepsilon_{ij} \) are Lagrange multipliers for orthogonality and normalization of radial wavefunctions. The detailed derivation of all these terms are presented in Appendix C.

Once the HF equation is constructed, we solve these equations self-consistently in a similar way to DFT pseudopotentials. The HF pseudowavefunctions \( \phi_{nl}^{\text{PS}}(r) \) are constructed using the same RRKJ procedure (Eq.(2.53)) as for the DFT pseudowavefunctions. The screened pseudopotential is obtained by inverting Eq.(3.5). Similar to DFT pseudopotentials, we descreen by subtracting the Hartree and exchange contributions of the valence electrons (c.f. Eq. 2.54)

\[
V_{\text{ion},l}^{\text{PS}}(r) = V_l^{\text{PS}}(r) - \frac{2}{r} Y_i[\{\phi_{\text{val}}\}](r) - \frac{2X_i[\{\phi_{\text{val}}\}](r)}{r \phi_i(r)},
\]

with \( Y_i \) and \( X_i \) obtained from Eq. 3.13. The HF pseudopotential constructed this way has a long-range non-Coulombic component of the tail, which does not decay as \( 1/r \). This is a consequence of the non-local nature of the Fock operator [63]. To resolve this issue, we make use of the localization procedure of Trail and Needs [62]. The tail is forced to
asymptotically approach $1/r$, and the potential is modified within the localization radius to ensure consistency with the all-electron eigenvalues [63].

### 3.2.3 PBE0 pseudopotentials

As hybrid functionals are a mix of HF and DFT ingredients, we generate hybrid pseudopotential using the HF pseudopotential approach as a foundation, making use of the spherical averaging procedure and localization procedure of the previous section and Ref. [63]. The PBE0 density functional [33] was developed based on the PBE exchange-correlation functional [31]; the PBE0 form is

$$
E_{xc}^{\text{PBE0}} = a E_{x}^{\text{HF}} + (1 - a) E_{x}^{\text{PBE}} + E_{c}^{\text{PBE}},
$$

where $a = 0.25$ for the PBE0 functional. As we use the spherical approximation for $E_{x}^{\text{HF}}$ (Eq. 3.9), we likewise evaluate the PBE exchange-correlation functional using a spherical approximation. Since $E_{x}^{\text{PBE}}$ is a functional of density only, this method consists of evaluating $E_{x}^{\text{PBE}}$ in Eq. 3.15 at the charge density, again taken to be the average over all possible magnetic quantum number configurations.

$$
\rho_{nl}(r) = \sum_{nlt} f_{ntm} |\psi_{nlt}(r)|^2 = \frac{1}{4\pi} \sum_{nli} f_{nli} |\phi_{nli}(r)|^2,
$$

where $\rho_{nl}(r)$ is the spherical symmetric charge density, $f_{nli} = w_i$ (as in Appendix B) is the occupation number for each orbital $(n_i l_i)$, and $f_{ntm} = f_{ntm'}$ is the occupation number for each magnetic quantum number $(nlm)$. Upon including $E_{x}^{\text{PBE}}$ and $E_{c}^{\text{PBE}}$ into the total energy expression Eq. 3.9, and taking functional derivatives, the coupled set of HF equations
(Eq. 3.13) becomes

\[
\hat{L}\phi_i(r) = \frac{2}{r} [Y_i(r)\phi_i(r) + \frac{1}{4} X_i(r)] + \frac{3}{4} \nu_{\text{PBE}}^x(r) + \nu_{\text{PBE}}^c(r) + \sum_{j=1}^{m} \delta_{ij} \delta_{ij} \epsilon_{ij} \phi_j(r),
\]

where the additional terms are the PBE exchange potential \( \nu_{\text{PBE}}^x(r) \) and the PBE correlation potential \( \nu_{\text{PBE}}^c(r) \). The self-consistent solution of these coupled equations is found iteratively, in a similar fashion to the HF equations (Eq. 3.13). At each iteration, we calculate the Fock exchange term \( (X_i(r)) \) from the wavefunctions of the previous iteration, and the PBE terms \( (\nu_{\text{PBE}}^x, \nu_{\text{PBE}}^c) \) from the density of the previous iteration. The pseudopotential construction is performed the same way as for HF pseudopotentials, including RRKJ pseudization, descreening, and localization of the non-Coulombic tail.

### 3.3 Testing of PBE0 pseudopotentials on molecular and solid state systems

We test the accuracy of our PBE0 pseudopotentials and the importance of pseudopotential density functional consistency for PBE0. We compare PBE calculations using PBE pseudopotentials (PBE), PBE0 calculations using PBE0 pseudopotentials (PBE0) and PBE0 calculations using PBE pseudopotentials (PBE-PBE0). The last case is currently the most widely used method of performing PBE0 calculations. The DFT code we use is QUANTUM-ESPRESSO [71]. Each single molecule is put into 20.0 Å cubic box, and its energy and geometry computed with kinetic energy cutoff \( E_{\text{cut}} = 25.0 \) Hartree. All these calculations are spin-polarized. The total energy convergence and force convergence are set to 0.005 mHartree/cell and 0.05 mHartree/Å. The reference all-electron calculations are performed using FHI-aims [1] with tight basis settings. The molecular and crystal structural opt-
mizations are converged within $3 \times 10^{-3}$ mHartree/cell for total energy, and the forces are converged within 0.003 mHartree/Å.

In Table 3.1, we show the bond lengths for diatomic molecules that belong to G2 data set [34] and compare each of our pseudopotential calculations with PBE0 all-electron values [72]. The use of PBE pseudopotential in PBE0 calculation gives MARE of 0.71%. Using the PBE0 functional with the PBE0 pseudopotential, the MARE reduces to 0.53%. This indicates that pseudopotential density functional consistently improves bond lengths for PBE0.
One of the reasons for using hybrid density functionals is that they predict band structures and ionization potentials (IP) more accurately than the PBE functional [73, 74, 66]. Table 3.2 shows the HOMO eigenvalues for diatomic molecules within the G2 dataset, calculated from different density functionals and compared with HOMO levels calculated from all-electron calculations. As expected, the difference between PBE HOMO eigenvalues and all-electron PBE0 values is the largest among the three computed cases. The use of consistent PBE0 pseudopotentials improves the MARE of the HOMO eigenvalues by a small amount (to 6.66% (PBE0) from 6.79% (PBE-PBE0)).
Table 3.1: The bond lengths of the diatomic molecules from G2 data set calculated from PBE, PBE-PBE0 and PBE0. The all-electron data are calculated using FHI-aims [1]. Units in Å. The MARE is calculated as MARE = $\frac{1}{N} \sum_{i}^{N} \frac{|b_i - b_{AE}|}{b_{AE}} \times 100$, where $N$ is the number of species, $b_i$ is the bond length of each species, and $b_{AE}$ is the all-electron value. The MAE is the average absolute deviation over the presented molecules and is calculated as $\text{MAE} = \frac{1}{N} \sum_{i}^{N} |b_i - b_{AE}|$. MARE and MAE of PBE calculations are taken relative to AE-PBE, while that of PBE0 calculations are taken relative to AE-PBE0. The experimental values are also listed for reference. The rest of the tables are of the same format.

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<th>PBE-PBE0</th>
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</tr>
<tr>
<td>CO</td>
<td>1.135</td>
<td>1.136</td>
<td>1.123</td>
<td>1.122</td>
<td>1.122</td>
<td>1.128</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.081</td>
<td>1.103</td>
<td>1.069</td>
<td>1.069</td>
<td>1.089</td>
<td>1.098</td>
</tr>
<tr>
<td>NO</td>
<td>1.132</td>
<td>1.157</td>
<td>1.113</td>
<td>1.138</td>
<td>1.139</td>
<td>1.151</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.212</td>
<td>1.218</td>
<td>1.218</td>
<td>1.217</td>
<td>1.192</td>
<td>1.207</td>
</tr>
<tr>
<td>F$_2$</td>
<td>1.420</td>
<td>1.413</td>
<td>1.382</td>
<td>1.382</td>
<td>1.376</td>
<td>1.412</td>
</tr>
</tbody>
</table>

MARE (%)  | 0.61 | 0.71 | 0.53 |
MAE (Å)   | 0.007| 0.008| 0.006|

a. Ref[72]
In Table 3.3, we present the HOMO-LUMO gap for the same dataset as in Table 3.2. Our PBE0 pseudopotentials reduce the MARE of the HOMO-LUMO gap to 4.55% (PBE0) from 7.96% (PBE-PBE0). Similar to bond length calculations, the consistency of the density functional between pseudopotential construction and DFT calculation reduces the error. While the use of PBE pseudopotential for PBE0 DFT calculation results in fair accuracy, it can be improved by using a pseudopotential constructed with a consistent density functional.
Table 3.2: HOMO eigenvalues with PBE, PBE-PBE0 and PBE0 methods. Energies are in eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>PBE</th>
<th>AE-PBE</th>
<th>PBE-PBE0</th>
<th>PBE0</th>
<th>AE-PBE0</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>-10.31</td>
<td>-10.34</td>
<td>-11.96</td>
<td>-11.96</td>
<td>-11.99</td>
</tr>
<tr>
<td>LiH</td>
<td>-3.89</td>
<td>-4.35</td>
<td>-5.45</td>
<td>-5.44</td>
<td>-5.44</td>
</tr>
<tr>
<td>BeH</td>
<td>-4.76</td>
<td>-4.68</td>
<td>-5.77</td>
<td>-5.20</td>
<td>-5.69</td>
</tr>
<tr>
<td>CH</td>
<td>-5.91</td>
<td>-5.84</td>
<td>-7.43</td>
<td>-7.43</td>
<td>-7.45</td>
</tr>
<tr>
<td>OH</td>
<td>-7.06</td>
<td>-7.14</td>
<td>-8.81</td>
<td>-8.72</td>
<td>-7.00</td>
</tr>
<tr>
<td>Li(_2)</td>
<td>-3.20</td>
<td>-3.16</td>
<td>-3.99</td>
<td>-3.75</td>
<td>-3.72</td>
</tr>
<tr>
<td>LiF</td>
<td>-6.08</td>
<td>-6.09</td>
<td>-7.77</td>
<td>-7.85</td>
<td>-7.96</td>
</tr>
<tr>
<td>CN</td>
<td>-9.30</td>
<td>-9.38</td>
<td>-10.74</td>
<td>-10.94</td>
<td>-9.32</td>
</tr>
<tr>
<td>CO</td>
<td>-9.01</td>
<td>-9.03</td>
<td>-10.41</td>
<td>-10.42</td>
<td>-10.72</td>
</tr>
<tr>
<td>N(_2)</td>
<td>-10.07</td>
<td>-10.22</td>
<td>-11.93</td>
<td>-12.20</td>
<td>-12.20</td>
</tr>
<tr>
<td>NO</td>
<td>-4.74</td>
<td>-4.50</td>
<td>-6.25</td>
<td>-6.29</td>
<td>-4.60</td>
</tr>
<tr>
<td>O(_2)</td>
<td>-6.71</td>
<td>-6.91</td>
<td>-8.68</td>
<td>-8.70</td>
<td>-8.91</td>
</tr>
<tr>
<td>MARE (%)</td>
<td>3.33</td>
<td>6.79</td>
<td>6.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAE (eV)</td>
<td>3.15</td>
<td>0.40</td>
<td>0.38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
We have also tested our pseudopotentials in solid-state calculations. The lattice constants and band gaps for some simple solids associated with first 20 elements in the periodic table are shown in Table 3.4 and Table 3.5. Similar to molecular bond lengths, the density functional consistency also influences the lattice constants of solids. By using consistent pseudopotentials the MARE of lattice constants of these solids are slightly improved to 0.57% (PBE0) from 0.66% (PBE-PBE0). As expected, the PBE calculation significantly underestimates the band gaps. The two PBE0 cases increase the band gaps by a large amount compared to PBE calculation. The effect of density functional consistency is even more important for the band gaps than for the lattice constants: the MARE of the band gaps are improved to 6.56% (PBE0) from 7.90% (PBE-PBE0). Together with the calculations from molecular properties, we may conclude that pseudopotential density functional inconsistency contributes a systematic error of the order of 1% for PBE0, for the systems tested.
Table 3.3: HOMO-LUMO gap (in eV) of diatomic molecules in G2 dataset with different functionals.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>PBE</th>
<th>AE-PBE</th>
<th>PBE-PBE0</th>
<th>PBE0</th>
<th>AE-PBE0</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>10.26</td>
<td>10.84</td>
<td>11.94</td>
<td>11.94</td>
<td>13.10</td>
<td>11.8³</td>
</tr>
<tr>
<td>LiH</td>
<td>2.57</td>
<td>2.81</td>
<td>4.04</td>
<td>4.48</td>
<td>4.45</td>
<td>4.0410²</td>
</tr>
<tr>
<td>BeH</td>
<td>2.64</td>
<td>2.31</td>
<td>4.44</td>
<td>4.42</td>
<td>4.15</td>
<td>4.200²</td>
</tr>
<tr>
<td>CH</td>
<td>2.06</td>
<td>1.77</td>
<td>3.95</td>
<td>3.51</td>
<td>3.60</td>
<td>-</td>
</tr>
<tr>
<td>NH</td>
<td>3.95</td>
<td>6.45</td>
<td>7.27</td>
<td>7.34</td>
<td>7.16</td>
<td>-</td>
</tr>
<tr>
<td>OH</td>
<td>1.12</td>
<td>6.54</td>
<td>4.77</td>
<td>4.92</td>
<td>4.25</td>
<td>-</td>
</tr>
<tr>
<td>FH</td>
<td>8.19</td>
<td>8.76</td>
<td>10.92</td>
<td>10.93</td>
<td>11.80</td>
<td>11.30³</td>
</tr>
<tr>
<td>Li₂</td>
<td>1.41</td>
<td>1.43</td>
<td>2.75</td>
<td>2.47</td>
<td>2.50</td>
<td>2.22²</td>
</tr>
<tr>
<td>LiF</td>
<td>4.29</td>
<td>4.62</td>
<td>6.41</td>
<td>6.50</td>
<td>7.02</td>
<td>6.16²</td>
</tr>
<tr>
<td>CN</td>
<td>1.99</td>
<td>1.72</td>
<td>4.67</td>
<td>4.74</td>
<td>4.48</td>
<td>9.78²</td>
</tr>
<tr>
<td>N₂</td>
<td>7.66</td>
<td>8.24</td>
<td>10.94</td>
<td>10.94</td>
<td>11.71</td>
<td>11.05²</td>
</tr>
<tr>
<td>NO</td>
<td>1.30</td>
<td>1.22</td>
<td>3.50</td>
<td>2.88</td>
<td>2.86</td>
<td>3.05²</td>
</tr>
<tr>
<td>O₂</td>
<td>2.40</td>
<td>2.31</td>
<td>5.74</td>
<td>6.09</td>
<td>6.10</td>
<td>6.06³</td>
</tr>
<tr>
<td>F₂</td>
<td>3.32</td>
<td>3.63</td>
<td>7.77</td>
<td>7.79</td>
<td>8.34</td>
<td>7.47²</td>
</tr>
</tbody>
</table>

| MARE (%) | 14.82 | 7.96 | 4.55 |
| MAE (eV) | 0.78  | 0.50 | 0.39 |

a. Ref[75]
b. Ref[76] G4 basis set
| c. Ref[77]
Table 3.4: Solid state calculation with PBE, PBE-PBE0 and PBE0. The lattice constants of simple solids associated with first 20 elements are listed. The lattice constant is in units of Å.

<table>
<thead>
<tr>
<th>Solids</th>
<th>PBE</th>
<th>AE-PBE</th>
<th>PBE-PBE0</th>
<th>PBE0</th>
<th>AE-PBE0</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>5.484</td>
<td>5.472</td>
<td>5.452</td>
<td>5.446</td>
<td>5.448</td>
<td>5.430</td>
</tr>
<tr>
<td>GaN</td>
<td>4.541</td>
<td>4.549</td>
<td>4.539</td>
<td>4.537</td>
<td>4.536</td>
<td>4.523</td>
</tr>
<tr>
<td>MgO</td>
<td>4.324</td>
<td>4.305</td>
<td>4.310</td>
<td>4.308</td>
<td>4.204</td>
<td>4.207</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.710</td>
<td>5.701</td>
<td>5.663</td>
<td>5.639</td>
<td>5.634</td>
<td>5.595</td>
</tr>
<tr>
<td>Graphene</td>
<td>2.476</td>
<td>2.469</td>
<td>2.460</td>
<td>2.460</td>
<td>2.453</td>
<td>2.464</td>
</tr>
<tr>
<td>SiC</td>
<td>4.403</td>
<td>4.404</td>
<td>4.375</td>
<td>4.370</td>
<td>4.349</td>
<td>4.358</td>
</tr>
</tbody>
</table>

MARE (%) | 0.17  | 0.66  | 0.57    |
MAE (Å)   | 0.007 | 0.027 | 0.023   |

a. Ref[59]
b. Ref[74]
c. Ref[78]
Table 3.5: Solid state calculation with PBE, PBE-PBE0 and PBE0. The band gap of simple solids within first 20 elements are listed. The band gap is in eV.

