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FIRST-PRINCIPLES STUDIES OF STRUCTURE–PROPERTY RELATIONSHIPS:
ENABLING DESIGN OF FUNCTIONAL MATERIALS

DISSERTATION

A Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

by

Qunfei Zhou

Lexington, Kentucky

Director: Dr. Matthew J. Beck, Professor of Chemical and Materials Engineering

Lexington, Kentucky

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ABSTRACT OF DISSERTATION

FIRST-PRINCIPLES STUDIES OF STRUCTURE–PROPERTY RELATIONSHIPS:
ENABLING DESIGN OF FUNCTIONAL MATERIALS

First-principles calculations based on quantum mechanics have been proved to be powerful for accurately regenerating experimental results, uncovering underlying myths of experimental phenomena, and accelerating the design of innovative materials. This work has been motivated by the demand to design next-generation thermionic emitting cathodes and techniques to allow for synthesis of photo-responsive polymers on complex surfaces with controlled thickness and patterns. For Os-coated tungsten thermionic dispenser cathodes, we used first-principles methods to explore the bulk and surface properties of W-Os alloys in order to explain the previously observed experimental phenomena that thermionic emission varies significantly with W-Os alloy composition. Meanwhile, we have developed a new quantum mechanical approach to quantitatively predict the thermionic emission current density from materials perspective without any semi-empirical approximations or complicated analytical models, which leads to better understanding of thermionic emission mechanism. The methods from this work could be used to accelerate the design of next-generation thermionic cathodes. For photo-responsive materials, we designed a novel type of azobenzene-containing monomer for light-mediated ring-opening metathesis polymerization (ROMP) toward the fabrication of patterned, photo-responsive polymers by controlling ring strain energy (RSE) of the monomer that drives ROMP. This allows for unprecedented remote, noninvasive, instantaneous spatial and temporal control of photo-responsive polymer deposition on complex surfaces. This work on the above two different materials systems showed the power of quantum mechanical calculations on predicting, understanding and discovering the structures and properties of both known and unknown materials in a fast, efficient and reliable way.

KEYWORDS: Density Functional Theory, Thermionic Emission, Dispenser Cathodes, Density of States, Photoisomerization, Ring Strain Energy

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July 18, 2016
FIRST-PRINCIPLES STUDIES OF STRUCTURE–PROPERTY RELATIONSHIPS:
ENABLING DESIGN OF FUNCTIONAL MATERIALS

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July 18, 2016
Date
“Emptiness is not nothingness. Emptiness is a type of existence. You must use this existential emptiness to fill yourself.”

Liu Cixin, The Three-Body Problem

“Ten thousand times the web could be destroyed, and ten thousand times the spider would rebuild it. There was neither annoyance nor despair, nor any delight, just as it had been for a billion years.”

Liu Cixin, The Dark Forest

“Time is the one thing that cannot be stopped. Like a sharp blade, it silently cuts through hard and soft, constantly advancing. Nothing is capable of jolting it even the slightest bit, but it changes everything.”

Liu Cixin, The Dark Forest
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acknowledgements</td>
<td>iii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xi</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 First-Principles Calculations on Materials Science</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Motivations</td>
<td>3</td>
</tr>
<tr>
<td>1.2.1 Os-Coated Tungsten Thermionic Dispenser Cathodes</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2 Azobenzene-Containing Photo-Responsive Materials</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Objectives</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Outline of Current Dissertation</td>
<td>9</td>
</tr>
<tr>
<td>2 Introduction to Computational Theories and Methods</td>
<td>11</td>
</tr>
<tr>
<td>2.1 The Schrödinger Equation and Hartree-Fock Method</td>
<td>11</td>
</tr>
<tr>
<td>2.2 Density Functional Theory (DFT)</td>
<td>13</td>
</tr>
<tr>
<td>2.3 Exchange-Correlation Functionals</td>
<td>16</td>
</tr>
<tr>
<td>2.4 Bloch Theorem</td>
<td>18</td>
</tr>
<tr>
<td>2.5 Pseudopotentials</td>
<td>20</td>
</tr>
<tr>
<td>2.6 Maximally Localized Wannier Functions</td>
<td>21</td>
</tr>
<tr>
<td>2.7 Orbital Wave Expansions</td>
<td>24</td>
</tr>
<tr>
<td>2.8 Time-Dependent Density Functional Theory (TD-DFT)</td>
<td>26</td>
</tr>
<tr>
<td>2.9 Cluster Expansion</td>
<td>27</td>
</tr>
<tr>
<td>3 Background</td>
<td>29</td>
</tr>
</tbody>
</table>
4.1 KPOINTS file ................................................................. 52
4.2 The lattice constants of the W-Os alloys obtained by quantum mecha-
nical calculations, compared with experimental results .................... 72
4.3 Work functions of (001) surfaces without ($\Phi_{sub}$) and with ($\Phi_{sub,Ba}$) Ba adsorption, for HCP Os, HCP WOs$_3$, tetragonal W$_3$Os and BCC W from our DFT calculations, compared with previous experimental data (exp.). $\Delta\Phi$ is the work function reduction by Ba adsorption from our calculations. ............................................. 83
4.4 Thermionic current densities $J$ from (001) surfaces of HCP Os, HCP WOs$_3$, tetragonal W$_3$Os and BCC W were calculated by adopting the calculated work function of the Ba adsorbed surfaces, $\Phi_{sub,Ba}$, and temperature of 1300 K. Our results (QM) are compared with previous experimental results (Exp.). Note that $J$(exp.) for HCP WOs$_3$ and tetragonal W$_3$Os are from cathodes with composition of surface layer in the range of HCP and tetragonal phase. ............................................. 93
5.1 Optimized geometries of trans and cis isomers of AB and ABn calculated in gas phase and with solvation effect of DCM, comparing with previous experimental results. ................................. 105
5.2 Bond angles (in degree) of the optimized closed and open trans and cis AB($m,n$) ring molecules with different linker sizes. NNC1 and NNC2 are two of the NNC angles of AB. $\Delta_{max}$ is the range over which each bond angle varies among the AB($m,n$) molecules. ................. 109
5.3 Enthalpies of AB(2,2) with AB and olefin linkers in cis/trans conformations. The enthalpies for the molecules are in Hartree. $\Delta H$ are in kcal/mol. $\Delta H_{\text{alkene}}$ indicates the enthalpy change due to the conformation change of olefin-linker from cis to trans. $\Delta H_{\text{AB}}$ indicates the enthalpy change due to the conformation change of AB from cis to trans.