<table>
<thead>
<tr>
<th>Solids</th>
<th>PBE</th>
<th>AE-PBE</th>
<th>PBE-PBE0</th>
<th>PBE0</th>
<th>AE-PBE0</th>
<th>Expt.(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.58</td>
<td>2.54</td>
<td>1.79</td>
<td>1.78</td>
<td>1.63</td>
<td>1.17</td>
</tr>
<tr>
<td>GaN</td>
<td>1.81</td>
<td>1.55</td>
<td>3.58</td>
<td>3.56</td>
<td>3.54</td>
<td>3.30</td>
</tr>
<tr>
<td>MgO</td>
<td>4.38</td>
<td>4.44</td>
<td>7.97</td>
<td>7.38</td>
<td>7.28</td>
<td>7.22</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.67</td>
<td>4.97</td>
<td>6.71</td>
<td>7.28</td>
<td>7.14</td>
<td>8.50(^b)</td>
</tr>
<tr>
<td>Diamond</td>
<td>5.63</td>
<td>5.58</td>
<td>5.53</td>
<td>5.54</td>
<td>6.08</td>
<td>5.48</td>
</tr>
<tr>
<td>BN (cubic)</td>
<td>4.49</td>
<td>4.45</td>
<td>6.58</td>
<td>6.56</td>
<td>6.54</td>
<td>6.22</td>
</tr>
<tr>
<td>SiC</td>
<td>1.34</td>
<td>1.38</td>
<td>2.98</td>
<td>2.96</td>
<td>2.95</td>
<td>2.42</td>
</tr>
<tr>
<td>MARE (%)</td>
<td>18.02</td>
<td>5.29</td>
<td>3.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAE (eV)</td>
<td>0.53</td>
<td>0.28</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Ref[59]

\(^b\) Ref[74]
3.4 Conclusion

We have developed the first consistent PBE0 pseudopotential and have successfully implemented it in the OPIUM pseudopotential generation code. We have also shown that our PBE0 pseudopotentials behave well when implementing them to DFT calculations. Our benchmarking tests on the G2 dataset and solids indicate that the systematic error associated with pseudopotential density functional consistency is of the order of 1%. Using the PBE0 pseudopotential in PBE0 DFT calculations leads to small improvements in bond length and lattice parameter accuracy. For these quantities, the errors of the pseudopotential calculations compared to all-electron calculations are typically less than 1%. Using consistent PBE0 pseudopotentials reduces these errors by around 0.1% (i.e. pseudopotential density functional consistency accounts for about $1/10^{th}$ of the 1% errors in these geometrical quantities). On the other hand, for the HOMO-LUMO gaps, the error of the pseudopotential calculations compared to all-electron calculations is 8%, and is reduced to 4.5% by using PBE0 pseudopotentials. Pseudopotential density functional consistency therefore accounts for a significant amount of the error between pseudopotential and all-electron calculations, for the electronic excitation energies. A similar trend is obtained for the bands gaps of solids tested. From these results, we conclude that using PBE pseudopotentials in PBE0 calculations leads to acceptable results for small molecules and simple solids, while using PBE0 pseudopotentials instead will likely result in a small consistent increase in accuracy. Future directions include further testing of PBE0 pseudopotentials for more complex systems, the inclusion of relativistic effects for heavy atoms, and the development of other hybrid functional pseudopotentials, including range-separated hybrids [79].
3.5 Appendix A: Derivation of Hartree-Fock average energy

As a preliminary to deriving the average energy formula Eq. 3.9, we collect several useful quantities. The Hartree potential due to an electron in the state \((nlm)\) is

\[
V_H^{(nlm)}(\vec{r}) = \int d^3r' \frac{|\psi_{nlm}(\vec{r'})|^2}{|\vec{r} - \vec{r'}|} = \int_0^\infty r'^2 dr' d\Omega \frac{\phi_{nl}(r')^2 |Y_{lm}(\Omega)|^2}{|\vec{r} - \vec{r'}|} \tag{3.18}
\]

Using the expansion with \(m\) here for getting ready for Eq. 3.20

\[
\frac{1}{|\vec{r} - \vec{r'}|} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{4\pi}{2k + 1} (-1)^m \frac{\frac{r_k}{r_{k+1}}}{Y_{k}^{-m}(\Omega)}Y_{k}^{m}(\Omega') \tag{3.19}
\]

where \(r_< (r_>)\) is the lesser (greater) of \(r\) and \(r'\), we write Eq. 3.18 as

\[
V_H^{(nlm)}(\vec{r}) = \sum_{k, l', m'} \int_0^\infty r'^2 dr' \frac{\phi_{nl}(r')^2}{r_{k+1}} \sqrt{\frac{4\pi}{2k + 1} Y_{k}^{0*}(\Omega) c^{k}(l, m', l, m') \phi_{nl}(r')^2} \tag{3.20}
\]

Here, we make use of the symbols

\[
c^{k}(l, m', l', m') = \sqrt{\frac{4\pi}{4k + 1} \int Y_{lm}^*(\Omega)Y_{k,m-m'}(\Omega)Y_{l'm'}(\Omega)d\Omega} \tag{3.21}
\]

for Gaunt’s formula, in terms of Wigner 3\(j\)-symbols. In the second line of Eq. 3.20, we

50
have separated the $k = 0$ and $k > 0$ components, because the latter vanishes when averaged over $m$. Therefore, the Hartree energy of a pair of electrons $(ij|i)$, in orbitals $(n_i, l_i)$ and $(n_j, l_j)$, averaged over the magnetic quantum number $m_j$ of the second electron, is simply

$$
\langle \langle ij | ij \rangle \rangle_{m_j} = \int_0^\infty dr \phi_{n_i l_i}(r)^2 \int_0^\infty dr' \frac{1}{r'} \phi_{n_j l_j}(r')^2 \tag{3.22}
$$

$$
= F^0(n_i l_i, n_j l_j)
$$

The exchange integral for a pair of electrons in orbitals $(n_i, l_i)$ and $(n_j, l_j)$ can be calculated in similar fashion. Using Eqs. 3.19 and 3.21, we get

$$
(ij|ji) = \int d^3 r d^3 r' \frac{\psi^*_{n_i l_i m_i}(\vec{r}) \psi_{n_i l_i m_j}(\vec{r}) \psi^*_{n_j l_j m_j}(\vec{r}') \psi_{n_j l_j m_i}(\vec{r}')}{|\vec{r} - \vec{r}'|}
$$

$$
= \sum_{kq} \int Y_{l_i m_i}(\Omega) Y_{l_j m_j}(\Omega) Y_{l_i m_i}(\Omega') Y_{l_j m_j}(\Omega') d\Omega \int Y^*_{l_i m_i}(\Omega') Y_{l_i m_i}(\Omega') Y_{l_j m_j}(\Omega') d\Omega'
$$

$$
= \sum_{kq} \frac{4\pi}{r_k^0 + 1} \frac{2k + 1}{2k + 1} \phi_{n_i l_i}(r) \phi_{n_j l_j}(r) \phi_{n_j l_i}(r') \phi_{n_i l_j}(r') dr dr'
$$

$$
= \sum_k c^k(l_i, m_i, l_j, m_j)^2 \int \frac{r_k^0}{r_k^0 + 1} \phi_{n_i l_i}(r) \phi_{n_j l_j}(r) \phi_{n_j l_i}(r') \phi_{n_i l_j}(r') dr dr'
$$

For the average of the exchange integral over $m_j$, we get

$$
\langle \langle ij | ji \rangle \rangle_{m_j} = \frac{1}{\sqrt{(2l_i + 1)(2l_j + 1)}} \sum_k c^k(l_i, 0, l_j, 0) G^k(n_i l_i, n_j l_j) \tag{3.24}
$$

To calculate the average total energy of an atomic configuration, we must consider the Hartree and exchange energies of all pairs of electrons. First consider the case where the electrons are in the same orbital $(n_i = n_j, l_i = l_j)$. In this case, since $G^k(n_i l_i, n_i l_i) = F^k(n_i l_i, n_i l_i)$, we can combine Eqs. 3.22, 3.11 and 3.24 to obtain

$$
\langle \langle ij | ij \rangle \rangle - \langle \langle ij | ji \rangle \rangle = \frac{w_i(w_i - 1)}{2} \sum_k f_k(l_i, l_i) F^k(n_i l_i, n_i l_i) \tag{3.25}
$$
where the numerical coefficients $f_k(l_i, l_i)$ are obtained from those in Eqs. 3.22, 3.24, and the prefactor $\frac{w_i(w_i-1)}{2}$ is the number of different electron pairs in orbital $i$.

For the case where the electrons in the pair are in different orbitals, the sum of Eqs. 3.22, 3.24 gives

$$
\langle (ij|ij) - (ij|ji) \rangle = w_i w_j \left( F^0(n_i, n_j l_j) + \sum_k g_k(l_i, l_j) G^k(n_i, n_j l_j) \right)
$$

(3.26)

where the coefficients $g_k(l_i, l_j)$ are given by Eq. 3.24. Collecting the terms in Eqs. 3.25, 3.26 with the single-particle energies results in the expression for the average total energy Eq. 3.9

### 3.6 Appendix B: Derivation of self-consistent Hartree-Fock equations

If the orbitals are not necessarily normalized, the average energy (as defined in Sec. 3.2.2) derived in Sec. 3.5 may be written in the form

$$
E_{av}^{HF} = \sum_i w_i I(n_i l_i, n_i l_i) \left( \frac{1}{\langle nl_i|nl_i \rangle} \right) + \sum_{i,k} a_{iik} F^k(n_i l_i, n_i l_i) \left( \frac{1}{\langle nl_i|nl_i \rangle} \right) + \sum_{i>j;k} b_{ijk} G^k(n_i l_i, n_j l_j) \left( \frac{1}{\langle nl_i|nl_i \rangle} \right) + \sum_{i>j;k} b_{ijk} G^k(n_i l_i, n_j l_j) \left( \frac{1}{\langle nl_i|nl_i \rangle} \right)
$$

(3.27)

We wish to find wavefunctions that minimize $E_{av}^{HF}$, under the constraint of wavefunction orthogonality. In other words, a pair of radial functions from orbitals with the same angular momentum, $(n_i, l_i)$ and $(n_j, l_j)$ with $l_i = l_j$, must be orthogonal. Using the Lagrange
multipliers \( \lambda_{ij} \), we therefore search for the stationary solutions of the functional

\[
K = E_{\text{av}}^{\text{HF}} + \sum_{i>j} \delta_{i,j} \lambda_{ij} \frac{\langle n_i l_i | n_j l_j \rangle}{\langle n_i l_i | n_i l_i \rangle^{1/2} \langle n_i l_i | n_i l_i \rangle^{1/2}} \tag{3.28}
\]

We now proceed to take functional derivatives of Eqs. 3.27, 3.28 with respect to variations in a radial function \( \phi_{nl}(r) \). We note that only a subset of terms in Eq. 3.27 involve \( nl \), and those that do all contain a factor of \( \langle n_i l_i | n_i l_i \rangle^{-1} \). We can therefore write those terms in the form \( \tilde{E}(nl) = \langle n_i l_i | n_i l_i \rangle^{-1} \tilde{F}(nl) \) with the variation

\[
\delta \tilde{E}(nl) = \langle n_i l_i | n_i l_i \rangle^{-1} \delta \tilde{F}(nl) + \delta [\langle n_i l_i | n_i l_i \rangle^{-1}] \tilde{F}(nl) \tag{3.29}
\]

and

\[
\delta \tilde{F}(nl) = w_{nl} \delta I(nl) + \sum_k a_{nl,nl,k} F^k(nl,nl) \delta[\langle nl | nl \rangle^{-1}] + \sum_k \frac{a_{nl,nl,k} \delta F^k(nl,nl)}{\langle nl | nl \rangle} \\
+ \sum_{n'l' \neq nl,k} a_{nl,n'l',k} F^k(nl,n'l') \frac{\langle n'l' | n'l' \rangle}{\langle n'l' | n'l' \rangle} + \sum_{n'l' \neq nl,k} b_{nl,n'l',k} \delta G^k(nl,n'l') \frac{\langle n'l' | n'l' \rangle}{\langle n'l' | n'l' \rangle} \tag{3.30}
\]

Furthermore, we have

\[
\delta [\langle n_i l_i | n_i l_i \rangle^{-1}] = -2 \int dr \frac{\phi_{nl}(r) \delta \phi_{nl}(r)}{\langle nl | nl \rangle^2} \tag{3.31}
\]

and

\[
\delta F^k(nl,n'l') = 2(1 + \delta_{nl,n'l'}) \int dr \phi_{nl}(r) \delta \phi_{nl}(r) \frac{1}{r} Y^k(n'l',nl,r) \tag{3.32}
\]

\[
\delta G^k(nl,n'l') = 2 \int dr \phi_{n'l'}(r) \delta \phi_{nl}(r) \frac{1}{r} Y^k(nl,n'l',r) \tag{3.33}
\]
where

$$Y^k(nl, n'l', r) = \int_0^r ds \frac{s^k}{r^k} \phi_{nl}(s) \phi_{n'l'}(s) + \int_r^\infty ds \frac{s^{k+1}}{s^{k+1}} \phi_{nl}(s) \phi_{n'l'}(s)$$ (3.34)

Finally, the variation of the terms involving the Lagrange multipliers in Eq. 3.28 is

$$\delta \left[ \sum_{n'} \lambda_{nl,n'l'} \langle nl|n'l' \rangle \langle nl|nl \rangle^{1/2} \langle n'l'|n'l'| \rangle^{1/2} \right] = \sum_{n'} \lambda_{nl,n'l'} \int dr \phi_{n'l'}(r) \delta \phi_{nl}(r)$$ (3.35)

The variational principle requires that the variation \( \delta K \) be stationary with respect to \( \delta \phi_{nl}(r) \). Collecting Eqs. 3.29–3.35, we obtain the Hartree-Fock equations (Eq. 3.13) where

$$Y_i(r) = \sum_{j,k} (1 + \delta_{nl_i,nl_j}) a_{nl_i,nl_j,k} Y^k(n_j l_j, n_j l_j, r) \frac{w_i}{\langle n_j l_j | n_j l_j \rangle}$$ (3.36)

$$X_i(r) = \sum_{j \neq i,k} b_{nl_i,nl_j,k} Y^k(n_i l_i, n_j l_j, r) \phi_{nl_j}(r) \frac{w_i}{\langle n_j l_j | n_j l_j \rangle}$$ (3.37)

and

$$\varepsilon_{ii} = \frac{2}{w_i} \left[ \tilde{E}(n_i l_i) - \sum_k a_{nl_i,nl_i,k} F^k(n_i l_i, n_i l_i) \frac{1}{\langle n_i l_i | n_i l_i \rangle^2} \right]$$ (3.38)

$$\varepsilon_{ij} = \frac{\lambda_{nl_i,nl_j} \langle n_i l_i | n_i l_i \rangle^{1/2}}{w_i \langle n_j l_j | n_j l_j \rangle^{1/2}}$$ (3.39)
Chapter 4

Van der Waals interactions in fullerene solids
4.1 Sublimation energy of fullerene and bulk modulus correction on fullerene solids lattice constants

4.1.1 Introduction

Sublimation is one of the basic properties of molecular solids. It is a common phenomenon that can be “observed” in our daily life, such as carbon dioxide (dry ice), snow and ice, iodine, naphthalene (a common ingredient in mothballs), etc. This property has been used for purification in industry. Nanostructured solids with high sublimation points, such as fullerenes [80], can be used as rapid cooling materials for rockets [81]. A good knowledge of this property is also important for our better understanding of long-range van der Waals (vdW) interaction, because intermolecular forces in most molecular solids essentially arise from the vdW interaction. However, calculation of this property presents a major challenge to conventional density functional theory (DFT), due to the missing of the long-range vdW interaction.

The vdW interaction is an important long-range correlation arising from instantaneous collective charge fluctuations on each object. It is ubiquitous and affects the properties of many molecules and solids, such as lattice constants [82], cohesive energies [83], or sublimation energies and physisorption [84]. It also plays an important role in the determination of higher-order structures of biomolecular chains that define their biological activities [85].

According to second-order perturbation theory, in the large separation, the vdW energy between two densities takes the asymptotic form, \( E_{vdW} = -\sum_{k=3}^{\infty} \frac{C_{2k}}{d^{2k}} \), where \( d \) is the separation between centers of the density pieces, and \( C_{2k} \) are the vdW coefficients. In the simulation of the vdW interaction, the main task is to calculate the vdW coefficients. Many methods have been proposed [86, 87, 88, 89, 90] to evaluate these coefficients. In particular, Becke and Johnson [91] proposed an exchange-hole dipole moment model, which can
generate accurate vdW coefficients for atoms [92] (with an error of 3\%) and molecules [93] (with an error of less than 10\%). Tkatchenko and Scheffler [94] proposed a method for intermolecular vdW coefficients, with an error of about 6\%. Recently, Tkatchenko et al. [95] have extended this method to include non-additive many-body (e.g., 3-body, 4-body) interactions, improving the performance of the Tkatchenko-Scheffler method for nanoscale systems. Tao, Perdew, and Ruzsinszky developed a solid-sphere model for the dynamic multipole polarizability, which generates for free atom pairs $C_6$, $C_8$, and $C_{10}$ in excellent agreement (3\%) with accurate reference values. Grimme and co-workers [96] developed a sophisticated pairwise-based dispersion-corrected DFT method (DFT-D), which well improves the accuracy of conventional DFT in quantum chemistry. Alternatively, Langreth and co-workers developed a nonlocal correlation functional to account for the long-range vdW interaction and combined it with a proper semilocal exchange functional. This combination is called vdW-DF and has been widely used in electronic structure calculations. Recently, many variants [97, 98] of this functional have been proposed and good improvement can be achieved with judicious choices for the exchange part.

With the development of vdW corrections to semilocal DFT, the applicability of DFT has been greatly extended and considerable progress has been made in electronic structure calculations [99, 100, 101, 102]. The aim of this work is to apply the vdW-corrected DFT to study the intermolecular interactions between fullerenes in the solid phase. Fullerenes are cage molecules of nanosize that have long been a topic of strong interest. Because all carbon atoms are distributed away from the center and the valence electrons are fully nonlocalized over the fullerene surface, the carbon atom in fullerenes are much more polarizable, compared to an isolated carbon atom, and the vdW coefficients between fullerenes exhibit strong non-additivity. It was shown that the vdW coefficients between large clusters strongly violate the prediction of a simple pairwise model and even the prediction of sophisticated pairwise models, but in a more moderate way. A solution to avoid the error...
due to the non-additivity is to treat molecules as whole systems, rather than as a sum of atom pairs. This treatment may not enable us to study intramolecular interactions, which allows for bond formation and breaking. However, it has great advantage for the study of the properties due to the intermolecular forces, in particular for nanostructured solids, in which it has been found that there exists strong non-additivity of vdW coefficients.

4.1.2 Theory and computational methods

Recently, it has been shown that the vdW coefficients between nanoclusters can be accurately generated from the conducting shell model. This model requires the input accurate static dipole polarizability and the average valence electron density. This requirement can be well satisfied with slowly varying densities. As such, the model is particularly suited for the vdW interactions between nonastructures, in which the electron density can be well modelled with the slowly varying density (paradigm of condensed matter physics). However, the conducting shell model is valid only for isolated nanostructures such as fullerene molecules. For nanostructured solids, screening from the valence electrons must be considered. Let us first consider a conducting shell of density uniform inside and zero outside the shell, placed in a continuous medium, with the dielectric function $\epsilon_1(iu)$. According to Refs. [103, 104, 82], the screened dynamic multipole polarizability of the shell takes the form of

$$\alpha_{l}^{sc}(iu) = \left( R^{2l+1} \frac{\omega_l^2}{\omega_l^2 + u^2} \frac{1 - \rho_l}{1 - \beta_l \rho_l} \right) \frac{1}{\epsilon_1(iu)} , \quad (4.1)$$

where $\beta_l = \frac{\omega_l^2 \bar{\omega}_l^2}{(\omega_l^2 + u^2)(\bar{\omega}_l^2 + u^2)}$, $\omega_l = \omega_p \sqrt{l/(2l+1)}$ is the plasmon frequency of a sphere, and $\bar{\omega}_l = \omega_p \sqrt{(l+1)/(2l+1)}$ is the plasmon frequency of a cavity, with $\omega_p = \sqrt{4\pi n}$ being the plasmon frequency of the extended uniform electron gas. (Atomic units are used unless otherwise explicitly stated.) $\rho_l = (1 - t/R)^{2l+1}$ is the shape function,
with $R$ being the outer radius of the shell and $t$ being the shell thickness. This model is valid for any value of $t$. The plasmon frequencies of the sphere and cavity can be calculated from the average valence electron density within the shell, which is given by $n = N/V$, with $N$ being the number of valence electrons of a fullerene, and $V$ being the shell volume calculated from $V = 4\pi R^3/3 - 4\pi (R - t)^3/3$. The outer effective (or vdW) radius $R$ may be obtained accurately from the quantum molecular dynamics [105]. In this work, the shell thickness $t = 3.4$ is taken from Ref. [106].