5.4 Excitation energies and oscillator strengths $f$ for AB, ABn, open and closed trans and cis AB(2,2) monomers.

5.5 DFT calculated $^1$H NMR chemical shifts for open and closed AB(2,2) monomers. The positions of the protons are labeled in Figure 5.15. Note that closed rings doesn’t have $g$ protons because $e$ protons are adjacent to the symmetric $e$ protons when the ring closed at the C=C double bond. The open AB(2,2) has been successfully synthesized by collaborators Ishan Fursule in Dr. Brad Berron’s group. And the experimental NMR results are included for comparison.
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>The current density $J$ as a function of W composition at the coatings, reproduced from previous study.</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>Photoisomerization of $\text{trans}$ (left) and $\text{cis}$ (right) diamino-azobenzene.</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>A brief sketch of ROMP. When RSE is too small, the cyclic monomer tends to be closed where no polymer forms. The right branch shows an example of ROMP when there is high enough RSE in the cyclic monomer.</td>
<td>7</td>
</tr>
<tr>
<td>3.1</td>
<td>Image (top) and brief sketch (bottom) of a tungsten dispenser cathode.</td>
<td>30</td>
</tr>
<tr>
<td>3.2</td>
<td>General model for electron transport.</td>
<td>34</td>
</tr>
<tr>
<td>3.3</td>
<td>An example of W(110) supercell slab used in DFT calculations for NEGF[39]. The bulk lead (tungsten, periodic) is on the left and vacuum on the right. The scattering region consists of two principal lead layers, one coupling with lead on the left and the other coupling with vacuum on the right, and a principal vacuum layer.</td>
<td>35</td>
</tr>
<tr>
<td>3.4</td>
<td>Os-W phase diagram at temperatures above 1000 °C, reproduced from the results of A. Taylor, et al. [140].</td>
<td>41</td>
</tr>
<tr>
<td>3.5</td>
<td>A summary of the mechanism of ROMP reaction.</td>
<td>45</td>
</tr>
<tr>
<td>4.1</td>
<td>Total energy of BCC W unit cell calculated using different number of $k$-points per reciprocal lattice vector.</td>
<td>52</td>
</tr>
<tr>
<td>4.2</td>
<td>The calculated ground-state energies as a function of cutoff energy.</td>
<td>53</td>
</tr>
<tr>
<td>4.3</td>
<td>Total energy of BCC W unit cell as a function of lattice constant.</td>
<td>54</td>
</tr>
<tr>
<td>4.4</td>
<td>A description of the W(001) surface slab, where $t_b$ and $t_v$ represents the thickness of bulk cells and vacuum, respectively.</td>
<td>58</td>
</tr>
</tbody>
</table>
4.5 Surface energy as a function of vacuum thickness $t_v$. The vacuum thickness described here represents how many repeated unit cells of BCC W in the vacuum along the surface normal. Thus the real vacuum thickness in Å is $t_v \times |z|$. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 60

4.6 Formation energies as a function of W atomic concentration of the configurations from HCP (a) and BCC (b) lattices. The convex hull (dashed blue line) connects the ground states (blue dots). . . . . . . . . . . . . . 67