The screening effect enters the dynamic polarizability via the frequency-dependent dielectric function $\epsilon_1(iu)$. The dielectric function is only known in two limits: the uniform-gas limit (metal) in which $\epsilon_1(iu) = 1 + \bar{\omega}_p^2/u^2$, and the low-density (vacuum or perfect insulator) limit, where $\epsilon_1(iu) = 1$. In the uniform-gas limit, electrons are fully delocalized so that the screening effect achieves maximum, while in the low-density or large energy-gap limit, electrons are fully localized on the objects so that $\epsilon_1(iu) \approx 1$ and no screening would be expected. However, the exact general form of $\epsilon_1(iu)$ remains unknown. Many methods have been proposed to simulate $\epsilon_1(iu)$. In this work, we use the following dielectric function [84]

$$\epsilon_1(iu) = 1 + \frac{\bar{\omega}_p^2}{u^2} \left\{ \frac{(1 - \Delta^2)y}{P} - \frac{\omega_g^2 - (\omega_g^2 + u^2)\Delta^2}{2u\sqrt{\omega_g^2 + u^2}} \ln I_+ \frac{I_+}{I_-} \right\}$$

$$+ \frac{2\bar{\omega}_p^2 \Delta}{u^2} \left\{ \frac{\omega_g}{u} \left[ \tan^{-1} \left( \frac{\omega_g P}{u} \right) - \tan^{-1} \left( \frac{\omega_g}{u} \right) \right] \right\}$$

$$+ \frac{1}{P - 1} \right\}, \quad (4.2)$$

where $I_\pm = [(1 + y^2)(1 + u^2/\omega_g^2)]^{1/2} \pm uy/\omega_g$, $y = 1/\Delta$, and $P = (1 + y^2)^{1/2}$. $\omega_g$ is the effective energy gap which will be defined below, and $\Delta = \omega_g/4\epsilon_F$, with $\epsilon_F = (3\pi^2 \bar{n})^{2/3}/2$ being the Fermi energy and $\bar{n}$ being the average valence electron density of
the solid. Notice that $\bar{n}$ and $n$ in Eq. (4.1) are different, the former is the bulk electron density, while the latter is the electron density within the shell of a fullerene. This formula was originally derived by Penn [107] based on the nearly-free electron gas, and later on it was modified by Breckenridge et al. [108] to satisfy the Kramers-Kronig relation. Recently, we have applied this model to the physical adsorption of atoms to surfaces. The calculated adsorption energies agree very well with experiments.

To ensure $\epsilon_1(iu)$ to be realistic, we determine $\omega_g$ by reproducing the static dielectric function $\epsilon_1(0)$ with the Penn model [107], $\epsilon_1(0) = 1 + (\omega_p^2/\omega_g^2)[(1 + \Delta^2)^{1/2} - \Delta]$, which is very close to the static limit of Eq.(4.2). Therefore, it will not make much difference between the two static limits. Although the model dielectric function was derived on the basis of the nearly-free electron gas, it should be quite realistic, even for the density away from the nearly-free electron gas, because of the recovery of the correct $\epsilon_1(0)$. This has been confirmed with our recent GW calculation, which shows that the model dielectric function of Eq. (Ref. [84]) agrees reasonably well with the GW values for many semiconductors, suggesting the general reliability of the model [Eq.(4.2)]. The $\epsilon_1(0)$ values of fullerenes can be estimated from the static dipole polarization using the Clausius-Mossotti formula [109, 110] $\alpha_1(0) = \frac{2}{3\pi\rho} \frac{\epsilon_1(0) - 1}{\epsilon_1(0) + 2}$. Here $\rho$ is the particle number density of a solid. For fcc solids, $\rho = 4/a^3$, where $a$ is the lattice constant, which can be calculated from semilocal DFT-LDA. The static polarization can be calculated from TDDFT or TDHF [111, 112]. For convenience, all the inputs $\alpha_1(0)$, $\epsilon_1(0)$, and $\omega_g$ are listed in Table 5.1.

Now we turn to the lattice constant calculation. Lattice constant is a very important geometrical parameter in electronic structure theory. Accurate prediction of this quantity is of general interest. In addition, lattice constant is also an important input in the present work. While the experimental values for the fullerene solids considered here are available in the literature, theoretical calculations are only found for C$_{60}$. To make the calculation to be predictable, we avoid any experimental input in the study of sublimation. Since the
Table 4.1: Input static polarizabilities (in a.u.) of fullerene molecules, static dielectric constants, energy gaps (in a.u.), and conventional cell lattice constants (in Å) of fullerene solids. All the data are from the present work, except as noted. M.R.E. = mean relative error.

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>$\alpha_1(0)$</th>
<th>$\epsilon_1(0)$</th>
<th>$\omega_g$</th>
<th>$a^{LDA}$</th>
<th>$a^{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{60}(I_h)</td>
<td>537&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.813</td>
<td>0.444</td>
<td>14.024</td>
<td>14.17&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>C_{70}(D_{5h})</td>
<td>685&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.260</td>
<td>0.410</td>
<td>14.837</td>
<td>15.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>C_{76}(D_{2})</td>
<td>756&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.309</td>
<td>0.405</td>
<td>15.297</td>
<td>15.475&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>C_{78}(C_{2v})</td>
<td>779&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.246</td>
<td>0.406</td>
<td>15.498</td>
<td>15.56&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>C_{84}(D_{2})</td>
<td>837&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.242</td>
<td>0.406</td>
<td>15.876</td>
<td>16.06&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>C_{96}(C_{2})</td>
<td>971&lt;sup&gt;e&lt;/sup&gt;</td>
<td>4.233</td>
<td>0.404</td>
<td>16.689</td>
<td>16.83&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>M.R.E.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−1%</td>
</tr>
</tbody>
</table>

<sup>a</sup> From Ref. [112].
<sup>b</sup> From Ref. [113].
<sup>c</sup> Interpolated between C_{76} and C_{78}.
<sup>d</sup> From Ref. [114].
<sup>e</sup> Interpolated between C_{90} and C_{100} values evaluated with TDLDA [111].
LDA lattice constants are usually more accurate [115] than those of the DFT-GGA, here we calculate the lattice constants with LDA, using the plane wave and pseudopotential based open-source code Quantum ESPRESSO [116]. The pseudopotential is generated using OPIUM [67]. Diamond is used as a trial to test the pseudopotential behavior. The lattice constant and bulk modulus are tested via LDA pseudopotential, whereas the cohesive energy is tested via GGA pseudopotential. LDA pseudopotential employs Perdew-Zunger exchange with cut-off radius $r_c = 0.74\text{Å}$ and energy cutoff $E_{\text{cut}} = 1361\text{ eV}$. The calculated lattice constant for diamond is 3.54Å with error of -0.84% in comparison with the experimental value, and the calculated bulk modulus is 460 GPa, 3.84% larger than the experimental value. For GGA pseudopotential, PBE exchange-correlation is employed with $r_c = 0.68\text{Å}$ and $E_{\text{cut}} = 1361\text{ eV}$. The cohesive energy for diamond is 6.46% larger than the experimental value. All the calculations are performed using variable cell relaxation. The total energy difference between two is around 0.2 meV/atom.

The LDA pseudopotential is therefore used to optimize the lattice structure of fullerene solids. In our calculations, an $8 \times 8 \times 8$ k-point grid is used. Our calculations show that, except for $C_{60}$, which has the perfect fcc structure, all other fullerenes give a slightly distorted fcc structure, due to the deviation of spherical symmetry. Consequently, the distortion results in some changes in lattice constants and solid angles of lattices, as shown in Table S1. However, except for $C_{70}$ whose deviation is 1.8°, the deviation of the solid angles for all other fullerenes considered is within 1°. Therefore, we may treat the distorted lattices as face-centered orthorhombic ($a \neq b \neq c$ and $\alpha \approx \beta \approx \gamma \approx 90°$). As we shall see below, this orientation has a small effect (about 10%) on the sublimation energies. In order to make direct comparison with experimental values [117, 118, 113], in the calculation of the vdW energy with the asymptotic expansion, we use the fcc lattice structure. The effective fcc lattice constants are obtained from the geometric mean of the distorted lattice constants. The results are reported in Table 5.1. From Table 5.1, we observe that the effective fcc lattice
constants are also too short by 1%, compared to experiments. This is consistent with other reports (e.g., Ref. [115]).

4.1.3 Results and discussion

The sublimation energy is defined as the energy difference between molecules in the gas phase and the solid phase. It essentially arises from the vdW interactions between fullerenes. The first theoretical study of this problem is the classical Monte Carlo calculation based on an empirical intermolecular potential. The calculated sublimation energies agree very well with experimental values. Recently, Hyldgaard [83] and co-workers calculated the cohesive energy of C\textsubscript{60} with several variants of vdW-DF functional. The result sensitively depends on the choice of the exchange part. In this work, we study the sublimation energy of the fullerenes, for which experimental values are available. This includes C\textsubscript{60}, C\textsubscript{70}, C\textsubscript{76}, C\textsubscript{78}, C\textsubscript{84}, and C\textsubscript{96}. Sublimation energy consists of two contributions: a smaller short-range part, which can be well described with semilocal DFT [119], and a larger long-range part, due to the vdW interaction. The short-range part arises from the orbital overlap of electrons between two fullerenes. Here we first calculate the short-range contribution with the GGA. The results are shown in Table 5.2. We observe from Table 5.2 that the short-range contribution is too small, compared to experimental values [120], suggesting that the orbital overlap of electrons between different fullerenes is negligible.
Figure 4.1: Comparison of the dynamic dipole polarizability $\alpha_{1}^{sc}(iu)$ of fullerenes in the solid phase with the dynamic dipole polarizability $\alpha_{1}(iu)$ of isolated fullerenes.
Table 4.2: Sublimation energies (in kcal/mol) of fullerene solids calculated with DFT+vdW, DFT-D2, and vdW-DF.

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>GGA</th>
<th>GGA+vdW</th>
<th>( \Delta H_{\text{sub}}^{\text{DFT-D2}} )</th>
<th>( \Delta H_{\text{sub}}^{\text{vdW-DF}} )</th>
<th>( \Delta H_{\text{sub}}^{\text{ref}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{60}(I_h) )</td>
<td>1.9</td>
<td>41.7</td>
<td>35.3</td>
<td>44.3</td>
<td>41.9 ± 3.3(^a)(0K)</td>
</tr>
<tr>
<td>( C_{70}(D_{5h}) )</td>
<td>1.8</td>
<td>50.1</td>
<td>39.3</td>
<td>50.1</td>
<td>47.8 ± 1.4(^a)(298K)</td>
</tr>
<tr>
<td>( C_{76}(D_2) )</td>
<td>1.7</td>
<td>51.0</td>
<td>40.8</td>
<td>51.0</td>
<td>49.3 ± 1(^a)(298K)</td>
</tr>
<tr>
<td>( C_{78}(C_{2v}) )</td>
<td>1.8</td>
<td>49.7</td>
<td>39.9</td>
<td>51.6</td>
<td>49.4(^b)(0K)</td>
</tr>
<tr>
<td>( C_{84}(D_2) )</td>
<td>1.8</td>
<td>49.8</td>
<td>42.5</td>
<td>55.6</td>
<td>53.8 ± 1.4(^a)(298K)</td>
</tr>
<tr>
<td>( C_{96}(C_2) )</td>
<td>1.9</td>
<td>50.0</td>
<td>47.0</td>
<td>60.1</td>
<td>53.1(^b)(0K)</td>
</tr>
</tbody>
</table>

\(^a\)From experiments [120]
\(^b\)Estimated from the classical Monte Carlo values [121].
Then we calculate the long-range vdW energy with the asymptotic formula, as described in the Introduction. The asymptotic expression is divergent in the small-separation limit, while the exact vdW energy is finite anywhere in space. To fix this problem, we usually multiply each term $C_{2k}/d^{2k}$ by a damping function $f(d)$. However, in this work we may apply the asymptotic formula directly to calculate the long-range part. This is because we are only concerned with the vdW energy at the equilibrium intermolecular distance and because, at equilibrium, the first-nearest neighbor intermolecular distance $d = a^{\text{LDA}}/(0.5292\sqrt{2})$ (18.7, 19.8, 20.4, 20.7, 21.2, and 22.3 for C$_{60}$, C$_{70}$, C$_{76}$, C$_{78}$, C$_{84}$, and C$_{96}$) is always larger than the average vdW diameters of fullerenes ($2R = 16.3, 17.6, 18.2, 18.4, 18.8,$ and 19.8). Applying a damping function [122] $f_d(d) = (1 - \exp[-c(d/d_{\text{vdW}})^3])^2$, where $c = 3.54$ and $d_{\text{vdW}} = 2R$ is the sum of the vdW radii, only reduces vdW effects by about 1%. The vdW coefficients between fullerene molecules in solids can be calculated [123] from the screened dynamic multipole polarizability of Eq. (4.1), with second-order perturbation formula $C_{2k}^{\text{sc}} = \sum_{l_1=1}^{k-2} \frac{(2k-2)!}{2\pi(2l_1)!(2l_2)!} \int_0^\infty \alpha^{\text{sc},A}_{l_1} (iu) \alpha^{\text{sc},B}_{l_2} (iu) \, du$. The long-range part is the vdW energy of a fullerene interacting with all other fullerenes in the solid. It is calculated up to the sixth-nearest neighbors. Since the convergence of the asymptotic series is very slow, we truncate the series for $k > 16$. This truncated order is far beyond the reach of other vdW methods. To see the screening effect, we calculate the vdW energy without screening. The results for C$_6$, C$_8$, and C$_{10}$ are listed in Table S2. Our calculations show that without screening, the vdW energy is surprisingly too large. This can be seen from the comparison of the screened dynamic polarizabilities with the unscreened ones, as shown in Fig. 4.1.

The sublimation energy is obtained by adding the DFT-GGA calculation (for short-range part) to the long-range part. From Table 5.2, we see that our screened vdW method, when combined with semilocal DFT, can yield the sublimation energies in good agreement with reference values [120, 121]. We also calculate the sublimation energies with the vdW-
DF and DFT-D2 (or GGA-D2) methods using the same pseudopotential for the LDA and GGA. The results are displayed in Table 5.2. From Table 5.2 we can see that the DFT+vdW method is slightly more accurate than vdW-DF, while DFT-D2 moderately underestimates the sublimation energies. Part of reason is that DFT-D2 only considers the leading-order \((C_6)\) contribution, while all higher-order terms have been neglected. The good performance of the vdW-DF nonlocal functional suggests that higher-order contributions seem to have been included in the long-range part of this functional. However, the leading-order coefficient of the vdW-DF has a significant error for molecules. It is interesting to note that the new version of vdW-DF, vdW-DF2, underestimates the sublimation energy of \(C_{60}\), as reported recently [83].

Experiment shows that at temperatures above 340K, fullerenes rotate rather freely in the fcc lattice [118]. To have a better understanding of this orientation effect [124], we calculate the long-range vdW energy of a fullerene with all other fullerenes in the effective fcc and distorted fcc structures, respectively. Our calculations (Table S3) show that the orientation of fullerenes can affect the vdW energy by about 5-6 kcal/mol on average, via distortion of the lattice. This leads to the increase of sublimation energy by about 10% (Tables S1,S3).

### 4.1.4 Conclusion

In conclusion, we have studied the sublimation energies of fullerenes with semilocal DFT, corrected with the dynamically screened vdW interaction. Our calculations show that the sublimation energies of fullerenes essentially arise from the vdW interaction. We find that there is strong screening effect on the vdW interaction. The reason is that the energy gap of fullerene solids are quite small (the largest energy gap is about 2eV, as found in \(C_{60}\), compared to many other solids formed with small molecules, although the intermolecular distance is large (in the order of nano meters). Our calculations also show that the higher-order contribution is very large. (If all higher-order terms are neglected, the screened leading-
order contribution only accounts for about 18% of the sublimation energy of C$_{60}$. To have a better understanding of this and the screening effect, we also performed calculations of the sublimation energies with vdW-DF (popular in solid-state calculations), and DFT-D2 (popular in quantum chemistry). We find that vdW-DF tends to yield larger sublimation energy and stronger bonding, while DFT-D2 tends to predicts weaker vdW bonding, compared to our DFT+vdW approach. This suggests the significance of the higher-contributions in fullerenes. Our method should be also valid for other nanostructured solids, such as alkali-metal clusters, in which the electron density is nearly homogeneous. For these clusters, the energy gap is expected to be small and thus there is strong screening from valence electrons.

4.2 Bulk modulus correction on lattice constants of fullerene solids

4.2.1 Introduction

Lattice constant is a fundamental structural property of a solid material. Accurately calculate the lattice constant using density functional theory (DFT) is still a challenging task especially for molecular solids due to incompletion of van der Waals (vdW) interaction implementation. In previous study [125], we introduced the dynamically screened vdW method to study the sublimation energy of fullerene solids. Here, we make use of such method to derive the lattice constant correction method on face-centered cubic (fcc) structure including bulk moduli computations. We apply the lattice constant corrections to fullerene crystal lattice systems ranging from C$_{60}$ to C$_{96}$. The error is found to be of the same level of that from DFT-D2 method [45]. Our method provides a fairly accurate lattice constants of molecular solids without involving vdW corrections in the geometric optimization process,
and a more accurate bulk modulus could lead to a more accurate lattice constant correction.

4.2.2 Theory and computational methods

In a pair interaction system with particle A and B, the vdW attraction energy can be written as,

\[ E_{\text{vdW}} = -\frac{C_6^{\text{AB}}}{R^6} - \frac{C_8^{\text{AB}}}{R^8} - \frac{C_{10}^{\text{AB}}}{R^{10}} - \cdots, \]  

(4.3)

where \( C_6^{\text{AB}}, C_8^{\text{AB}} \) and \( C_{10}^{\text{AB}} \) are long-range coefficients and \( R \) is the distance between A and B. The coefficients can be obtained by calculating the particle dynamical multipole polarizability [53]. In our model system with fullerene molecules in the fcc lattice, we consider fullerene as a classical spherical shell with electron density localized around the shell. The classical dynamical multipole polarizability including the screening effect is given as,

\[ \alpha_l^{\text{SC}}(iu) = \left( R^{2l+1} \frac{\omega_l^2}{\omega_l^2 + u^2} \frac{1 - \rho_l}{1 - \beta_l \rho_l} \right) \frac{1}{\epsilon_1(iu)}, \]  

(4.4)

where \( \alpha_l^{\text{SC}}(iu) \) is the multipole polarizability under screened (SC) condition with multiple of \( l \) varying the imaginary part of low frequency \( u \). \( \omega_l \) is the plasmon frequency of a solid sphere, \( \rho_l \) is a shape function taking the form of

\[ \rho_l = (1 - t/R)^{2l+1} \]  

(4.5)

with \( t \) as the thickness of the cavity shell, and \( \beta_l \), the frequency coupling between a sphere and a cavity, can be written as,

\[ \beta_l = \frac{\omega_l^2 \omega_l^2}{(\omega_l^2 + u^2)(\tilde{\omega}_l^2 + u^2)} \]  

(4.6)
where $\tilde{\omega}_l$ is the plasmon frequency of the cavity shape. $\epsilon_1$ is the imaginary part of the dielectric constant of the material.