4.7 The ECIs (a) of the clusters: pairs (b), triplets (c) and quadruplets (d) for the cluster expansion in HCP lattice. . . . . . . . . . . . . . . 68

4.8 Formation energies as a function of W concentration for all the calculated W-Os configurations with various atomic arrangements. The blue and red convex hulls are constructed from HCP and BCC-based configurations, respectively. The black one is the absolute convex hull connecting the two ground-state alloys. . . . . . . . . . . . . . . 69

4.9 Primitive cells of the predicted stable structures, with W atoms in red and Os atoms in yellow. The crystal structure type is represented in the form of chemical-formula●Pearson-symbol(space group) . . . . . . . . . . . . . 70

4.10 The atomic arrangement of $W_{22}Os_8$●tP30(P4_2mm) (a); The standard unit cell(red), primitive cell(green) and hexagonal cell(deep blue) drawn in the oF32 WOs7 crystal lattice. The size of W atoms has been enlarged in order to distinguish them from Os atoms. Atoms in green color belong to the primitive cell and deep blue atoms belong to the HCP cell. . . 73

4.11 Formation energies of the ground states of W-Os-Ru ternary alloys from HCP (blue) and BCC (red) lattices. . . . . . . . . . . . . . . 74

4.12 Primitive cells of the ground-state structures, with W atoms in red, Os atoms in yellow and Ru atoms in green. . . . . . . . . . . . . . . 75

xii
4.13 Density of states of hcp Os (a), the predicted ground-state structures
(W-Os binary alloys in black line and W-Os-Ru ternary alloys in other
colors) (b)∼(g), and bcc W (h). The vertical blue dashed lines are posi-
tions of the Fermi level. ................................. 76

4.14 Top and side view of the supercell slabs:(a) W (001)/Ba; (b) Os (001)/Ba;
(c) hcp WO$_3$ (001)/Ba top surface; (d) hcp WO$_3$ (001)/Ba bottom sur-
face; (e) tetragonal W$_3$Os (001)/Ba top surface; (f) tetragonal W$_3$Os
(001)/Ba bottom surface; (g) side view of W (001)/Ba supercell slab. 80

4.15 Electro-static potential for the (001) surface slabs of (a) HCP Os, (b)
HCP WO$_3$, (c) tetragonal W$_3$Os and (d) BCC W with and without Ba
adsorption. The corresponding surface super-cells are shown at the top
of each plot. .................................................. 82

4.16 Ba adsorption energies on (001) surfaces of HCP Os (0 at.% W), HCP
WO$_3$ (25 at.% W), tetragonal W$_3$Os (75 at.% W) and BCC W (100
at.% W). .......................................................... 85

4.17 The $\ln J$ ∼ $\Phi$ relationship for HCP WO$_3$ (a) and tetragonal W$_3$Os (b)
along different emission directions using our new approach comparing
that from the Richardson equation. .......................... 91

4.18 The difference in thermionic emission current density from our method
and that from Richardson equation ($J_R$), depicted as $dJ/J = (J_R -
J)/J$, as a function of work function. The insets enlarges to see more
clearly the differences at lower work functions (1 eV ∼ 4 eV). ......... 92

4.19 Work function of Ba adsorbed surfaces (dark) and current density (blue)
as a function of W concentration. ............................ 94

5.1 The structure of open-AB$(m,n)$ .......................... 98

5.2 Optimized Geometries of (A) $trans$ AB; (B) $cis$ AB; (C) $trans$ ABn; (D)
$cis$ ABn. ...................................................... 104
5.3 Optimized geometries of the linkers with DCM solvation. . . . . . . . . 106
5.4 The lengths of the linkers (linked by the black line) as a function of
$(m,n)$ values, and the end-to-end length of ABn (see the red data points).
Those linkers are all obtained considering the solvation effects of DCM. 106
5.5 The optimized geometries of the closed and open AB$(m,n)$ ring molecules
in cis and trans conformations with $m=n$. . . . . . . . . . . . . . . . . . . . . 107
5.6 The optimized geometries of the closed and open AB$(m,n)$ ring molecules
in cis and trans conformations with $m \neq n$. . . . . . . . . . . . . . . . . . . . . 108
5.7 Geometries of the closed cis (A) and trans (B) AB(2,2) monomers with
alkenes in cis conformations calculated with solvation effect of DCM. . 110
5.8 Enthalpy of formation for closed and open cis AB$(m,n)$ (a) and trans
AB$(m,n)$ (b). . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 111
5.9 The enthalpy differences between trans and cis AB$(m,n)$, $\Delta H = H[cis
AB(m,n)] - H[trans AB(m,n)]$. . . . . . . . . . . . . . . . . . . . . . . . . . . . 112
5.10 Calculated ring strain energies for the closed-trans and closed-cis AB$(m,n)$. 114
5.11 TDDFT calculated UV-Visble absorption spectra for trans and cis AB,
ABn, open and closed AB(2,2) monomers. For trans isomers, only
closed-trans AB(2,2) has two absorption peaks, as seen in the inset. . . 116
5.12 Potential energy curves for (A) AB, (B) ABn, (C) open and (D) closed
AB(2,2) along the rotation pathway. There are two minimums for each
PEC at ground state $S_0$. The left minimum corresponds to cis isomers
and right minimum is the trans isomers. . . . . . . . . . . . . . . . . . . . . 119
5.13 Potential energy curves for (A) AB, (B) ABn, (C) open and (D) closed
AB(2,2) along the inversion pathway. The left minimum at $S_0$ corre-
sponds to cis isomers and right minimum is the trans isomers. . . . . 119
5.14 The molecular orbitals involved in the photoisomerization of closed AB(2,2): (A) HOMO and (B) LUMO of cis AB(2,2); (C) HOMO and (D) LUMO of trans AB(2,2).