The lattice constant correction can be evaluated related to the bulk modulus of the solid system. We start from the derivation of the equation of state to obtain the lattice constant correction. We represent the true lattice constant as $a_0$, the calculated lattice constant as $a$, the lattice constant correction as $\Delta a$, and $a = a_0 + \Delta a$. The total energy in terms of lattice volume, $v$, can be written as,

$$E_{\text{tot}}(v) = E_{\text{vdW}}(v) + E_{\text{DFT}}(v). \quad (4.7)$$

We apply Taylor’s expansion to both the $E_{\text{vdW}}(v)$ and $E_{\text{DFT}}(v)$ around $v_0$, where $v_0 = \frac{1}{4}a_0^3$ since the lattice is a fcc structure. Then, $E_{\text{DFT}}(v)$ can be rewritten as,

$$E_{\text{DFT}}(v) = E_{\text{DFT}}(v_0) + \frac{dE_{\text{DFT}}(v)}{dv}\bigg|_{v=v_0} \Delta v + \frac{1}{2} \frac{d^2E_{\text{DFT}}(v)}{dv^2}\bigg|_{v=v_0} (\Delta v)^2, \quad (4.8)$$

and the bulk modulus $B_0$ is

$$B_0 = v \frac{d^2E_{\text{DFT}}(v)}{dv^2}\bigg|_{v=v_0}. \quad (4.9)$$

Also, the change of volume $\Delta v$ is

$$\Delta v = \frac{d(\Delta v)}{da} = \frac{3}{4}a^2 \Delta a. \quad (4.10)$$

Substituting Eq. 4.10 into Eq. 4.8, we obtain the final equation of $E_{\text{DFT}}(v)$ as

$$E_{\text{DFT}}(v) = E_{\text{DFT}}(v_0) + \frac{9}{8}B_0a_0(\Delta a)^2. \quad (4.11)$$
As for the formulation of $E_{\text{vdW}}(v)$, we follow the same strategy as the above to have

$$\frac{1}{2} \frac{d^2 E_{\text{vdW}}(v)}{dv^2} \bigg|_{v=v_0} (\Delta v)^2 = \frac{9}{8} \Delta B a_0 (\Delta a)^2. \tag{4.12}$$

Thus, the total energy can be rewritten as

$$E_{\text{tot}}(v) = E(v_0) + \frac{3}{4} \frac{dE_{\text{vdW}}(v)}{dv} \bigg|_{v=v_0} a_0^2 \Delta a + \frac{9}{8} (B_0 + \Delta B) a_0 (\Delta a)^2. \tag{4.13}$$

Since the total energy, $E_{\text{tot}}$, reaches minimum at equilibrium volume, the first derivative of $E_{\text{tot}}$ with respect to $v$ is,

$$\frac{dE_{\text{tot}}(v)}{dv} = 0, \tag{4.14}$$

and

$$\frac{dE_{\text{tot}}(a)}{da} = 0. \tag{4.15}$$

Continuing the derivation based on $E_{\text{tot}}$, we obtain the lattice constant correction, $\Delta a$ as

$$\Delta a = -\frac{4}{9} \frac{dE_{\text{vdW}}(a)}{da} \bigg|_{a=a_0}, \tag{4.16}$$

with the correction of bulk modulus $\Delta B$ as

$$\Delta B = v_0 \left\{ \frac{d}{da} \left( \frac{dE_{\text{vdW}}}{da} \frac{4}{3a^2} \right) \right\} \frac{4}{3a^2}. \tag{4.17}$$

In this investigation, density functional theory (DFT) calculations were performed using Quantum ESPRESSO package [71] with norm conserving pseudopotentials from OPIUM code [67]. A 680 eV of plane-wave cutoff was used, and the electronic exchange correlation energy was calculated with generalized gradient approximated (GGA) density functional of Perdew, Burke, and Ernzerhof [31]. Two types of vdW interaction forms, such as vdW-DF
functional [126, 127, 128] and DFT-D2 [45] are computed for the fullerene solid systems. Lattice constant correction is computed based on DFT+vdW [125]. An $8 \times 8 \times 8$ Monkhorst-Pack [129] k-point mesh was used for variable cell relaxation of each fullerene solid bulk.

### 4.2.3 Results and discussion

Eq. 4.16 and Eq. 4.17 only require two inputs: the lattice constant value computed from DFT and the bulk modulus calculated based on the total energies from DFT. Tab. 4.3 provides the lattice constants of series of fullerene molecular solids calculated with PBE functional. The lattice constant correction computed followed Eq. 4.16 is listed on the second column. The corrected lattice constants show, very small, less than 1.3% of relative errors compare to experimental lattice constants [113, 114]. The large error comes from $C_{60}$ and $C_{96}$ is due to the bulk modulus analysis consist of a bit larger error compare to other species.

We also provide lattice constants values calculated by DFT-D2 and vdW-DF methods. As shown in Tab. 4.4, DFT-D2 method based lattice constant shows relative errors that are generally less than 0.5% compare to the experimental values. The lattice constants calculated by vdW-DF method shows almost three times larger of the error compare to both DFT-D2 and our DFT+vdW lattice correction method. The comparison also shows that our correction method possess the similar level of accuracy with DFT-D2 method.

These results indicate that without computing vdW energies with DFT calculations, the fairly accurate lattice constants of molecular solids such as fullerene solids can be obtained from simply calculating GGA lattice constants and applying post-process vdW analytical corrections.
Table 4.3: DFT+vdW method computed lattice constants for fullerene fcc lattices ranging from C60 to C96.

<table>
<thead>
<tr>
<th></th>
<th>(a^\text{GGA} (\text{Å}))</th>
<th>(\Delta a)</th>
<th>correct (a_0)</th>
<th>(a_0^\text{exp.})</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{60})</td>
<td>15.45209</td>
<td>1.46356</td>
<td>13.98853</td>
<td>14.17(^a)</td>
<td>-1.28066</td>
</tr>
<tr>
<td>C(_{70})</td>
<td>16.56335</td>
<td>1.50754</td>
<td>15.05581</td>
<td>15.01(^a)</td>
<td>0.30520</td>
</tr>
<tr>
<td>C(_{76})</td>
<td>17.19825</td>
<td>1.64618</td>
<td>15.55207</td>
<td>15.48(^a)</td>
<td>0.46557</td>
</tr>
<tr>
<td>C(_{78})</td>
<td>17.30416</td>
<td>1.62152</td>
<td>15.68264</td>
<td>15.56(^b)</td>
<td>0.78817</td>
</tr>
<tr>
<td>C(_{84})</td>
<td>17.67456</td>
<td>1.64806</td>
<td>16.02650</td>
<td>16.06(^a)</td>
<td>-0.20859</td>
</tr>
<tr>
<td>C(_{96})</td>
<td>18.52117</td>
<td>1.89690</td>
<td>16.62427</td>
<td>16.83(^a)</td>
<td>-1.22240</td>
</tr>
</tbody>
</table>

\(^a\)From Ref. [113].
\(^b\)From Ref. [114].
4.2.4 Conclusions

We provide a lattice constant correction method for fcc lattice molecular crystals via bulk modulus correction from vdW interactions. The corrected lattice constants of sampled fullerene molecular crystals are at the same level of accuracy compare to that of DFT-D2 method with the relative error of less than 1.5%. The less accurate lattice constant values of C$_{60}$ and C$_{90}$ are due to less accurate bulk modulus of the two crystals. Our lattice constant correction method can be extended to any molecular crystals with fcc lattice structure, and the strategy of deriving the lattice constant correction can apply to other type of lattice structures.
Table 4.4: Lattice constants of fullerene fcc systems with DFT-D2 method and vdW-DF method.

<table>
<thead>
<tr>
<th></th>
<th>DFT-D2</th>
<th>% error</th>
<th>vdW-DF</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C60</td>
<td>14.18</td>
<td>0.071</td>
<td>14.52</td>
<td>2.470</td>
</tr>
<tr>
<td>C70</td>
<td>14.95</td>
<td>-0.400</td>
<td>15.28</td>
<td>1.799</td>
</tr>
<tr>
<td>C76</td>
<td>15.49</td>
<td>-0.450</td>
<td>15.82</td>
<td>2.196</td>
</tr>
<tr>
<td>C78</td>
<td>15.66</td>
<td>-0.643</td>
<td>15.97</td>
<td>2.635</td>
</tr>
<tr>
<td>C84</td>
<td>16.03</td>
<td>-0.187</td>
<td>16.34</td>
<td>1.743</td>
</tr>
<tr>
<td>C96</td>
<td>16.87</td>
<td>0.238</td>
<td>17.18</td>
<td>2.080</td>
</tr>
</tbody>
</table>
Chapter 5

First principle study of adsorption:
Benzene on RuO$_2$(110) surface
5.1 Introduction

Over the past twenty years, the RuO$_2$(110) surface has become a key model system for transition metal oxide catalysis\[130]. Its high electrical conductivity and high bulk modulus\[131] make this metal oxide a suitable material for application in microelectromechanical and nanoelectromechanical systems (MEMS/NEMS) devices. But as shown experimentally\[10], hydrocarbon tribopolymer layers form as benzene is introduced into the atmosphere. This tribopolymer increases the electrical contact resistance, which leads to electrical failure of the switches. This obstacle is yet to be solved, and the mechanism of tribopolymer formation remains unclear. Since aspects such as atmospheric composition and gas pressures have been shown to affect the contamination rate of the switches\[?], studying the adsorption of gases on the contact surfaces will provide crucial understanding of the initial step of tribopolymer formation.

The surface catalytic properties of RuO$_2$(110) have been well studied for small molecules. Molecules including CO \[132, 133, 134\], H$_2$O \[135, 136\], O$_2$ \[137\], N$_2$ \[132\], methanol \[138\], CO$_2$ \[139\], NO \[140\], ethylene \[141\], NH$_3$ \[142\], HCl \[143\] and H$_2$ \[144\] are reported to be adsorbed from the gas phase directly to a single catalytically active atom on the surface. For benzene, there is a similar but slightly different mechanism of adsorption, in which the adsorbed molecule has a collective interaction with multiple surface atoms. This arises partly because the benzene molecule is a comparatively larger molecule than the previously studied ones, covering many surface atoms. This study of benzene chemisorption is motivated by recent breakthroughs in NEMS devices and the importance of discovering tribopolymer-resistant surfaces. This long-term goal requires understanding of the components and their interactions. The complexity of benzene adsorption on RuO$_2$ due to the large molecular size and the rich surface structure mandates in-depth study and extends the recent literature on RuO$_2$ surface structure and small-molecule chemisorption.
In this work, we investigate the adsorption of benzene on the RuO$_2$(110) surface. Our proposed adsorption mechanisms incorporate the effect of varying benzene coverage and O content of the RuO$_2$ reconstruction. The surface terminations and oxygen coverages are determined by previous studies [145], and adsorption Gibbs free energies were calculated by density functional theory (DFT) to study the thermodynamic properties of benzene adsorption under different conditions. In addition, we generate a phase diagram to predict the most favored benzene coverage.

5.2 Computational Methods

5.2.1 DFT calculations

In this investigation, density functional theory (DFT) calculations are performed using the Quantum ESPRESSO package [71] with designed nonlocal pseudopotentials [?, ?] from the OPIUM code [67]. A 50 Ry plane wave cutoff is used, and the electronic exchange correlation energy is calculated with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [31]. Later, the vdW correction methods, such as DFTD3 [44, 45, 46] and TS [48], were applied to all the modeled systems. An $8 \times 8 \times 8$ Monkhorst-Pack [129] k-point mesh is used for variable cell relaxation of bulk RuO$_2$, and an $8 \times 8 \times 1$ k-point mesh is used for all the other calculations such as the slab, adsorption, and molecule relaxation studies.

5.2.2 Surface structure and adsorption energy model systems

The stoichiometric RuO$_2$(110)-$O^{bridge}$ surface was previously considered to be the most stable surface at ambient conditions, but recent works show that the stable surface structure depends on the chemical potential of oxygen [145, 133]. As shown in FIG 5.1, three
types of RuO$_2$(110) surface structures are stable: RuO$_2$(110)-Ru, RuO$_2$(110)-O$^{\text{bridge}}$, and RuO$_2$(110)-O$^{\text{cus}}$. Lower oxygen chemical potential leads to exposed surface metal atoms in the RuO$_2$(110)-Ru surface structure. With increasing oxygen chemical potential, the oxygen atoms will cover surface sites, forming the RuO$_2$(110)-O$^{\text{bridge}}$ and RuO$_2$(110)-O$^{\text{cus}}$ structures.

In the bulk structure of RuO$_2$, O is bonded to three Ru atoms, producing the $sp^2$ hybridization, and Ru is bonded to six O atoms, forming $d^2sp^3$ hybridization. From this information, one can predict the catalytically active sites on each surface, since the reactivity of a metal oxide surface is related to the undercoordinated metal and O atoms [146]. Observing the RuO$_2$(110)-Ru surface, the five-fold, coordinatively unsaturated site Ru$^{\text{cus,5f}}$ and the four-fold bridge Ru$^{\text{bridge,4f}}$ atoms are undercoordinated. This makes the surface Ru atoms catalytically active. Also, even though O$^{3f}$ is fully bonded with three Ru atoms, other works show that it could be a site for weak hydrogen bonding [147]. On the RuO$_2$(110)-O$^{\text{bridge}}$ surface, one can observe that while Ru$^{\text{bridge,6f}}$ is fully coordinated, the other surface atoms are not, keeping them catalytically active. For the RuO$_2$(110)-O$^{\text{cus}}$ surface, all the Ru atoms are fully coordinated, but O$^{\text{bridge}}$ and O$^{\text{cus}}$ atoms are undercoordinated, bonding with only two and one Ru atoms respectively.

Before studying surface adsorption, the bulk RuO$_2$ is relaxed using the variable cell relaxation method and the GGA functional. The cell parameters of bulk RuO$_2$ are calculated to be $a = b = 4.47$ Å, $c = 3.08$ Å which agree well with experimental X-ray diffraction values of $a = b = 4.49$ Å, $c = 3.10$ Å [148]. Using bulk in-plane lattice parameters, a symmetric surface slab structure is constructed using three layers of Ru. For the surface, the relaxed Ru$^{\text{bridge,6f}}$-O$^{\text{bridge}}$ length is 1.88 Å and Ru$^{\text{cus,6f}}$-O$^{\text{cus}}$ is 1.68 Å. The $z$-axis cell parameter for the slab is set to 30 Å which separates the benzene molecules on the top and bottom surfaces by at least 14 Å for all cases. This distance ensures that there is no interaction between benzene molecules above and below the slab.
Figure 5.1: Three possible terminations of the RuO$_2$ rutile (110) plane are studied: RuO$_2$(110)-Ru(left), stoichiometric RuO$_2$(110)-O$^{\text{bridge}}$(middle) and RuO$_2$(110)-O$^{\text{cus}}$(right).
The adsorption energies are calculated for every adsorption relaxation:

\[ E_{\text{ads}} = E_{\text{slab}+\text{molecule}} - E_{\text{slab}} - E_{\text{molecule}}, \]  

(5.1)

where \( E_{\text{ads}} \) is the adsorption energy, \( E_{\text{slab}+\text{molecule}} \) is the total energy of the relaxed structure of the slab with the benzene molecule, \( E_{\text{slab}} \) is the energy of the relaxed slab structure, and \( E_{\text{molecule}} \) is the energy of molecule overlayer with same periodicity as the adsorbed system. The negative value of the adsorption energy indicates that adsorption is energetically favorable.

5.2.3 Surface adsorption sites

Three types of adsorption sites, hollow, bridge and top, are determined based on the benzene position relative to the surface Ru atoms. The hollow site is where the three surface Ru atoms are covered by the benzene C atoms. The bridge site is where the benzene C-C bond is on top of the Ru atom. And the top sites are where the center of the benzene ring is directly above the Ru atom. We label six distinct sites for each surface as hollow1, hollow2, top1, top2, bridge1, bridge2. The benzene molecules are initially placed 3 Å above the Ru atoms of the RuO\(_2\)(110) surface. The lateral starting coordinates (Fig. 5.2) are labelled as follows.

The hollow sites are located with the center of the benzene ring directly on top of a Ru three-fold hollow site. Specifically, the hollow1 site has a O\(^{3f}\) atom inside the carbon ring, whereas hollow2 is without an O\(^{3f}\) atom in the carbon ring. The top sites are placed so that the center of the benzene ring is directly on top of a particular surface atom, depending on the surface structure. For the RuO\(_2\)(110)-Ru and RuO\(_2\)(110)-O\(^{\text{bridge}}\) surfaces, the top1 site has the benzene ring centered over the Ru\(^{\text{cus},5f}\) atom, and for the RuO\(_2\)(110)-O\(^{\text{cus}}\) surface the top1 site has the benzene ring over the O\(^{\text{cus}}\) atom, which is directly above the Ru atom,
(this O\textsuperscript{cus} is marked as blue in Fig. 2c). For the RuO\textsubscript{2}(110)-Ru surface, the top2 site is over the Ru\textsuperscript{bridge,4f} atom, and for the RuO\textsubscript{2}(110)-O\textsuperscript{bridge} and RuO\textsubscript{2}(110)-O\textsuperscript{cus} surfaces, the top2 is over the Ru\textsuperscript{bridge,6f} atom. The bridge sites have the center of the benzene ring directly above the midpoint of two surface Ru atoms. Bridge1 is between adjacent Ru\textsuperscript{cus} atoms, and bridge2 is between Ru\textsuperscript{bridge} atoms. For the RuO\textsubscript{2}(110)-O\textsuperscript{bridge} and RuO\textsubscript{2}(110)-O\textsuperscript{cus} surfaces, the bridge2 site contains O\textsuperscript{bridge} connecting the Ru\textsuperscript{bridge} atoms, marked as blue in Fig. 2b. The schematic of site naming is shown in Fig. 5.2, and benzene molecules are placed so that two of the C-C bonds would be along [\overline{1}10].

To choose the periodic unit cell size for our calculations, we calculate the nearest distance between two hydrogen atoms on nearby benzene molecules in the periodic $1 \times 1$, $1 \times 2$, and $\sqrt{5} \times \sqrt{5}$ cells. For the case of one benzene per $1 \times 1$ cell, the nearest distance is less than 1 Å, which is unreasonable. The $1 \times 2$ and $\sqrt{5} \times \sqrt{5}$ cells give minimum distances of 1.34 Å and 4.11 Å between two hydrogen atoms on adjacent benzenes, respectively. Accordingly, $1 \times 2$ and $\sqrt{5} \times \sqrt{5}$ surface cells are modeled in this study. Additionally, to compare and confirm the results of $\sqrt{5} \times \sqrt{5}$ cells, we also include the $2 \times 3$ surface adsorption calculations to represent low coverage.

5.3 Results

5.3.1 Energy and geometry of benzene adsorption on RuO\textsubscript{2}(110) surface

We start by investigating the adsorption of benzene on the RuO\textsubscript{2}(110) surface using the GGA functional (Tab. 5.1). The relaxation pathways of benzene on the most reduced surface, RuO\textsubscript{2}(110)-Ru, using a $1 \times 2$ periodic cell are quite interesting and highlight important adsorption interactions. The site with the strongest adsorption energy is the hollow2 site,
Figure 5.2: Site naming scheme for all three RuO$_2$(110) surfaces. The figures are all shown in top view. (a) Site naming for RuO$_2$(110)-Ru surface (b) RuO$_2$(110)-O$^{\text{bridge}}$ (c) RuO$_2$(110)-O$^{\text{cus}}$ (d) figure with benzene placed on each site on the surface of RuO$_2$(110)-Ru. Each blue square with arrow indicates a surface oxygen that is added, going from reduced to oxidized forms of the surface.
since in this position the C atoms of benzene and Ru surface atoms can maximize their strong attraction without much interference from surface O atoms. The strong interactions of C atom $p_z$ orbitals and the Ru $d_{yz}$ orbitals are shown in Fig. 5.3.
Table 5.1: Adsorption energies of benzene (bz) on a periodic $1 \times 2$ surface of RuO$_2$(110)-Ru, RuO$_2$(110)-O$^{\text{bridge}}$, and RuO$_2$(110)-O$^{\text{cus}}$ using the GGA functional.