5.15 The $^1$H protons in AB(2,2) molecules. Note that the molecule is symmetric around N=N thus only half of the molecule is shown, same for closed AB(2,2) with no $g$ protons.
Chapter 1  Introduction

1.1  First-Principles Calculations on Materials Science

The advancement of materials science is essential to the development of quantum computing, both hardware and software. For example, implementation of advanced solid state hardware like superconducting circuits makes high-performance computing possible with improved efficiency and accuracy at decreased costs and sizes[1, 2], e.g., a smart phone people use everyday today has more computing power than the Apollo computers that took man to the moon in 1967. A new heterostructure of graphene and hexagonal boron nitride material[3, 4] that is able to emit single pulse of quantum light have been discovered to be promising for the creation of powerful quantum optical computers of the future—beam data at the speed of light with no heat or energy wasted as for traditional electronic computers[3].

In return, the more and more powerful supercomputers and advanced quantum mechanical methods enable fast, efficient and reliable computations on exploring and understanding composition-structure-property relationships of materials governing their applications, as well as accelerating the discovery/design of novel and more advanced materials and properties. One good example is the materials genome project that makes use of high-throughput computation[6–9] to allow for accelerated searching and design of various innovative materials (alloys, energy materials, solid electrolytes for batteries), which would be otherwise complex, expensive and time-consuming to be achieved by experiments. An open quantum materials database (OQMD) of high-throughput DFT calculated energies of thousands of ICSD structures and prototypical structures has been developed for accelerating materials design and discovery[10]. The absolute mean error of DFT calculations comparing with experimental studies by examining more than
one thousand structures is 0.096 eV/atom (the absolute mean error for experimental results themselves from different experimental techniques is 0.082 eV/atom)[11]. A number of quantum materials database like OQMD can be downloaded or accessed online[10, 12].

Quantum mechanical computations allow for studying materials at the level of atoms and molecules by describing their quantum behaviors using first-principles methods that requires no input information of experimental parameters. The quantum mechanical methods have advanced remarkably, from calculating only simple hydrogen-like atoms in 1930s to calculating efficiently for systems with up to thousands of atoms as a result of the development of density functional theory (DFT)[13], which will be introduced in Chapter 2. It has been considerably used for exploring the geometric structures, energetics and electronic properties of various materials, such as metals and metal alloys[14–16], semiconductors[17] as well as organic molecules[18–20].

Here in this dissertation, we are going to make use of advanced quantum mechanical methods for the purpose of innovative materials design, including: 1) explore the geometrical structures of materials and their relationship with electronic structure for comprehensive understanding of properties, including phenomena observed in experiments that have not yet been explicitly explained; 2) design or develop new approaches for the design of innovative materials according to the structure-property relationships that governing the applications discovered by first-principles calculations. 3) Provide insights and/or references for future experimental studies.

Specifically, this work involves the research of two systems: a) understanding the composition-structure-property relationships for W-Os alloys governing the thermionic emission of Os-coated tungsten dispenser cathodes. An approach for screening or discovering better cathode materials has been developed which could be used to accelerate
the design of next-generation thermionic cathodes; b) design of an optimal azobenzene-containing monomer allowing for unprecedented reversible, spatial and temporal control of patterned, photo-responsive polymers synthesis through light-mediated ring-opening metathesis polymerization (ROMP).

1.2 Motivations

Motivation of this work comes from (1) the demand of designing next-generation thermionic dispenser cathodes for higher-power vacuum electron devices and (2) the need to design a new monomer with modulated RSE for the controlled ROMP synthesis of photo-responsive polymers on complex surfaces. Both of those two studies would otherwise be complex, time-consuming and expensive for experimental-only studies.

1.2.1 Os-Coated Tungsten Thermionic Dispenser Cathodes

Refractory metals, such as Os, Ru, W have been attractive to industry especially in high-temperature-operating devices due to their high melting points of more than 3000 K[21] and low vapor pressure[22]. And their alloys exhibit superior physical and mechanical properties, especially at elevated temperatures. One of the most important applications of those refractory metals is the thermionic tungsten dispenser cathodes which produce high current density electron beams when being heated.

Thermionic tungsten dispenser cathodes are widely used in high-power electron devices, such as high-power microwave tubes, electron linear accelerators and travelling wave tubes[23, 24] due to their good thermal properties, high and stable emission capabilities[25]. Due to the demand for higher power electron devices, more durable and powerful thermionic cathodes with higher emission current density, more stable and uniform electron emission at lower possible operating temperature[26] are desired. Researchers and industries have made a lot of efforts trying to understand the thermionic emission mechanism and discover novel electron emitting materials for designing better
thermionic cathodes. Studies have found that during operation, there are Ba or BaO adsorptions on the cathode surface which is believed to decrease the work function of W of about 2 eV[15, 27–30]. P. Zalm[31] first discovered that cathodes coated with metals of high work functions such as Re, Ru, Os largely improve the thermionic emission. The improvement in electron emission current density was found to be a result of the formation of W-Os alloys by diffusion of W into the Os coatings[31, 32]. Since then, the role of W-Os alloys in tungsten dispenser cathode has been widely investigated. Intriguingly, thermionic emission from Os-coated first increases with increasing W content at the cathode surface, then decreases dramatically after reaching maximum at around 30~40 at.% W[27, 33, 34] at the operating temperature of about 1050 °C[34]. The end of life of the cathode is observed when the W atomic concentration is over 80% or with the appearance of a W-Os tetragonal structure[35, 36]. The variation of thermionic current density with composition is shown in Figure 1.1, which is reproduced from the experimental study of D. Brion[33].

![Figure 1.1: The current density J as a function of W composition at the coatings, reproduced from previous study.](image-url)

Although the phenomena described above of the thermionic emission properties of
the W-Os alloys varying with different compositions have been observed for more than thirty years, a comprehensive understanding on the mechanism of thermionic emission is still needed and key questions remain: why thermionic emission varies with W-Os composition? Is it the appearance of W-Os tetragonal phase lead to end-of-life of cathodes? If so, why? Why does metals/alloys coatings with higher work function lead to better thermionic emission?

Meanwhile, quantitative calculation of the thermionic emission has been elusive in the past. Most of the methods depended on semi-emperical approximations with complex numerical and analytical models[37, 38]. Johannes Voss, et al.[39] has developed a quantum mechanical method based on non-equilibrium Green’s function (NEGF) for accurately predicting thermionic emission current density without any semi-empirical approximations as previous methods. However, this method is limited on uncovering the materials properties governing thermionic emission.

Addressing the key questions related to Os-coated tungsten dispenser cathodes and developing a new approach to calculate the thermionic emission current density from materials perspective are important for the understanding of thermionic emission mechanism and design of next-generation cathodes. Although the currently most advanced cathodes are the Scandante cathodes, which can achieve thermionic current density of over 100 A/cm²[40–44], much higher than that of Os-coated tungsten dispenser cathodes with a current density of less than 20 A/cm², thermionic emission from scandate cathodes has found to be unstable and non-uniform[45], which limits its wide application in industry. Understanding the thermionic emission mechanism by addressing the questions on Os-coated tungsten dispenser cathodes could contribute to discovering/design of improved thermionic cathodes and probably the understanding of problems for scandate cathodes.
1.2.2 Azobenzene-Containing Photo-Responsive Materials

Azobenzene (AB)-containing materials have gained considerable interests both in scientific researches and industries due to the photo-responsive behavior which enables manipulation on the molecular scale[46–48]. This responsive behavior is attributed to the reversible isomerization of *trans* and *cis* azobenzene by adjusting the wavelength of the light. Under visible light, the azobenzene is stable at *trans* conformation, which can be transformed to *cis* conformation under ultra-violet (UV) light, see Figure 1.2 for diamino-azobenzene. Azobenzene-containing polymeric materials have the ability of rapid, reversible and large geometry changes[49–51], which makes azobenzene and its derivatives attractive in a variety of applications such as reversible information storage[52, 53], molecular switches[54], surface coatings[55], responsive polymers[56, 57], membrane separations[58, 59], molecular motors in drug delivery or nano-scale machines[60–62], in molecular and optoelectronic devices[63–66], and photo-active artificial muscles[67, 68].

![Figure 1.2: Photoisomerization of trans (left) and cis (right) diamino-azobenzene.](image)

Previous approaches for preparing responsive polymer materials are typically spin coating and solution casting[69, 70], which limits the responsive polymers to two-dimensional films with defect-free thickness that are usually beyond the penetration length of UV light (or other response-inducing light) resulting in only part of the film become photo-responsive. While mechanical responses in three-dimensional complex
geometries are usually desired[69–71]. Thus new techniques to prepare defect-free thin films with controllable thickness on complex three-dimensional geometries allowing spatial actuation and polymerization is needed. Ring-opening metathesis polymerization (ROMP) is a powerful and widely used method for the controlled synthesis of polymer materials and films[72–78]. This technique overcomes the limitations of the spin-coating and solution casting methods and is capable of growing uniform films with controllable thickness appropriate for photoactuation on complex surfaces[70, 71].