<table>
<thead>
<tr>
<th></th>
<th>RuO$_2$(110)-Ru/bz (eV)</th>
<th>RuO$_2$(110)-O$^{\text{bridge}}$/bz (eV)</th>
<th>RuO$_2$(110)-O$^{\text{cus}}$/bz (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hollow1</td>
<td>-0.20</td>
<td>-0.23</td>
<td>-0.06</td>
</tr>
<tr>
<td>hollow2</td>
<td>-0.39</td>
<td>-0.23</td>
<td>-0.08</td>
</tr>
<tr>
<td>top1</td>
<td>-0.20</td>
<td>-0.24</td>
<td>-0.06</td>
</tr>
<tr>
<td>top2</td>
<td>-0.05</td>
<td>-0.01</td>
<td>-0.08</td>
</tr>
<tr>
<td>bridge1</td>
<td>-0.14</td>
<td>-0.22</td>
<td>-0.05</td>
</tr>
<tr>
<td>bridge2</td>
<td>-0.03</td>
<td>-0.01</td>
<td>-0.09</td>
</tr>
</tbody>
</table>
Figure 5.3: Projected density of states of benzene adsorbed on the $1 \times 2$ supercell of the (a) RuO$_2$(110)-Ru and (b) RuO$_2$(110)-O$^{\text{cus}}$ surfaces. The C atom orbitals on the benzene ring and the closest Ru surface atom orbitals are shown. Note the orbital interaction between the $p_z$ orbitals of C and $d_{zy}$ orbital of Ru near the Fermi energy. The C atom that is closest to the surface and its closest surface O atom orbitals are shown. Note the C atom orbital of benzene is close to an isolated molecule, indicating that no chemical bond forms, and hence presenting physisorptive phenomenon on the oxidized surface.
The adsorption relaxation of benzene on the hollow2 site of RuO$_2$(110)-Ru surface follows three steps. The first step is the attraction of C and Ru. This makes the benzene molecule tilt so that two C atoms get closer to the two Ru$^{\text{bridge,4f}}$ atoms. The benzene H atoms do not show much attraction toward the surface at this point. The second observed behavior is the slight rotation of benzene, by $\approx 11.9^\circ$. The third step strengthens adsorption, as the benzene molecule moves closer to the surface. In this step, in addition to the two C already attracted to the Ru$^{\text{bridge,4f}}$ atoms, the C on the other side of the ring is attracted toward the Ru$^{\text{cus,5f}}$. Also, the H atoms of the benzene ring are slightly attracted towards the O$^{3f}$ atoms. At this step, the benzene molecule deforms significantly.

Other than adsorption on hollow2 of the RuO$_2$(110)-Ru surface in a $1 \times 2$ cell, all the other sites show a similar behavior (Tab. 5.2). For the other sites, the first step is the rotation of benzene by $\approx 12^\circ$. The second step is the benzene tilting by $\approx 20^\circ$. For all cases on the RuO$_2$(110)-Ru surface, the attraction of C and surface Ru atoms (Ru$^{\text{cus,5f}}$ and Ru$^{\text{bridge,4f}}$) is observed, but it is not as strong as hollow2. Also, some H atoms on the benzene are attracted to the O$^{3f}$ atoms on the surface, as was predicted from previous DFT work on O$^{3f}$ as a hydrogen bonding site[147]. On all sites of RuO$_2$(110)-Ru including the hollow2, during and after the adsorption, the molecule does not move from its initial site to find its most favorable site. Instead it generally stays on its initial site, and the largest lateral movement that occurs is the rotation of the molecule.

To study the chemisorption and physisorption mechanisms with less intermolecular interaction, the adsorption is studied in a $\sqrt{5} \times \sqrt{5}$ supercell of the RuO$_2$(110)-Ru slab using the GGA functional. For the hollow2 site, the final structure shows a very similar geometry to the $1 \times 2$, but with significantly enhanced chemisorption energy of -0.63 eV. Also, there is no rotation of benzene during the relaxation. For the top1 site, one of the most strongly physisorbed (-0.20 eV) sites on the $1 \times 2$ cell of RuO$_2$(110)-Ru surface, the calculated adsorption energy on the $\sqrt{5} \times \sqrt{5}$ supercell increases (-0.27 eV). This stronger
Table 5.2: Adsorption energies of benzene with $1 \times 2$, $\sqrt{5} \times \sqrt{5}$, and $2 \times 3$ periodicities on the RuO$_2$(110)-Ru hollow2, RuO$_2$(110)-O$^{\text{bridge}}$ top1, and RuO$_2$(110)-O$^{\text{cub}}$ bridge2 using the GGA functionals and vDW corrected values with TS method. Note that the large difference between GGA and vDW corrected energies demonstrates that the long-range vDW attraction plays a major role in benzene adsorbs on RuO$_2$ surface.

<table>
<thead>
<tr>
<th></th>
<th>RuO$_2$(110)-Ru/</th>
<th>RuO$_2$(110)-O$^{\text{bridge}}$/</th>
<th>RuO$_2$(110)-O$^{\text{cub}}$/</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hollow2 (eV)</td>
<td>top1 (eV)</td>
<td>bridge2 (eV)</td>
</tr>
<tr>
<td>$1 \times 2$-GGA</td>
<td>-0.39</td>
<td>-0.24</td>
<td>-0.09</td>
</tr>
<tr>
<td>$1 \times 2$-TS</td>
<td>-1.40</td>
<td>-0.66</td>
<td>-0.65</td>
</tr>
<tr>
<td>$\sqrt{5} \times \sqrt{5}$-GGA</td>
<td>-0.63</td>
<td>-0.28</td>
<td>-0.13</td>
</tr>
<tr>
<td>$\sqrt{5} \times \sqrt{5}$-TS</td>
<td>-1.68</td>
<td>-1.06</td>
<td>-0.82</td>
</tr>
<tr>
<td>$2 \times 3$-GGA</td>
<td>-0.63</td>
<td>-0.30</td>
<td>-0.15</td>
</tr>
<tr>
<td>$2 \times 3$-TS</td>
<td>-1.61</td>
<td>-1.06</td>
<td>-0.84</td>
</tr>
</tbody>
</table>
adsorption energy with lower coverage indicates a reduction of molecular interaction and increased interaction with the surface. Since the changes of the adsorption energies from a $1 \times 2$ to a $\sqrt{5} \times \sqrt{5}$ cell are significant, the adsorption of benzene in a $2 \times 3$ cell is also calculated. The geometry and the energy in the $2 \times 3$ supercell are very similar to the $\sqrt{5} \times \sqrt{5}$ surface in all cases.

For further investigation of chemisorption on the reduced surface, we account for the van der Waals (vdW) interaction in the calculation by using DFTD2 [45] and TS [48] methods. In the periodic $1 \times 2$ and $\sqrt{5} \times \sqrt{5}$ supercell, the benzene adopts similar geometries regardless of the inclusion of vdw correction, as shown in Fig. 5.4. The hollow2 site proves to be a chemisorption site because of the strong carbon-metal bonds. For confirmation, benzene adsorption is also examined in the $2 \times 3$ supercell using the DFTD2 and TS methods. The geometric and energetic results are very similar to those on the $\sqrt{5} \times \sqrt{5}$ supercell.

On the oxidized surfaces (RuO$_2$(110)-O$^{\text{bridge}}$ and RuO$_2$(110)-O$^{\text{cus}}$), O atoms gain electrons and Ru atoms lose electrons. This makes the O atoms interfere with the Ru-C attraction, weakening it. In addition, the O$^{\text{bridge}}$ and O$^{\text{cus}}$ atoms attract the H atoms of the benzene, forming weak hydrogen bonds, as also shown in other DFT studies[149]. We again start our investigation using the GGA functional on the $1 \times 2$ cell. The relaxation pathways for benzene on the $1 \times 2$ cell of oxidized surfaces are very similar regardless of the site, suggesting physisorption. The first step is the repulsion of benzene from the surface without any changes to its geometry, rotation, or tilt. The extent of the benzene displacement away from the surface varies among sites from 0.5 Å to 2 Å. This repulsion arises from the interaction between the surface O atoms and C atoms on the benzene, also shown by the projected density of states in FIG 5.3. The second step consists of benzene molecule rotation by $\approx 25^\circ$, induced by intermolecular interactions. The last step is the molecular tilting, which maximizes the H bonding between the surface O atoms and H
Figure 5.4: Top and side views of the equilibrium structure of benzene adsorbed on the hollow2 site of the RuO$_2$(110)-Ru surface with different periodic cell sizes using GGA functionals. (a) $1 \times 2$ supercell of the RuO$_2$(110)-Ru surface using the GGA functional. (b) $\sqrt{5} \times \sqrt{5}$ supercell of the RuO$_2$(110)-Ru surface using the GGA functional. vdW calculations using DFTD2 and TS have similar geometries.
atoms of benzene. The tilting is \( \approx 46^{\circ} \), which is greater than on the RuO\(_2\)(110)-Ru surface. Again, the benzene molecules do not move around laterally, but stay on their initial site. Besides the relaxation pathways, a minor difference between the two oxidized surfaces is that the RuO\(_2\)(110)-O\(_{\text{cus}}\) surface has a slightly weaker benzene binding energy than the RuO\(_2\)(110)-O\(_{\text{bridge}}\).

To further study the adsorption on oxidized RuO\(_2\) with reduced intermolecular interaction, the sites with the most stable energies in the \( 1 \times 2 \) cell were chosen for study in \( \sqrt{5} \times \sqrt{5} \) cells (top1 of RuO\(_2\)(110)-O\(_{\text{bridge}}\) and bridge2 of RuO\(_2\)(110)-O\(_{\text{cus}}\)), using the GGA functional. The GGA adsorption energy in the \( \sqrt{5} \times \sqrt{5} \) cell of the RuO\(_2\)(110)-O\(_{\text{bridge}}\) top1 surface is -0.28 eV, and for RuO\(_2\)(110)-O\(_{\text{cus}}\) bridge2 it is -0.13 eV. During the relaxation on this larger cell, intermolecular interaction is weak, so the molecules do not tilt or rotate. In addition, to observe the effects of vdW interactions on oxidized RuO\(_2\), the DFTD2 and TS methods are applied to the \( 1 \times 2, \sqrt{5} \times \sqrt{5}, \) and \( 2 \times 3 \) cells of the top1 site of the RuO\(_2\)(110)-O\(_{\text{bridge}}\) surface and the bridge2 site of the RuO\(_2\)(110)-O\(_{\text{cus}}\) surface. The trends of both the energy and the geometry of the relaxed structure conform to the GGA results for oxidized RuO\(_2\)(110) surfaces, as shown in Fig. 5.5.

### 5.3.2 Adsorption structure stability phase diagram

The preferred coverages that minimize the Gibbs free energy of adsorption for varying oxygen and benzene chemical potentials are given in Fig. 5.6. We express the Gibbs free energy in terms of benzene and oxygen chemical potentials as following [150],

\[
\Delta G^{\text{ads}}(\Delta \mu_\text{O}, \Delta \mu_\text{bz}) = - \frac{1}{A} \Delta E^{\text{ads}}_{\text{O,bz}@\text{slab}} + \frac{N_\text{O}}{A} \Delta \mu_\text{O} + \frac{N_\text{bz}}{A} \Delta \mu_\text{bz},
\]

where \( \Delta G^{\text{ads}}(\Delta \mu_\text{O}, \Delta \mu_\text{bz}) \) is the benzene adsorption Gibbs free energy as a function of chemical potential of oxygen (\( \Delta \mu_\text{O} \)) and benzene (\( \Delta \mu_\text{bz} \)), \( A \) is the surface area of the slab,
Figure 5.5: Top and side views of the final structure of benzene adsorbed on the bridge2 site of the RuO$_2$(110)-O$^{\text{cus}}$ surface of different periodic cell sizes using GGA. (a) $1 \times 2$ supercell (b) $\sqrt{5} \times \sqrt{5}$ supercell. vdW calculations using DFTD2 and TS show the similar geometries.
$\Delta E_{\text{ads}}^{\text{O,bz@slab}}$ is the adsorption energy of O atoms and benzene molecules on the reduced surface, $N_O$ is the number of O atoms, and $N_{bz}$ is the number of benzene molecules. The chemical potential of benzene and oxygen corresponds to pressure which can be expressed as,

$$\Delta \mu_{bz} = \mu_{bz}^0 + k_B T \ln \left( \frac{P_{bz}}{P_0} \right),$$

and

$$\Delta \mu_O = \mu_O^0 + \frac{1}{2} k_B T \ln \left( \frac{P_{O_2}}{P_0} \right),$$

where $\mu_{bz}^0$ and $\mu_{O_2}^0$ are the standard chemical potential of benzene and oxygen gas molecules, and $p_0$ is the pressure of 1 atm. The standard chemical potential for oxygen can be obtained from the experimental thermodynamic table [151]. For the standard chemical potential of benzene, the value is approximated from experimental standard Gibbs free energy [152]. In the surface phase diagram, we plot the stability ranges of benzene overlayers on RuO$_2$(110) with different periodicities and of extents of oxidation. The pressure corresponding to the chemical potential is shown assuming room temperature ($T=300$ K). In Fig. 5.6, we show the surface phase diagram based on DFTD2 calculations. Starting from the lower left, where the chemical potentials of both benzene and oxygen are very low, RuO$_2$(110)-Ru is the most stable surface. As increases to the right, the most stable phase goes from RuO$_2$(110)-Ru, to RuO$_2$(110)-O$_{\text{bridge}}$, and then to RuO$_2$(110)-O$_{\text{cus}}$, which is consistent with previous findings [145]. Along the benzene chemical potential axis at low $\mu_O$, the RuO$_2$(110)-Ru surface with benzene adsorption at different coverages is shown. As $\mu_{\text{benzene}}$ increases, higher coverage is favored. Note that $2\times3$ surface adsorption phase for RuO$_2$-Ru and RuO$_2$-O$_{\text{bridge}}$ does not appear on the graph due to almost equivalent adsorption condition and energetics with $\sqrt{5} \times \sqrt{5}$ periodic cell. Moving diagonally up and to the right, we can observe the change of the surface termination (RuO$_2$(110)-Ru to RuO$_2$(110)-O$_{\text{cus}}$). At high chemical potential of both species, we can observe increase of the benzene
coverage on the RuO$_2$(110)-O$^{\text{cus}}$ surface (RuO$_2$(110)-O$^{\text{cus}}$(2×3) to RuO$_2$(110)-O$^{\text{cus}}$(1×2)). The low coverage 2×3 surface with one benzene per six primitive cells is only favorable on the RuO$_2$(110)-O$^{\text{cus}}$ surface. The top right corner indicates that when both $\mu_{\text{benzene}}$ and $\mu_O$ are high, the most stable surface is RuO$_2$(110)-O$^{\text{cus}}$ with high molecular coverage. The scale for benzene pressure is converted to the experimental values in unit of PPM [10]. The PPM units of pressure of benzene gas is converted based on the ideal gas law as shown in following [153],

$$1 \text{ PPM} = \frac{1}{1} \mu \text{moles gas} \frac{1}{1} \text{mole air} = \frac{V_n}{M} 1 \mu \text{g gas} \frac{1}{1} \text{L air} ,$$ 

(5.5)

where $T$ is temperature, $M$ is the molar mass of the gas, and $V_n$ is the molar volume of the gas taking the form of

$$V_n = \frac{RT}{p} .$$

(5.6)

At the pressure, $p = 1$ atm, and room temperature (300 K), 1 PPM = 3.151 × 10$^{-7}$ atm for benzene gas.

Based on the surface phase diagram, we may conclude that for most of the experimental conditions, the RuO$_2$(110)-O$^{\text{cus}}$ surface is the stable phase. And with such a fully oxidized surface, the density of the adsorbed benzene layer depends on the benzene pressure.

### 5.4 Conclusion

We investigate the surface adsorption of benzene on RuO$_2$(110). The adsorption mechanism of benzene on RuO$_2$(110) depends on the site, O coverage, and the benzene coverage. Clear trends emerge: the C and Ru atoms attract strongly, while benzene H and oxide O atoms have a weaker attraction. Also, increasing the benzene coverage makes the molecules interact with each other, reducing surface bonding. As the surface becomes more oxidized, the O surface atoms make the benzene adsorption weaker. Benzene can strongly chemisorb...
Figure 5.6: The benzene adsorption surface phase diagram of the RuO$_2$(110) surface. Each color indicates a distinct surface adsorption condition. The legend shows both O and benzene coverage. The partial pressure scales for benzene and oxygen are at 300 K.
to the Ru-terminated surface. However, full surface oxidation leads to benzene physisorption. With understanding of benzene adsorption geometries, energies, and their relation to the surface oxidation, we can develop realistic models of the formation of tribopolymer on metal oxide contacts and provide useful information for further dynamical studies.
Chapter 6

Molecule-Adsorbed Topological Insulator and Metal Surfaces: a Comparative First Principles Study
6.1 Introduction

Topological insulators (TIs) are a newly-identified class of solids,[154, 155] in which strong spin-orbit coupling (SOC) leads to a state of matter which is distinct from ordinary ("trivial") insulators. Even though in both trivial and topological insulators electrons cannot conduct in the bulk, TI surfaces support metallic electronic states that are “protected” by constraints of time-reversal symmetry. [156, 157, 158, 159, 160] These metallic surface states are unique in that they exhibit spin-momentum locking and electron back-scattering from them is suppressed, requiring a spinflip. Metallic surface states at TI surfaces also differ from surface states at conventional metal surfaces in that they arise in an otherwise forbidden gap, whereas in a metal the consequences of surface states can be (and close to the surface often are) overwhelmed by the density of evanescent metallic bulk states at the surface. [161]

One way to modify surface electronic properties, which has been studied extensively, is via the adsorption of molecules (see, e.g., Refs. [162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172]). Generally, molecule adsorption allows one to harness the power and flexibility of organic chemistry to tailor desired surface properties. Extensive research has shown that this is indeed possible and, furthermore, often results in novel collective effects emerging from various forms of molecule-surface interaction (see, e.g., Refs. [173, 174, 175, 176, 177, 178, 179]). With this in mind, recent years have seen several important studies of the effect of molecular adsorption on TI surfaces.[180, 181, 182, 183, 184, 185, 186] While some studies [183, 186] emphasized surface protection by an organic overlayer, most of this effort has been focused on the interaction of TI surfaces with magnetic molecules, especially phthalocyanines. This is important because the interaction of magnetic molecules with ordinary metallic surfaces has already been shown to result in unusual magnetic effects [187, 188, 179, 189, 190] and because magnetic impurities break the time-reversal...
symmetry protecting TI surfaces.