![Figure 1.3: A brief sketch of ROMP. When RSE is too small, the cyclic monomer tends to be closed where no polymer forms. The right branch shows an example of ROMP when there is high enough RSE in the cyclic monomer.](image)

During ROMP, a closed ring-shaped olefin can be opened up at the presence of Grubbs catalyst. This process has been found to be driven by ring strain energy (RSE), which needs to be sufficiently large enough for ROMP to occur, as shown in Figure 1.3[75, 77]. Thus this could be harnessed to activate or deactivate ROMP if it were possible to control or modulate RSE. To the knowledge of the authors, no such control of strain-promoted reactions has been previously described.

### 1.3 Objectives

For Os-coated tungsten dispenser cathodes, the objectives include: first, determine the stable structures of W-Os alloys with various composition using first-principles calculations and compare with known experimental results; second, calculate thermionic
emission related properties, e.g., electronic structure for every stable structure, and explore the relationship to thermionic emission; third, developing new quantum mechanical methods to quantitatively predict the thermionic current density with incorporation of different properties of Os-W alloys; fourth, based on the structure-property relationships and factors for thermionic current density calculations, answer the key questions raised in previous section 1.2.1; finally, developing approaches for the screening/designing of innovative thermionic emitting materials based on the structure-property relationships and thermionic emission mechanism.

![Scheme 1.1: The proposed cyclic monomers in cis conformation consist of cis ABn and alkene-α, ω-dioic acid chloride linkers. Here the linkers are denoted as L(m,n) where m and n are the number of methylene groups at the two sides of the C=C double bond. The cyclic monomer with linker L(m,n) is denoted as AB(m,n) with cis AB(m,n) and trans AB(m,n) for AB of cis and trans conformation, respectively. Only cis AB(m,n) is shown here but same applies for cyclic trans AB(m,n), composed of trans ABn and linker L(m,n). This scheme shows the constitution instead of synthesis of the monomers.](image-url)

For ROMP synthesis of photo-responsive polymers, an optimal monomer with controlled RSE need to be determined using quantum chemical calculations. The proposed monomer for light-mediated ROMP consists of 4,4′-diaminoazobenzene (ABn) combined with alkene-α, ω-dioic acid chloride linkers [denoted L(m,n)] that connect the two amino groups of the ABn to form an AB-containing ring molecule [denoted AB(m,n)], see Scheme 1.1. The length of the linker is determined by the number of methylene groups—m and n—on either side of the C=C double bond, which will also affect the RSE of the ring-shaped monomers. For suitable linker lengths, the RSEs of trans AB(m,n) ring molecules are expected to be significantly larger than that of cis AB(m,n)
because of the larger distance between the two -NH$_2$ for trans ABn. Therefore, the RSEs of those AB(m,n) monomers will be able to be intentionally controlled through the photoisomerization of azobenzene. In this way, the activation and deactivation—effectively the rate—of catalyst-induced ROMP can be directly and elegantly controlled by exposure of suitable AB(m,n) monomers to different wavelengths of light.

In order to identify the optimal monomer, or more specifically, the optimal linker length maximizing photo-mediated control of ROMP, cyclic molecules AB(1,1), AB(1,2), AB(2,2), AB(2,3), AB(3,3), AB(3,4), AB(4,4) and AB(5,5) have been investigated in this study. The criteria for optimal functional azobenzene-containing monomers are: (i) stable in a closed-ring configuration that (ii) exhibits low RSE with AB in cis conformation, but also high RSE with AB in trans conformation; (iii) photoisomerization of AB must still be possible and controllable when AB is in the ring monomer. In seeking to satisfy those criteria, geometries and energy properties of those ring-shaped monomers have to be firstly determined in order for evaluation of stability and RSE (criterion i and ii). Then the wavelengths for photoisomerization of trans-to-cis and vice versa need to be identified by exploring the photoisomerization mechanism in order to address criterion iii.

1.4 Outline of Current Dissertation

Following is a brief outline of current dissertation. As for this chapter 1, a brief introduction of: the applications of first-principles calculations; unsolved key questions related to thermionic cathodes; photo-responsive polymer films and related problems, is first given. And then the motivation and objectives of this dissertation to solve the key questions and problems raised using first-principles calculations are also specified.

Chapter 2 introduces briefly the quantum mechanical methods and theories behind the first-principles calculations. Calculating processes will be detailed in Chapters 4
and 5 to allow, hopefully, anyone who is interested in this dissertation to understand how those computational results are obtained and how accurate they can be.

Chapter 3 gives a brief review of the background for both thermionic cathodes and azobenzene-containing photo-responsive materials, including: 1) concepts and theories that will be discussed throughout this dissertation; 2) an introduction of previous researches, both experimental and computational (or theoretical).

Chapter 4 discusses the studies on Os-coated tungsten thermionic cathodes, including determined stable structures, density of states (DOS) that related to thermionic emission, surface work functions of W-Os alloy surfaces with/without Ba adsorption, and finally a new approach to quantitatively predict the thermionic current density. All those results and discussions gave a comprehensive understanding of relative effects of bulk and surface properties on thermionic emission.

Chapter 5 discusses the identification of an optimal azobenzene-containing monomer by addressing the three criteria listed in section 1.3. This novel monomer allows for light-mediated ROMP toward spatial and temporal control of synthesis of patterned, photo-responsive polymers.

Chapter 6 concludes the dissertation and specifies future work on thermionic cathodes and the promising application of azobenzene-containg cyclic monomer on other RSE-related chemistry.
Chapter 2  Introduction to Computational Theories and Methods

First-principles methods have been widely used and proved powerful in computational materials science for the calculation of structures, properties of real materials systems and improving the physical understanding of underlying mechanisms. These methods are based on well-established fundamental quantum mechanics, one of the most profound scientific development of the twentieth century that have been confirmed by repeated experiments. No semi-classical approximation is required but only the information of atomic number and approximate positions of species in the system. This section briefly introduces basics of the theories, especially density functional theory (DFT) that all the calculations in this dissertation based on, including different theorems for treating solids and organic molecules that will both be discussed in the following chapters of this dissertation. The detailed calculation approaches for determining the accuracy, structures and exploring various properties of the W-Os alloys and azobenzene-containing photo-responsive materials will be introduced in Chapter 4 and 5, respectively.

2.1  The Schrödinger Equation and Hartree-Fock Method

In quantum mechanics, describing the properties of a system requires only information about the atomic number and approximate positions of the atoms constituting the system. The position of an atom includes that of the nucleus and distribution of the atom’s electrons. Since the mass of individual electrons are much smaller than atomic nuclei, the response of electrons to changes in surroundings is much faster than that of the nuclei. As a result, the atomic nuclei and electrons can be treated separately.
into individual mathematical problems—Born–Oppenheimer (BO) approximation. For a system with multiple electrons interacting with a set of nuclei, a) with fixed positions of atomic nuclei, equations describing the motions of electrons can be solved to obtain the lowest energy state and total electron density; b) with this electron density, we can change the positions of the nuclei to obtain the lowest energy configuration. By repeating process a) and b), the lowest energy state, or configuration of the system (both the electrons and nuclei), which is called the ground state, is obtained.

The quantum state of a system can be described by Schrödinger equation:

\[ \hat{H} \Psi = E \Psi \]  \hspace{1cm} (2.1)

where E is the total energy of the system, and H is the Hamiltonian, or total energy operator. \( \Psi \) is a set of eigenfunctions of the Hamiltonian, which is a function of the positions of the electrons in a N-electron system, for example, \( \Psi = \Psi(r_1, ..., r_N) \) that describes all information of the system. \( \Psi \) is known as wave function because it shares lots of characteristics with classical waves. If \( \Psi \) in Eq. 2.1 can be solved, then all physical properties of the system can be obtained from \( \Psi \) by using appropriate operators.

A more complete expression of Eq. 2.1 for a N-electron system is:

\[ \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r_i, r_j) \] \( \Psi = E \Psi \) \hspace{1cm} (2.2)

where Hamiltonian is replaced by a description of three types of energies, in order, electron kinetic energy, interaction energy between electron and the set of atomic nuclei, and interaction energy between different electrons.

Solving the Schrödinger equation for practical systems is not easy and many brilliant scientists have made a lot of efforts on it. Hartree[79] simplified the N-electron full wave function as a product of individual one-electron wave functions: \( \Psi = \Psi_1(r) \Psi_2(r), ..., \Psi_N(r) \). This is called Hartree product. However, the Schrödinger equation is a
many-body problem. Even with Hartree product, $\Psi$ is still $3N$ dimensional and the number of electrons $N$ in a system can be very large (much larger than the number of atoms). Besides, determination of the electron-electron interactions, the third term of Hamiltonian in Eq. 2.2, requires the consideration of all the individual $\Psi_i(r)$ simultaneously.