The topologically-protected nature of states at the TI surface has also triggered suggestions for a broad range of applications,[191] including heterogeneous catalysis.[192, 193, 194] It is therefore of particular interest to study how the surface states of a TI interact with the energy levels of an adsorbed molecule and how this may affect the electronic structure at the interface. To the best of our knowledge, so far only little work,[180, 185] has been devoted to understanding the consequences of the unique TI surface states for the molecule-surface state interaction. Here, we wish to compare and contrast molecule-TI and molecule-metal interactions from first principles, using density functional theory (DFT). We consider modifications in the electronic structure brought about by the adsorption of benzene, a simple closed-shell prototypical organic molecule, on Bi$_2$Te$_3$ (a prototypical TI), Au (a prototypical inert metal), and Pt (a prototypical catalytic metal). We find that benzene adsorption on Bi$_2$Te$_3$ is significantly weaker than on the metallic surfaces, consistent with a minimal perturbation of the electronic structure at the surface of the topological insulator, revealed by a detailed analysis of the interaction of the molecular orbitals with the topological surface states.

6.2 Computational Details

All DFT calculations were performed within the generalized-gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.[195] In order to account for the benzene-substrate dispersive interaction, we have augmented the PBE functional with the surfac-screened version [196] of the Tkatchenko-Scheffler [197] pair-wise dispersive correction, which we denote as PBE+TS$_{surf}$. All calculations were performed using the VASP code,[198] a plane-wave code, in which ion-electron interactions are treated with the projector augmented wave (PAW) approach.[199, 200] A kinetic energy cutoff of 550 eV was used for
plane-wave basis set expansion. Spin-orbit coupling was explicitly included in all calculations, as implemented within the PAW method in the VASP code.[201]

The Bi$_2$Te$_3$(111) surface was represented using a $4\times4$ super-cell containing a slab that comprises four quintuple layer (QL) units, each of which consists of alternating Bi and Te layers, as shown in Fig. 6.1. In each atomic layer, the atoms form a triangular lattice such that their in-plane positions are commensurate with the (111) surface of a face-centered-cubic lattice. Together with the adsorbed benzene molecule, the supercell contains 332 atoms. Atoms of the benzene molecule and the two top-most QLs were allowed to relax until forces smaller than 5 meV/Å were obtained, with all other atoms fixed at their bulk positions. Au and Pt (111) surfaces were represented using a $6\times6$ super-cell containing a slab comprising four layers. Atoms of the benzene molecule and all metal atoms except those of the bottom-most layer were allowed to relax until forces smaller than 5 meV/Å were obtained, with all other atoms fixed at their bulk position. A $4\times4\times1$ Monkhorst-Pack[202] k-point mesh was used for Brillouin zone integration.

In order to identify the TI surface bands, each wave function at a given energy band and $\vec{k}_\parallel$ (momentum parallel to the surface) was projected onto spherical harmonics around each ion.[203] TI surface bands were identified based on a 60% critical percentage of the projections onto the 3 top (or bottom) layers of the surface. The threshold value was chosen such that the surface states identified within the energy window do not change significantly with the variation of the given threshold.[204]

---

[1] The surface is grown along the (111) direction of the rhombohedral unit cell of Bi$_2$Te$_3$. However, once the $4 \times 4$ supercell is formed along xy plane, normal to the surface is defined as (001) which is same as (111) of the unit cell.
Figure 6.1: Unit cell of four quintuple layers of $\text{Bi}_2\text{Te}_3$ with a single adsorbed benzene molecule. $\text{Bi}$, $\text{Te}$, $\text{C}$, and $\text{H}$ atom are represented by magenta, green, brown, and pink balls, respectively. Inset: top view of the position and orientation of the benzene molecule on the top surface.
6.3 Results and Discussion

We find the optimized faced-centered-cubic (FCC) lattice parameters of Au and Pt to be 4.15 and 3.94 Å respectively. These values are in good agreement with past theory and experiment.[205] Using these lattice parameters, we constructed a supercell containing 4 layers along the (111) direction and 20 Å of vacuum normal to surface, for each system. For these metallic slabs a $6 \times 6$ supercell in the $xy$ plane was used so as to approach the low-coverage limit of a single benzene molecule adsorbed on each surface. For Bi$_2$Te$_3$, the optimal lattice constants were found to be $a=b=c=10.46$ Å and $\alpha=\beta=\gamma=20.05^\circ$, consistent with past theoretical and experimental reports.[204, 206]

We first consider the molecule-adsorbed transition metal surfaces, Bz/Pt(111) and Bz/Au(111), known as a more strongly bound and a more weakly bound system, respectively.[207] It is well-known that both the Au(111) and Pt(111) surfaces are thermodynamically stable under ambient conditions. The most stable chemisorption site for benzene on Pt(111) is the hollow site, consistent with the results of prior calculations.[205, 208] On the Au(111) surface, benzene is mostly physisorbed on the surface.[205] The total energy of the Bz/Au(111) surface for different adsorption sites, on top, bridge, and hcp-hollow, differ by less than 10 meV, which is also consistent with previous work.[205] For an even comparison with Pt, we place benzene on the hollow site. The average distances between carbon (hydrogen) atoms and Pt atoms on top layer is 2.19 Å (2.61 Å), which is also consistent with previously reported values.[205, 208] For the Au(111) surface, the average distance of carbon and hydrogen atoms from the top-most layer differs by less than 0.01 Å, i.e. the benzene molecule remains flat, with adsorption height of 3.15 Å. For the chosen adsorption site, the calculated adsorption energy and structural details of the adsorption geometry are given in Table 6.1.

We now turn our attention to the benzene-adsorbed Bi$_2$Te$_3$(111) surface. First, in order
Table 6.1: Comparison of the adsorption energy \((E_{ad})\) and average normal distance of carbon \((d_{CM})\) and hydrogen \((d_{HM})\) atoms from the topmost atomic layer of Bz/Pt(111), Bz/Au(111), and Bz/Bi\(_2\)Te\(_3\)(111) systems. The adsorption energy \(E_{ad}\) is defined as \(E_{ad} = E_{Sys} - E_{Surf} - E_{Mol}\), where Sys, Surf, and Mol refer to the molecule-adsorbed surface, pristine surface, and gas-phase benzene molecule, respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>(E_{ad}) (eV)</th>
<th>(d_{CM}) (Å)</th>
<th>(d_{HM}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bz/Pt(111)</td>
<td>-2.25</td>
<td>2.19</td>
<td>2.61</td>
</tr>
<tr>
<td>Bz/Au(111)</td>
<td>-0.52</td>
<td>3.14</td>
<td>3.15</td>
</tr>
<tr>
<td>Bz/Bi(_2)Te(_3)(111)</td>
<td>-0.28</td>
<td>2.96</td>
<td>2.97</td>
</tr>
</tbody>
</table>
to identify the surface states of Bi$_2$Te$_3$, we consider the pristine surface consisting of 4 QLs along the (111) direction, with a $1\times1$ unit cell along the $xy$ plane. The calculated band structure, including SOC effects, is in good agreement with Fig. 2 of Ref. [204]. Generally, the wave function of a surface state decays rapidly inside the bulk. But in case of a thin TI surface, states emanating from the top and bottom surfaces may couple, leading to an energy gap at the Dirac point. Calculations we performed for Bi$_2$Te$_3$(111) surfaces with increasing thickness confirmed that at 4 QLs the magnitude of this energy gap diminishes practically to zero and the dispersion of the surface bands is essentially saturated (see details given in the Supplementary Material), which is in agreement with previously reported first-principles results.[204, 209, 210, 211] Next, we introduce the benzene molecule to the Bi$_2$Te$_3$ surface. The equilibrium distance between benzene and the Bi$_2$Te$_3$(111) surface is found to be 2.9 Å. Similar to Bz/Au(111), the distances of different C or H atoms of the benzene molecule and Te atoms at the top layer of the Bi$_2$Te$_3$ surface do not differ by more than 0.02 Å from each other. Table 6.1 lists corresponding values for the Bz/Bi$_2$Te$_3$(111) system. Our calculation finds different adsorption sites for the benzene molecule on the Bi$_2$Te$_3$ surface to be energetically close (total energy difference between any two adsorption sites of less than 7 meV). In the following, we choose the adsorption site to be on top. The adsorbed molecule is placed such that one Te atom is exactly below the center of the six C atoms of benzene. The adsorption height of the TI is between those on Pt and Au, but the adsorption energy on Bi$_2$Te$_3$ is only 0.28 eV, significantly lower than for the metals.

In order to understand these adsorption trends in terms of surface electronic structure, Fig. 6.2 shows the density of states projected onto the slab and onto the $\pi$ states of the benzene molecule for all three systems studied here. The computed discrete $\pi$-system energy states of the gas-phase benzene molecule, shifted to align with the states of the adsorbed molecule, are also shown for comparison. Note that it is well-known that the
PBE functional fails to predict the metal-induced renormalization of the molecular gap, which facilitates the comparison but precludes quantitative determination of level alignment with respect to the Fermi level.[212, 213, 214, 215, 216] For Pt, the $\pi$-state-projected DOS spreads over a broad range of energy (more than 8 eV) both below and above the Fermi energy, indicating significant hybridization,[217] primarily between Pt $d$-states and benzene $\pi$-states. It is well-established that in case of a transition metal surface having partially filled $d$-states, the average energy of the $d$-states relative to the Fermi level is a good measure for the strength of chemisorption.[218] This is reflected in the Bz/Pt111 system, in which the $d$-bands lying close to the Fermi energy significantly hybridize with the $\pi$ states of the adsorbed benzene molecule. For Au, however, the molecular resonances broaden with respect to the gas-phase but remain relatively narrow in energy. For Bi$_2$Te$_3$, the molecular resonances are even narrower, indicating an even smaller perturbation of the molecular electronic structure. This provides clear evidence for chemisorption on the Pt surface, physisorption on the Au surface, and weak physisorption on the Bi$_2$Te$_3$ surface. This picture is fully consistent with the above-discussed ordering of the adsorption energies. Furthermore, near the Fermi level, the DOS projected on the $d$ orbitals of the Pt atoms at the top surface that are closest to the benzene molecule is lower than the DOS projected on other surface Pt atoms that are farther away from the molecule, indicating hybridization of the former with benzene molecular orbitals. This difference is smaller for Au and virtually zero for the Te atoms at the top of the Bi$_2$Te$_3$ surface, again confirming the relative ordering of the adsorption strengths.

To gain further insight into the benzene-TI interaction, we have compared the electronic structure of the molecule-adsorbed surface with that of a structure where the benzene molecule is kept at a large distance ($\approx 10$ Å) from the surface, such that the molecule-surface interaction is surely negligible. Fig. 6.3 shows the band structure calculated for the two cases (for completeness, a similar comparison for the two metals is given in the
Figure 6.2: (a) Density of states (DOS) curves projected onto the slab (black solid line) and the carbon $\pi$ states of the benzene molecule (blue dashed line) adsorbed on the (111) surface of (a) Pt, (b) Au, (c) Bi$_2$Te$_3$. Vertical lines (red) represent the computed $\pi$ state energy levels of the free benzene molecule. Energies are reported with respect to the Fermi level, $E_F$. 
Supplementary Material). The degeneracy of the top-surface and bottom-surface states crossing the Fermi level around the $\Gamma$ point is lifted upon benzene adsorption, due to the interaction between the molecule and one of the states of the top surface. Nevertheless, the general nature of the band dispersion around the Fermi energy does not differ substantially, consistent with the topological protection of the surface and the closed-shell molecular electronic structure. We note that for a nearly full-monolayer coverage of the H$_2$Pc (free-base phthalocyanine) on the Bi$_2$Se$_3$ surface, a molecular adsorption height of 2.5 Å and negligible overlap between the frontier orbitals of the molecule and the TI surface have been reported,[185] in agreement with the nature of the results reported here.

A different perspective on the extent of molecule-substrate interaction is given by the spatial distribution of the charge density. This electronic charge distribution around the benzene molecule, projected on the carbon-atom-containing plane of the benzene molecule, for the gas-phase and the three surface-adsorbed molecules, is given in Fig. 6.4. In the figure, isovalue surfaces of the charge density, for the four cases depicted, are plotted. Clearly, the charge distribution for the Bz/Bi$_2$Te$_3$(111) system is very close to that of the gas-phase molecule, indicating weak physisorption. That of Bz/Au(111) exhibits some charge loss to the substrate, in line with stronger physisorption, and that of Bz/Pt(111) exhibits significantly larger charge loss, in line with chemisorption. This trend of relative strength of molecule-substrate interaction is fully consistent with that inferred in Fig. 6.2 from DOS considerations.
Figure 6.3: Band structure of a benzene-adsorbed Bi$_2$Te$_3$(111) surface for two different adsorbate heights, (a) 10 Å and (b) 2.9 Å. The interaction between the TI surface and the benzene molecule splits the degenerate topological surface states band near the Γ point at the Fermi level. Red circles in panel (a) represent the surface state character of the bands, with radius proportional to the relative surface contribution.
Additional insights into the strength and nature of the molecule-substrate interaction can be obtained using a perturbation model, as suggested in Ref. [219]. This model is based on expressing the Hamiltonian of the molecule-adsorbed substrate, \( H_{ads} \), as

\[
H_{ads} = H_{iso} + V, \tag{6.1}
\]

where \( H_{iso} \) is the Hamiltonian of the non-interacting substrate and single molecule (in the same geometry as that of the real system), such that \( V \) represents the coupling between the molecule and substrate. Treating \( V \) as a perturbation, and assuming that substrate-molecule interaction proceeds mostly via the frontier orbitals of the benzene molecule, second-order perturbation theory yields an approximate expression for the adsorption energy:

\[
E_{chem} = \sum_{i=HOMO-n}^{HOMO} \int_{\epsilon_F}^{+\infty} \frac{n_{slab}(\epsilon)|V_{CB}|^2}{\epsilon - \epsilon^{(i)}_{benzene}} d\epsilon + \sum_{i=LUMO}^{LUMO+m} \int_{-\infty}^{\epsilon_F} \frac{n_{slab}(\epsilon)|V_{VB}|^2}{\epsilon^{(i)}_{benzene} - \epsilon} d\epsilon \tag{6.2}
\]

where \( n_{slab}(\epsilon) \) is the density of states of the slab model, \( V_{VB} \) represents matrix elements of the coupling between valence band states and molecular states that are from lowest unoccupied molecular orbital (LUMO) to \( m \)-th states higher, \( V_{CB} \) represents matrix elements of the coupling between conduction band states and molecular states that are from \( n \)-th lower states up to highest occupied molecular state (HOMO), and \( \epsilon^{(i)}_{benzene} \) is the corresponding energy of various molecular states. The first term in Eq. (6.2) corresponds to electron donation from the benzene occupied states to the substrate and the second term corresponds to back-donation of electrons from the substrate to the benzene unoccupied states. Note that \( m \) and \( n \) values are the number of states considered to be interacting with substrate strongly near HOMO and LUMO of the molecule. They vary with molecular species and substrates. In our case, the choice of the those numbers can be viewed directly from Fig. 6.5. In particular, \( n = 2 \) for all the supercell systems we discussed, whereas \( m = 3 \) for Bz/Pt(111)
Figure 6.4: Electronic charge density projected on the carbon-atom-containing plane of the benzene molecule. From left to right, the panels correspond to Bz/Pt(111), Bz/Au(111), Bz/Bi$_2$Te$_3$(111), and the gas-phase benzene molecule. The color-bar represents iso-surface values ($e/\text{Bohr}^3$) of the charge density.
and Bz/Bi$_2$Te$_3$(111) system and $m = 4$ for Bz/Au(111).

Adsorption energies of the three substrate-molecule systems, obtained from the perturbation model, are summarized in Table 6.2. Clearly, the energies predicted from the model are reasonably close to those obtained from the treatment of the full system. Interestingly, the adsorption energy contributions of the Bz/Bi$_2$Te$_3$(111) system are qualitatively similar to the Bz/Pt(111) one, with non-negligible donation (larger) and back-donation (smaller) contributions to the adsorption energy, whereas for Bz/Au(111) mainly weak back-donation is observed.

Further insight into this behavior is afforded by considering the coupling matrix elements evaluated using the molecular states and substrate states for benzene interacting with the Pt, Au and Bi$_2$Te$_3$ surfaces, as shown in Fig. 6.5. For the Bz/Pt(111) system, strong coupling terms corresponding to both donation and back donation are found, consistent with the stronger nature of the Pt-benzene interaction. For the Bz/Au(111), however, most of the strong coupling elements are at the lower right corner of Fig. 6.5(b), corresponding to weaker back donation. Most interestingly in our context, for the TI-benzene system the behavior of the coupling matrix elements is qualitatively very similar to that of Bz/Pt(111), but with much smaller magnitude in terms of energy gain owing to electron transfer, i.e., with much lower chemical interaction (note that the color bar for panel (c) in Fig. 6.5 represents a smaller range of matrix element magnitudes). The latter is fundamental for understanding surface chemical activity and catalysis [220]. This provides an additional perspective for how the TI metallic states promote the same kind of interaction as that of more reactive metals, but will not necessarily be useful toward surface reactivity enhancement as the interaction is very weak indeed.

Finally, we note that in light of the importance of $d$-states in the interaction between benzene and Pt, a topic of interest for further research would be the strength of adsorption of benzene on a TI surface in which the topological band inversion involves $d$ states. We
Table 6.2: Energy contributions, in eV, to the adsorption energy from a perturbation model. “OCC” and “UCC” represent occupied molecular states (OCC) and unoccupied molecular states (UCC) and correspond to the energy gained from benzene electron donation and substrate back-donation, respectively. “Total” is their sum and “DFT” is the non-perturbative adsorption energy calculated using DFT.

<table>
<thead>
<tr>
<th></th>
<th>OCC</th>
<th>UCC</th>
<th>Total</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bz/Pt(111)</td>
<td>2.417</td>
<td>0.773</td>
<td>3.190</td>
<td>2.25</td>
</tr>
<tr>
<td>Bz/Au(111)</td>
<td>0.009</td>
<td>0.469</td>
<td>0.478</td>
<td>0.52</td>
</tr>
<tr>
<td>Bz/Bi$_2$Te$_3$(111)</td>
<td>0.197</td>
<td>0.057</td>
<td>0.254</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Figure 6.5: Coupling matrix element magnitudes describing the interaction between a benzene molecule and an (a) Pt(111), (b) Au(111), (c) Bi₂Te₃(111) substrate. x-axis: energy of molecular state. y-axis: energy of substrate state. color-scale: magnitude of the coupling matrix element. Eigenenergies for each substrate and benzene state have been shifted so as to obtained an aligned vacuum level. Zero denotes the position of the Fermi level. The blue and magenta dashed line frames denote molecule donation terms and substrate back-donation terms, respectively.
are aware of two recent reports of such TI materials, NaBaBi\cite{221} and IrBi$_3$\cite{222} showing topological band inversion involving $d$-state at high pressure. At ambient pressure, however, these compounds either remain in the normal metallic state (IrBi$_3$) or undergo topological band inversion involving $p$ states (NaBaBi).

### 6.4 Conclusions

In conclusion, we considered benzene adsorbed on three different types of (111) surfaces: Bi$_2$Te$_3$ a prototypical example of a three-dimensional TI, and two conventional metals, Pt and Au. We identified clear adsorption trends: chemisorption for Pt, physisorption for Au, and weak physisorption for Bi$_2$Te$_3$. This was inferred by combining insights from DFT based calculations of the adsorption energy, analysis of the density of states, analysis of the charge density corresponding to the molecular $\pi$-system, and a model calculation based on perturbation theory. Specifically for the TI surface, the result shows that the presence of metallic surface states is not a sufficient condition for surface reactivity. The same methodology can be used to study more complex molecule-adsorbed TI surfaces.
Chapter 7

The mechanism of benzene tribopolymerization on the RuO$_2$ (110) surface
7.1 Introduction

Nano– and microelectromechanical system (NEMS and MEMS) switches are potential next–generation electronic computing devices that could offer improved computational efficiency, due to their small scale, low power consumption, and high speed [4, 5, 6, 7, 223, 224, 225]. Different from complementary metal–oxide semiconductor (CMOS) transistors, the on and off states of NEMS and MEMS are modulated by the closing and opening of the contacts, which could bridge the source and drain terminals into a closed circuit. In such an operation, there is essentially no open–circuit leakage or energy dissipation. However, after some switching cycles, tribopolymer (a kind of polymer caused by pressing and rubbing contacts together mechanically) forms on the surfaces of the contacts and severely reduces their conductivity [3]. This effect hampers the practical application of NEMS and MEMS, and therefore understanding the underlying mechanism of tribopolymer formation is an on–going research challenge.

Tribopolymerization has been primarily studied in the context of lubricant additives; theoretical models have been developed by using both classical and quantum molecular dynamics [226, 227, 228, 229]. Some of the essential steps in tribopolymerization involve chemical bond breaking and formation. Therefore, first–principles based methods are a powerful tool with distinct advantages for understanding the tribopolymer formation mechanism. Our previous study based on density functional theory calculations [17] demonstrated that reactive metals (Pt) can adsorb contamination gas molecules onto its surface and anchor them tightly. Mechanical load during contact closure along with the effect of the metal as a catalyst together trigger the polymerization reaction [17]. Generally, conductive metal oxides, especially those with oxygen terminations, have less reactive and catalytic surfaces. Contamination gas molecules are less likely to be adsorbed, let alone undergo reaction. However, recent experimental study observed a trace amount of polymer...
formed on RuO$_2$ contacts, especially when the benzene concentration is high [10]. This indicates that tribopolymer formation on conductive oxide surfaces has a different and not well understood mechanism. In this study, we perform DFT calculations modeling a mechanical switching cycle, which involves a closure and detachment of the contacts, and propose reaction pathways for tribopolymer formation on RuO$_2$(110). Moreover, based on our proposed reaction path and calculated activation energies, we provide an estimate of tribopolymer formation rates at different contaminant gas concentrations and stresses.

### 7.2 Computational Methods

Density functional theory (DFT) calculations are performed with the QUANTUM-ESPRESSO code [71]. Norm-conserving, optimized [38], designed nonlocal [40] pseudopotentials are constructed with the OPIUM code [67] for all the elements in the system. The exchange-correlation energy of electrons is included via the generalized gradient approximation (GGA) density functional of Perdew, Burke, and Ernzerhof [31]. The van der Waals interaction correction is included by applying DFT-D2 method [45, 230]. The kinetic energy cutoff is 680 eV. The self-consistent relaxation calculations are converged to a total force threshold of 5 meV/Å. For the bulk structure, an $8 \times 8 \times 8$ Monkhorst-Pack mesh of $k$–points is used. The optimized lattice parameters of RuO$_2$ ($P42/mnm$) are $a=b=4.4681$ Å, $c=3.0832$ Å and $\alpha=90.0^\circ$; the lattice parameters agree with the experimental values $a=b=4.4919$ Å, $c=3.1066$ Å and $\alpha=90.0^\circ$ [231] with an error of 0.53% in the $a$, $b$–directions and 0.75% in the $c$–direction.

For the surface model of the metal oxides, we use symmetric slabs for the RuO$_2$(110)-O$_{cvd}$ surface, as shown in Fig. 7.2 (a), since such a surface is the most stable case under experimental conditions [145, 232]. The ‘cvd’ in RuO$_2$(110)-O$_{cvd}$ refers to fully oxygen-“covered” the surface. The surface structure contains three rutile (RuO)-O bilayers capped
with O. Benzene is chosen as the background contamination gas, since it comes from NEMS packaging and causes the most severe contamination [233]. The surface is fully relaxed with a 20 Å vacuum space between slabs, and a $8 \times 8 \times 1$ $k$-point grid is used to integrate the Brillouin zone.

In order to apply normal stress in simulations, we performed multiple steps of structural relaxation on the supercell successively reducing the z-direction cell length. For each step of relaxation, we reduce the supercell height and the inter?layer distances of the metal oxide slab. As shown in Fig.7.2 (b), we keep the vacuum space fixed at the beginning and reduce each atomic interlayer spacing in the RuO$_2$ slab by $\Delta a = 0.02$ Å. Here, we constructed the slab with 11 layers of atoms, so that the unit cell is reduced by 0.2 Å from the previous supercell. After relaxation, the strong Ru–O bonds tend to recover to their original inter–layer distances, and the vacuum space decreases due to pressure from this interlayer expansion. As a result, the contamination gas molecules in the vacuum space sense the mechanical load along the same direction. Note that each relaxation step takes the end structure of previous step as the starting point and utilizes atomic wavefunctions as the starting wavefunctions.

After acquiring the reaction path from the compression computational experiments, the activation energy is computed with the nudged elastic band (NEB) method, to estimate the polymerization rates [234, 235].

### 7.3 Results and discussions

#### 7.3.1 Computational Mechanical Cycle

To search all the possible reaction paths, we started with two different initial benzene registries, which are referred to as full–overlap and non–overlap respectively, as shown in
Figure 7.1: Supercells for model surface and compression analysis. (a) Ball–and–stick model of the RuO$_2$(110)–O$_{cvd}$ surface with a full oxygen coverage. The superscripts ‘ot’, ‘3f’ and ‘brg’ refer to on–the–top, three–fold coordinated, and bridging oxygens respectively. (b) Schematic representation of our computational compression model. The initial supercell is 30 Å long with a 20 Å vacuum space. The three O–Ru bilayers slab contains 11 atomic layers, judging by the location of atoms along the z–direction. To simulate compression, the length of the supercell is reduced by $\Delta a$, with each inter–layer distance reduced by $\frac{\Delta a}{n-1}$, where $n$ is the number of atomic layers. The length of the centre vacuum region does not change before relaxation. Oxygen atoms are in red and Ru atoms are in light grey, whereas C atoms are in brown and H atoms are in pink.
Figure 7.2: Schematic picture demonstrating a mechanical cycling, which involves a compression and an expansion process. The upper panel shows the full–overlap case, in which the upper and lower benzene molecules are mirror images of each other. The lower panel shows the non–overlap case, in which there is no overlap between the two benzene molecules. On the left of both upper and lower panels, $2 \times 2 \times 1$ supercell is shown for describing two initial benzene adsorption registries on the RuO$_2$–O$^{\text{cvd}}$ surface. Only the nearest layers to the molecules are shown. The supercell length is changed between 30.0 Å and 14.0 Å. Compression and expansion have the same step size change. In each step, the change of the supercell length is 2 Å between $c = 30.0$ Å and $c = 18.0$ Å. This change is reduced to 0.2 Å for $15.0 < c < 16.0$ Å, and further reduced to 0.1 Å when $c < 15.0$ Å, in order to have a more detailed observation of the reaction. Note that the RuO$_2$ surface slab is shown in stick style, with red representing O atoms and grey for Ru atoms.
Computational mechanical switching cycles for both registries is also shown in Fig. 7.2. The supercell height is compressed down to 14 Å, which is 53% of the original cell height, and this height range (30 Å → 14 Å) is considered to be large enough to demonstrate crucial steps of tribopolymerization. During the compression from \( c = 30 \) Å to \( c = 14 \) Å, benzene molecules in the two registries behave approximately the same. Upon compression from \( c = 30 \) Å to \( c = 14.6 \) Å, the molecules rotate and slide due to the inter–molecular repulsion, and finally become approximately parallel to the surface. Upon further compression (\( c = 14.6 \) Å to \( c = 14.0 \) Å), the originally physisorbed benzene molecules begin to chemically bond with surface oxygen atoms.

As the cell length is further compressed below 14.6 Å, the two benzene molecules dimerize by forming a C–C bond. The structure of this intermediate state formed by the linkage of two benzene molecules varies with the initial registry. For a compression cycle starting with a full–overlap registry, there are hydrogen atom migrations between the bottom and the top benzene molecules, as shown in Fig. 7.3 (a). For the non–overlap initial registry compression, no such H atom migrations are observed during the intermediate state formation, as shown in Fig. 7.3 (b).

Furthermore, the decompression process (\( c = 14 \) Å to \( c = 30 \) Å) demonstrates two different phenomena after the formation of the intermediate structure. We found that, during the expansion, the intermediate biphenyl–like structure will either split into two adsorbed benzene molecules or become a biphenyl–like structure with an oxanorbornadiene segment, depending on its structure. For the intermediate state with H migrations (whose structural evolution and the denomination of atoms are shown in detail in Fig. 7.3 (c)), the two O atoms which bond with the ortho–C and meta–C are extracted from the substrate. The \( \text{O}^{\text{breg}} \) atom attached to the ortho–C originally also bonds to the meta–C atom, transforming the lower benzene ring into an oxanorbornadiene segment. This oxidized biphenyl–like molecule demonstrates that benzene molecules react under stress to form a complex poly-
Figure 7.3: Ball–and–stick model showing different intermediate–state structures. For clarity, we use thin lines to represent the RuO$_2$ substrate. (a) Intermediate state with H migrations. The green arrows show the hydrogen atom migrations between bottom and upper benzenes. (b) Intermediate state without H migrations. Only C–C bond forms between the upper and lower benzenes, as shown in the blue circle. (c) the intermediate state molecule (left) and its structural change (right) during a mechanical cycling. The carbon atom connecting the upper and lower benzene is labeled as $\alpha$-C. The ortho-C attaches to O$^{bg}$, and the meta-C attaches to O$^{nt}$.
meric precursor, which is the rudiment of tribopolymer. Tribopolymer formation, therefore, involves a chain reaction of this molecule linkage process. H migration, during the formation of the intermediate state, plays an important role in inducing O extraction reaction. After H atoms migrate away from the ortho–C and meta–C, these two carbon atoms share more electrons and form stronger chemical bonds with the surface O atoms, thereby weakening the chemical bonds between O atoms and the RuO$_2$ substrate. As a result, during expansion, two O atoms will be extracted from the surface and an oxanorbornadiene segment forms. For an intermediate state without H migrations, the biphenyl–like structure splits into two strongly chemisorbed benzene molecules, which could also lead to further polymerization as more cycles are applied. Since the polymerization process for strongly chemisorbed molecules is well studied in our previous work [17], we will not discuss it further.

7.3.2 Chemical Kinetics

We will now focus on the case in which an oxidized biphenyl–like molecule is produced, and estimate the time–scale of tribopolymerization. This reaction involves two steps. First, the benzene molecules change from weakly physisorbed gas molecules, which interact with the contacts by weak Van der Waals interaction, to strongly–chemisorbed adsorbates,

$$C_6H_6(g) \rightarrow C_6H_6(ads), \quad (7.1)$$

and then two chemically adsorbed benzene molecules follow a second–order reaction as,

$$2C_6H_6(ads) \rightarrow C_{12}H_{12}(ads), \quad (7.2)$$
Gas chemisorption depends on the partial pressure and the chemisorption energy. We consider the simplest relationship, the Langmuir isotherm, between benzene molecule surface coverage, \( \theta \), and to benzene pressure, \( p_{C_6H_6} \), as follows:

\[
\theta_0 = \frac{p_{C_6H_6}}{p_{C_6H_6} + p_0},
\]

(7.3)

where \( \theta_0 \) represents the initial equilibrium coverage, \( p_{C_6H_6} \) is the initial partial pressure of benzene in the gas phase and \( p_0 \) takes the form as,

\[
p_0 = \left( \frac{2\pi m k_B T}{h^2} \right)^\frac{1}{2} k_B T \exp \left( -\frac{E_{ads}}{k_B T} \right). \]

(7.4)

Here, \( m \) is the molecular weight of benzene, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( h \) is Planck’s constant, and \( E_{ads} \) is the adsorption energy of benzene on the surface. The rate constant, \( k \), for the intermediate state formation (Eq. 7.2), treated by transition state theory, can be written as,

\[
k = \frac{k_B T}{h} \exp \left( -\frac{\Delta E(\sigma)}{k_B T} \right),
\]

(7.5)

where \( \Delta E \) is the activation energy under applied normal stress, \( \sigma \). Since Eq. 7.2 is a second-order reaction, the rate law can be written as

\[
\text{rate} = -\frac{d\theta(t)}{dt} = 2k\theta(t)^2,
\]

(7.6)

where \( \theta \) is the surface coverage of adsorbed benzene and \( k \) is the rate constant.

Here, we introduce the reaction half–life time (\( t_{1/2} \)), which is defined as the time that
half of the surface adsorbates are consumed for tribopolymerization. $t_{1/2}$ is expressed as

$$t_{1/2} = \frac{1}{2k\theta_0}. \quad (7.7)$$

To acquire $k$, we calculate $\Delta E(\sigma)$ at different supercell lengths with the NEB method, as shown in Fig. 7.4 (a). We observe that the activation energy is lower for a smaller supercell. Normal stress vs. supercell length is also plotted. During the compression, the normal stress increases linearly and plateaus around 15.0 GPa. Further compression causes the normal stress drop to 11.66 GPa, indicating that the molecule–linkage reaction occurs. This stress, 15.0 GPa, is the threshold for a zero–barrier reaction, above which polymerization reaction will occur spontaneously. This value (15.0 GPa) is also consistent with the estimated stress in experiments [236, 9].

By using Eq. 7.5 and Eq. 7.7, we calculated reaction rate constant $k$ and corresponding reaction half–life at different benzene partial pressures and applied normal stresses, as shown in Fig. 7.4 (b) and Fig. 7.4 (c). Smaller applied stresses and contamination gas molecule partial pressures lead to slower tribopolymer formation. The half–life decreases exponentially with benzene partial pressure, and plateaus at and above $1 \times 10^{-4}$ atm, indicating the saturation of surface adsorption sites. Normal stress, which could affect the half–life by several orders of magnitude, is more influential than partial pressure. Therefore, techniques for reducing normal mechanical load, such as controlling the momentum of NEMS contacts and fabricating flatter contact surfaces (high spots on the surfaces may cause the stress to peak there) will be of great significance.
Figure 7.4: (a) The activation energy (red dots) and normal stress (blue squares) vs. supercell length. The purple dashed line is the linear fit of the activation energy. (b) Calculated normal-stress-dependent reaction rates. The threshold stress for a zero-barrier reaction change is 15 GPa. The blue dashed lines are the linear fits. (c) Reaction half-life under different benzene partial pressures and normal stresses.
7.4 Conclusion

We carry out DFT calculations to reveal the tribopolymer formation mechanism on the RuO$_2$(110)-O$_{cvd}$ surface. We find that normal stress changes molecular adsorption from weak physisorption to strong chemisorption, and sufficient stress (15 GPa) will cause benzene molecules link to form an intermediate biphenyl–like state, which can adopt two different structures. One, with H migration, will change to a biphenyl–like molecule with an oxabicyclic segment, which is the rudiment of tribopolymer. Another structure, without H migration will split into two adsorbed benzene molecules. Further, we predict the reaction rates based on the transition–state theory and second–order rate law. This study provides more insights about the mechanochemical reactions of tribopolymerization on conductive oxides.
Chapter 8

Tribopolymerization of benzene on Pt$_3$Si(001) surfaces
8.1 Introduction

Silicides, especially thin films, have long been recognized as an efficient and reliable material for microelectronics [237]. Platinum silicides as one of the kind reveals the potential of a good candidate for nano-electro-mechanical system (NEMS) devices due to their low surface wear, high temperature stability, and resist to surface corrosion [238]. They are easy to synthesis in thin film layers by solid-state diffusion [239, 18]. Platinum silicides occur in variety of species based on various stoichiometric combinations between Pt and Si. Through solid-state diffusion, three type of materials based on the stoichiometry, PtSi, Pt$_2$Si and Pt$_3$Si can be obtained. The fundamental properties for PtSi and Pt$_2$Si have studied in deep, for example the formation process via thermal processing or chemical vapor deposition [240, 241, 242] and investigation of electrical performance and stabilities when interfacing with multiple substrates [243, 244, 245, 246, 247, 248]. Theoretical studies also make many contributions to figure out the electronic structures, elastic properties and thermodynamic properties for PtSi and Pt$_2$Si [249, 250, 251, 252, 253]. However, the investigation on Pt$_3$Si is mildly incomplete. Our recent study shows that Pt$_3$Si possesses the best conductivity over PtSi and Pt$_2$Si [19], which bring us the attention to thorough study for Pt$_3$Si both in experimental point of view and in theoretical and computational perspective.

Tribopolymer, that forms on the Micro- or Nano-electrical-mechanical system (MEMS/NEMS) devices during mechanical switching cycles, is a major concern to MEMS/NEMS feasibility, due to such a polymer is sticky and insulating [9, ?]. Since the both MEMS and NEMS are close to atomic scale, sampling tribopolymer from those devices for measurement is a tough task. A rough prediction has made by the experimentalists that the tribopolymer consists of hydrocarbon long chains. However, the specific composition and reaction mechanism of the hydrocarbon long-chain remain unclear. Theoretical computation, such as density functional theory (DFT) method, is powerful tool to predict electronic
structure and reaction mechanisms of chemical substances at a reasonable level of accuracy and is available for fairly large scale systems. Previously, we have investigated the tribopolymer formation mechanism of metal and metal oxide surfaces [17, 254], and have found that tribopolymer formation undergoes dehydrogenation and radical species linkage using benzene as an initial contamination source. In this work, we perform a comprehensive study of fundamental Pt$_3$Si surface properties using DFT calculations, including determining the thermodynamically stable surface direction of Pt$_3$Si, surface oxidation, and compression analysis for tribopolymer formation.

8.2 Computational methods

All Density functional theory (DFT) calculations are performed with the generalized gradient approximation (GGA) density functional of Perdew, Burke, and Ernzerhof [31] in the QUANTUM-ESPRESSO code [71]. The plane-wave norm-conserving pseudopotential [38, 38] is generated using OPIUM code [67] software package for all the elements in the system. The van der Waals interaction correction is included by applying DFT-D2 method [45, 230]. The kinetic energy cutoff is 680 eV. The self-consistent relaxation calculations are converged to a total force threshold of 1 meV/Å, with the total energy convergence of 5 meV/atom. For the bulk structures are calculated use an $8 \times 8 \times 8$ Monkhorst-Pack mesh of $k$–points. The optimized lattice parameters of Pt$_3$Si($P_4/mmb(127)$) are $a=b=5.49$ Å, $c=7.86$ Å and $\alpha=90.0^\circ$; the lattice parameters agree with the experimental values $a=b=4.46$ Å, $c=7.86$ Å and $\alpha=90.0^\circ$ [255] with an error of 0.49% in the $a$, $b$–directions and 0.02% in the $c$–direction.

For the surface models of Pt$_3$Si, we used both symmetric slabs and asymmetric slabs depending on the surface termination we were varying during the calculation of the energies for surface free energy diagram generation. For symmetric slabs, we used twice of the
length of slab as vacuum space length. For asymmetric slabs, we used one and half of the length of the slab for vacuum and applied artificial dipole field correction [256] to avoid the interaction between between upper and lower layer of the slab. We performed ionic position relaxation of each slab with a $8 \times 8 \times 1$ $k$–point grid for Brillouin zone (BZ) integration. The reaction path for surface oxidation kinetics was computed by applying nudged elastic band (NEB) method [234, 235]. In compression analysis, we applied normal stress the same method as illustrated in Chapter 7.

8.3 Results and discussions

8.3.1 Surface free energy of Pt$_3$Si

The surface free energy is calculated as

$$\gamma(T, p) = \frac{1}{2A}[E_{\text{slab}}(T, p, N_{\text{Pt}}, N_{\text{Si}}) - N_{\text{Si}}E_{\text{bulk}}^{\text{Pt}_3\text{Si}} + (xN_{\text{Si}} - N_{\text{Pt}})(E_{\text{bulk}}^{\text{Pt}} + \Delta\mu_{\text{Pt}})],$$  \hspace{1cm} (8.1)

where $\gamma(T, p)$ is the surface free energy in terms of temperature and pressure, $A$ is the surface energy of the slab supercell, $E_{\text{slab}}$ is the total energy of the slab, $E_{\text{bulk}}^{\text{Pt}_3\text{Si}}$ is the total energy of bulk Pt$_3$Si, $E_{\text{bulk}}^{\text{Pt}}$ is the total energy of bulk Pt, and $\Delta\mu_{\text{Pt}}$ is the amount of chemical potential change of Pt in the Pt$_3$Si slab. $N_{\text{Pt}}$ and $N_{\text{Si}}$ are number of Pt and Si atoms in the slab, and $x$ is chemical formula ratio of Pt$_x$Si with $x = 3$ for Pt$_3$Si. Fig.8.1 shows the surface free energy with respect to different terminations of Pt$_3$Si surface of (001), (100), (110) and (101). From $\gamma$ against $\mu_{\text{Pt}}$ diagram, we find that the most stable surface among the sampled slab structures is Pt$_3$Si(001) with a chess-board-like termination of Pt$_2$Si$_2$ structure (see 8.2) towards the formation of Pt bulk (“Pt Rich” in Fig. 8.1) condition.

Once the stable surface structures are determined for all platinum silicides, we apply compressive and tensile strain along [001] direction to obtain the normal stress, where
Figure 8.1: Surface free energy under Pt chemical potential with different surface terminations of Pt$_3$Si, including (100), (001), (101), and (110) surface directions. The vertical dashed line to the left labeled as "Pt Poor" indicates the formation bulk Si, while the vertical dashed line to the right labeled as "Pt Rich" indicates the formation of bulk Pt. The horizontal dashed line at zero is the reference of zero surface free energy. The violet solid line indicates the case for Pt$_3$Si(001) surface, and it is the most stable surface.
Figure 8.2: Ball-and-stick structure of Pt$_3$Si(001) slab model. The top layer and the rest for the slab is separated by a greyish-black transparent plain. The light gray atoms are Pt, and the blue atoms are Si.
compressive strain is to symmetrically push the slab inward and tensile strain is to push outward. In Fig. 8.3, the compressive stress curve show a larger elastic deformation region than the tensile stress curve. The non-linear increment starting at 42 GPa in the compressive curve indicates the material densification. On the other hand, the tensile curve plateaus at 15% of the tensile strain and follows a sudden drop shows the tensile strength is roughly 15 GPa. Please see Appendix 8.5 for additional discussion of tensile strength calculations.

Fig. 8.3 also shows that the compressive stress is greater than tensile stress by almost three times, and hence Pt$_3$Si is able to tolerate large compression stress. In fact, such mechanical property matches the requirement of MEMS/NEMS devices material being mechanically robust.

### 8.3.2 Oxidation of Pt$_3$Si(001) surfaces

The experimental results have shown less oxidation evidence for Pt$_3$Si surface, and the surface tends to stay clean. To simulate the adsorption of oxygen atoms on Pt$_3$Si(001), we use Pt$_3$Si(001)(1×1) as shown in Fig. 8.4(a). The chess-board-like surface structure separates the adsorption sites into four regions with each region of the same chemical environment. In our case, we consider two oxidation conditions by having oxygen atom coverage of 0.25 mono-layer (ML) to 0.5 ML. If we count those four regions as four general adsorption sites, 0.25 ML and 0.5 ML correspond to adding one oxygen atom on either of adsorption site and two oxygen atoms on any two of the four sites. The oxygen atom is brought to the surface one at a time from a few angstrom away of the surface until it fully adsorbed on the surface, and then the second atom comes in following the same steps as previously. In Fig. 8.4(b) and Fig. 8.4(c), we show the stable adsorption structure for 0.25 ML and 0.5 ML coverage of O atoms. On 0.25 ML oxidized surface, oxygen adatom occupies one of the hollow site. The surface chess-board-like structure transforms to a diamond-shaped structure. The oxygen atom forms a bridge between two Si atoms and
Figure 8.3: Normal stress versus tensile strain and compressive strain. Only the absolute stress value is taken the stress. The normal stress changes with compressive strain is in red, whereas the stress changes with tensile strain is in green. The linear portion of the both red and green curves indicate the elastic deformation regions.
Figure 8.4: Top layer of stable oxidized Pt$_3$Si(001) surfaces with different oxygen coverages. The supercell is expanded to $4\times4$ for clear visualization. (a) is pure Pt$_3$Si(001) surface for reference. The black dashed line encompasses a $1\times1$ supercell. The pink shaded circle covers one of the adsorption sites. (b) is the stable structure with 0.25 ML oxygen coverage; (c) is 0.5 ML coverage surface structure. The Pt atoms are in light grey, Si atoms are in dark blue, and O atoms are in red.
drags them closer to each other, which causes the nearby Pt-Si square to expand. When the Pt$_3$Si(001)-O structure is stabilized, the second oxygen atom is added to the system. The surface undergoes significant reconstruction and forms a five-membered rings between Pt, Si and O atoms on the surface. In both cases, oxygen atoms show the sign of $sp^2$ hybridization.

To investigate the oxidation thermodynamics of the Pt$_3$Si(001) surface, we obtain the adsorption Gibbs free energies [150] with different O-atom adsorption. The energy profile with respect to reaction coordination is shown in Fig. 8.5. The definition of adsorption Gibbs energy is the difference between the surface free energies of the clean surface and the adsorbed surface. The energies are plotted via the change of a singly oxygen chemical potential ($\mu_O$). In general as $\mu_O$ increasing, surface tends to be more oxidized. $\mu_O \rightarrow 0$ indicates the liquid oxygen state. At $\mu_O=-2.39$ eV, the bulk SiO$_2$ is formed. Before the surface Si atoms are fully oxidized to turn into SiO$_2$, the 0.25 ML O-covered surface is generally shows a lower Gibbs free energy compare to that of 0.5 ML O-covered surface. This indicates that the 0.25 ML O-covered surface can be majorly energetically favored over 0.5 ML O-covered surface until the formation of SiO$_2$ on the surface.

Our study shows that Pt$_3$Si(001) surface prefers 0.25 ML oxygen coverage, but further oxidation is kinetically hindered. It turns out that even with partially oxidized surface, the surface can still conducting electron as good as bare surface. Fig. 8.6 shows the surface density of states (DOS) of Pt$_3$Si(001) surface with and without surface oxidation. The 0.25 ML O-covered surface even higher electron density contribution near the Fermi level rather than bare Pt$_3$Si surface. This indicates the material like Pt$_3$Si is less picky about the environment and can bare with a certain level of surface corrosion.
Figure 8.5: The adsorption Gibbs free energy profile of Pt$_3$Si(001) oxidation with respect to change of oxygen chemical potential. The energy curve for 0.25 ML O-covered surface is in black, and 0.5 ML O-covered surface is in red. The horizontal line across 0 indicates the clean surface with no adsorption of oxygen. The vertical line at $\mu_O = -2.39$ eV indicates the formation of bulk SiO$_2$. The shaded area is the bulk phase of SiO$_2$. The highlighted green curve shows the lowest Gibbs free energy at given $\mu_O$. 
Figure 8.6: Surface density of states (DOS) of Pt$_3$Si(001) with and without oxidation. The inlet shows the supercell slab of 0.25 ML O-coverage.
8.3.3 Compression analysis of Pt₃Si(001) with benzene

It has been shown in Appendix 8.6 that benzene on oxidized Pt₃Si(001) surface presents a weak physisorption over which the bare surface shows a strong interaction with benzene. We now investigate tribopolymer formation on the oxidized surfaces given that the partially oxidation is usually unavoidable. Since the initial adsorption of benzene on Pt₃Si(001)-O surfaces is very weak and is of the same scale compare to that on RuO₂(110)Ocvd surface [232], we hypothesize that tribopolymer formation process should be similar.

During our computation of compression, we apply compressive strain along [001] direction to the benzene/Pt₃Si(001)-O(0.25ML) system in order to model the closing gap stage of mechanical cycle of MENS/NEMS devices. The detailed compression process is presented in Appendix 8.7. As the compressive strain is applied on the supercell, benzene molecules adsorbed on the upper and lower ends of the slab move away from each other to reduce the repulsive effect from the vdW interaction. At the normal stress of 4.6 GPa, benzene is forced to start forming chemical bonds with the surface due to vacuum space is confined and Pt atoms, a highly active metal adsorbs benzene strongly, are exposed on the surface. The normal stress curve (see Fig. 8.7) presents a slope change at supper cell length of 26.0 Å indicating benzene molecules transforms from physisorption to chemisorption. Continuing compressing the supercell, benzene molecules stay chemisorbed even pass the stress of 25.0 GPa, which is a stress threshold of Pt(111) forms tribopolymer with benzene [17].

The sign of forming new species within benzene/Pt₃Si(001)-O(0.25ML) system starts at the normal stress increasing to 55.3 GPa. In Fig.8.8, the lower adsorbed benzene molecule transfers a hydrogen atom to the nearby surface oxygen atom and opens up an active radical position for upper benzene to attack to form a new C–C single bond. In the meantime, the upper benzene looses another hydrogen atom to the lower benzene to form a –CH₂– group as shown in the high-lighted circle on the right of Fig. 8.8. In short, the entire process
Figure 8.7: Normal stress change versus compressive strain applied on the supercell. The ball-and-stick pictures indicates the corresponding cell configurations for the given normal stress. The arrow is pointing to the compression to higher stress direction.
involves two hydrogen atoms transfer to either the surface species or the other benzene molecule and a C–C single bond formation linking the upper and lower benzene. Such a process with formed new species are similar to what has been explained in both Ref [17] and Chapter 7. Note that, the stress required for the new species to occur is beyond the region of elastic deformation for Pt$_3$Si along [001] direction (\( \leq 45 \) GPa), which indicates the tribopolymer formation for Pt$_3$Si(001) not only has run over the material regular functioning limitation but also way beyond the experimental limitation.

8.4 Conclusion

In conclusion, we conduct DFT calculation to investigate Pt$_3$Si viability for MEMS/NEMS devices in terms of tribopolymer formation analysis. We investigate the surface free energy of various surface structures of Pt$_3$Si and determine the thermodynamically stable surface is along [001] direction with Pt$_2$Si$_2$ chess-board-like surface profile. Our study also shows Pt$_3$Si(001) surface prefers partial oxidation and can still maintain conductivity when oxidation occurs. In addition, the partially oxidized Pt$_3$Si(001) present low tendency of tribopolymer formation. All these characters of the surface material provide us the strong evidence that Pt$_3$Si could be a very promising material for MEMS/NEMS devices utilization. Our research also provides a thorough understanding of tribopolymer formation on metallic surfaces and expresses a fundamental routine process for tribopolymer analysis from the first principle point of view. Our method can be extend to any type of surface material, which may open many doors for material design and discovery.
Figure 8.8: Ball-and-stick structure of intermediate state species formation of benzene/Pt$_3$Si(001)-O(0.25ML) system. The color scheme of different elements in turn are: grey for Pt, blue for Si, red for O, brown for C and pink for H. The light green ovals marked on the left structure indicate the potential active position for the tribopolymer formation, whereas the oval on the right indicate the formation of –CH$_2$– group on the lower benzene when attracting the hydrogen atom from the upper benzene. The arrow in green shows the hydrogen transfer from benzene to nearby surface oxygen.
8.5 Appendix A: Theoretical prediction of tensile strength of solids

The tensile strength of solids can be theoretically calculated by using the following form [257, 258],

\[
\sigma_t = \left( \frac{\tilde{E}\gamma}{S_0} \right)^{1/2},
\]

(8.2)

where \(\sigma_t\) is the tensile strength, \(\gamma\) is the surface free energy, \(\tilde{E}\) is the Young’s modulus of the material and \(S_0\) is the interlay distance along the direction of applied strain. Hence, the tensile strain at fracture can also be calculated as,

\[
\epsilon_t = \frac{\pi}{2} \left( \frac{\sigma_t}{\tilde{E}} \right).
\]

(8.3)

Based on our surface free energy diagram, we obtain the tensile strength changes with chemical potential of Pt, \(\mu_{Pt}\), as shown in Fig. 8.9. Each point on the curve is calculated by taking the corresponding surface free energy of given \(\mu_{Pt}\) for Pt\(_3\)Si(001) surface as shown in Fig. 8.2. The interlayer distance is approximated to be unchanged during varying \(\mu_{Pt}\). Our simulated tensile strength for Pt\(_3\)Si in the [001] direction is 15 GPa, which is close to the lower bound of the tensile strength predicated by Eq. 8.2.

8.6 Appendix B: Benzene adsorption on Pt\(_3\)Si(001)-O(0.25ML) surfaces

Once the pure surface properties are well understand, we proceed to study the surface exposing to tribopolymer contaminants. Benzene as a contamination source is introduced on the surface. We calculate the adsorption energy of benzene on Pt\(_3\)Si(001)-O(0.25ML)
Figure 8.9: The tensile strength of Pt₃Si in direction of [001]. The horizontal blue dashed line indicates the tensile strength value simulated by applying tensile strain.
surface considering the different initial registries shown in Fig. 8.10. The adsorption energy is calculated as,

\[ E_{\text{ads}} = E_{\text{benzene@surface}} - E_{\text{surface}} - E_{\text{benzene}}, \]  

where \( E_{\text{ads}} \) is the adsorption energy, \( E_{\text{benzene@surface}} \) is the total energy of benzene adsorbs on the surface, \( E_{\text{surface}} \) is the total energy of Pt\(_3\)Si surface, and \( E_{\text{benzene}} \) is the total energy of a single benzene molecule. We list the adsorption energy in Tab. 8.1 for adsorption of benzene on bare and oxidized surfaces. The bare surface adsorption energy is one order of magnitude larger than that of partially oxidized surface. The bare surface tends to chemically interact with benzene molecule via Si–C strong bonding on the surface. However, the partially oxidized surface such as Pt\(_3\)Si(001) with 0.25 ML O coverage (Pt\(_3\)Si(001)-O(0.25ML)) resists the adsorption of benzene.
Figure 8.10: Initial benzene registries on Pt$_3$Si(001)-O(0.25ML) surface. Three different adsorption sites are (a) Pt–Si hollow between head-to-head aligned Si–O–Si bond, named as hollow1, (b) Pt–Si hollow between side-to-side aligned Si–O–Si bond, named as hollow2, and (c) directly on top of Si–O–Si bond, named as O-bridge.
8.7 Appendix C: Compression computation process of benzene/Pt$_3$Si(001)-O(0.25ML) system

We focus on three special cases of benzene/Pt$_3$Si(001)-O(0.25ML) system to study the tri-bopolymer formation mechanism. Fig. 8.11 (a) shows the initial condition of the supercell of these cases, and they are named as “Overlap”, “Shift”, and “Non-overlap” respectively. Using the “Overlap” case as a reference, the “Shift” and “Non-overlap” cases are set that two benzene molecules are separated a few distance apart horizontally. The “Shift” case is with benzene molecules partially overlapped with each other, whereas the “Non-overlap” case is benzene molecules almost not overlapping. The compressive strain is applied on each of the interlay spacings, and, in the mean time, the vacuum spacing is reduced too. We use the same compression steps as explained in Chapter 7. Fig. 8.11 (b) lists the key steps supercell structure configurations as the increment of the stress. The chemisorption of benzene happens at 5 GPa of the stress, and benzene binds on the surface via Pt atoms on the surface. The stress versus compressive strain curve, in Fig. 8.11 (c), shows that the initial registry of the benzene molecule does not make a difference on the compression feature.
Table 8.1: Adsorption energy of benzene Pt$_3$Si(001) surfaces with different surface registries. The bare surface adsorption energy if provided at last column of the table. All energies are in eV.

<table>
<thead>
<tr>
<th></th>
<th>Hollow1</th>
<th>Hollow2</th>
<th>O-bridge</th>
<th>Bare</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ads}$</td>
<td>-0.09</td>
<td>-0.03</td>
<td>-0.02</td>
<td>-2.17</td>
</tr>
</tbody>
</table>
Figure 8.11: Compression process details for benzene/Pt₃Si(001)-O(0.25ML) system. (a) The ball-and-stick structures for three cases for benzene initial registries on Pt₃Si surface. (b) The ball-and-stick structures showing detailed compression process. The blue arrow indicates the direction of normal stress increment. The zoomed-in structure where the two dash arrows point to is the top-view of the lower surface with chemisorbed benzene. (c) Normal stress versus cell compressive strain for three initial registry cases as shown in (a).
Chapter 9

Future work
9.1 Electromechanical tribopolymerization on MEMS/NEMS thin film materials

We have comprehensively studied the initial surface condition and have tribopolymerization mechanism on MEMS/NEMS surface materials under pure mechanical stress. However, the electrochemistry combined with mechanical effects have not been considered yet. Due to the MEMS/NEMS devices will eventually perform hot-switching, opening and closing the air gap during with charged electrodes, electrochemical effect is an ignorable factor for the future tribopolymerization study. On possible route is to develop a hybrid model which combines quantum chemistry and classical molecular dynamics to studying both tribopolymer formation and tribopolymer growth as previously found for molybdenum dithiocarbamate (MoDTC) on Fe(001) surface [259]. Based on the hybrid model, we could introduce a simple electron transport model, such as drude model, to modify the hybrid quantum chemical/classical model to simulate the electromechanical effect on tribopolymer formation.

9.2 Machine learning algorithm for searching tribopolymer resistant materials

We have gained knowledge of tribopolymerization on metal/metal oxides/metal silicides that chemisorption of contaminants could lead to high tendency of polymer formation. We could use molecular binding strength as a descriptor to build a machine learning algorithm and further determine the tribopolymer resistant material. In particular, we could carry out a comprehensive analysis of binding strength of a group of molecular species on various surfaces. From the random forest model [260], we could figure out the key features of the surface, such as layer symmetries, surface charge, surface structure parameters, affect on
molecular binding strength. From then, a more concrete material searching criteria could be built and new materials for MEMS/NEMS could be proposed.

9.3 Hybrid pseudopotential development

The PBE0 functional pseudopotential development pave a way to the range-separated hybrid functional pseudopotential development. So far, such project has already been initiated. The task is to find a valid Hartree potential representation for the short-range part. Meta-gga functional pseudopotential implementation should be easy. Since the exchange-correlation functional library is available at LibXC, the effort for us is to create a channels for spin-dependent wavefunction inputs. In terms of pseudopotential algorithm development, one could also consider the machine learning approach for optimizing the pseudopotential generation parameters.
Bibliography


[116] 


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