Hartree-Fock (HF) method was developed to determine the N-body wave function using a single Slater determinant when particles are fermions or as single permanent of $N$ spin-orbitals in the case of bosons. The Slater determinant for a N-body wave function can be described as:

$$
\Psi_{HF}(r_1\sigma_1, \cdots, r_N\sigma_N) = \frac{1}{\sqrt{N}} \left| \begin{array}{cccc}
\Psi_1(r_1\sigma_1) & \cdots & \Psi_1(r_N\sigma_N) \\
\Psi_2(r_1\sigma_1) & \cdots & \Psi_2(r_N\sigma_N) \\
\vdots & \ddots & \vdots \\
\Psi_N(r_1\sigma_1) & \cdots & \Psi_N(r_N\sigma_N) 
\end{array} \right| (2.3)
$$

where $\sigma$ is the spin of the electron and each $\Psi_i$ inside the determinant is the solution of an effective one-particle Hamiltonian for a electron in the effective potential formed from the electrostatic field of all the other electrons in the system. In this case, the electron self-interaction, which was included in the electron-electron interaction previously, is eliminated. However, though the HF method accounted for effects of electron exchange, the correlation of electrons with opposite spin was not fully accounted for.

An alternative formulation for solving the many-body problem of a practical system is DFT, which has successfully incorporated the electron exchange-correlation functions to overcome the limitations of HF method.

### 2.2 Density Functional Theory (DFT)

In experiments, for a set of $N$ electrons, it is not the position of each individual electron, or which electron is in $r_i$, but the probability of this set of electrons having coordinates
$r_1, r_2, ..., r_N$ that is of physical interest. This quantity can be described using the electron density, $n(r)$, which can be obtained from the individual electron wave functions:

$$n(r) = 2 \sum_i \Psi_i^*(r) \Psi_i(r)$$

(2.4)

where inside the summation, $\Psi_i^*(r) \Psi_i(r)$ is the probability of an electron in $\Psi_i(r)$ locating at position $r$. The factor 2 is because each individual electron wave function can be occupied by two electrons with different spins (spin up and spin down), according to Pauli exclusion principle.

One of the two fundamental mathematical theorems that the entire field of DFT rests on is the Hohenberg-Kohn theorem, which states that: ‘The ground-state energy from Schrödinger’s equation is a unique functional of the electron density’[13]. A functional is a function of another function. As in this case, the electron density $n(r)$ is a function of the spatial variable $r$. Then the function of $n(r)$ is a functional. This is meaningful and simplifies remarkably for solving Schrödinger equation, or more precisely, finding the ground-state energy. First, electron density $n(r)$ is a quantity that is physically observable. Second, the problem has been reduced to $n(r)$ of 3 variables (3 spatial dimension) from 3N-dimension of $\Psi$.

The second fundamental theorem of Hohenberg-Kohn defines what the functional that introduced in the first theorem actually is: ‘The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation’[13]. In this case, the problem becomes finding the right electron density that minimizes the total energy.

At this point, it is still a tough task to fully solve the Schrödinger equation, until the Kohn-Sham equation that find the right electron density by solving a set of equations,
each only involves a single electron. The Kohn-Sham equations are expressed as:

\[
\left[ \frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{XC}(\vec{r}) \right] \Psi_i(\vec{r}) = \epsilon_i \Psi_i(\vec{r})
\]  \hspace{1cm} (2.5)

The main difference of Eq. 2.5 from Eq. 2.2 is that there is no summations in the Kohn-Sham equations because \( \Psi_i(\vec{r}) \) are single-electron wave functions. The first two terms inside the bracket is the kinetic energy of electron and the interaction between the electron and the set of atomic nuclei in the system, respectively, same as in Eq. 2.2. The third term, the Hartree potential, defines the Coulomb interaction between the electron considered in the Kohn-Sham equation and the total electron density of all the electrons in the system:

\[
V_H(\vec{r}) = \frac{e^2}{\epsilon} \int n(\vec{r}') \frac{d^3 r'}{|\vec{r} - \vec{r}'|} d^3 r'
\]  \hspace{1cm} (2.6)

Thus \( V_H(\vec{r}) \) involves the Coulomb repulsion between the electron and itself because this electron contributes to the total electron density as well. This is unphysical, and thus the fourth term inside the bracket, \( V_{XC}(\vec{r}) \) is used to correct this effects and all other quantum mechanical effects. Thus it is called the exchange-correlation potential that defines the exchange and correlation contributions to Kohn-Sham equations. It has the form of:

\[
V_{XC}(\vec{r}) = \frac{\delta E_{XC}(\vec{r})}{\delta n(\vec{r})}
\]  \hspace{1cm} (2.7)

where \( E_{XC}(\vec{r}) \) is called the exchange-correlation energy.

According to the above discussion, to solve the wave functions in Kohn-Sham equation, Eq. 2.5, we first need to know what the total electron density is in order to determine the potentials that described in Eq. 2.5. However, to find out the total electron density, we need the wave functions according to Eq. 2.4. This turns out to be circular. To solve this problem, an iterative way has been used by the following steps:

- taking an initial guess of electron density, \( n(\vec{r}) \) and a fixed external potential.
• This electron density determines the effective potential for the Hamiltonian and solve Eq. 2.5 for the electron wave functions.

• A new total electron density can be obtained from the wave functions from previous step using Eq. 2.4.

• This new electron density is compared with the initial input electron density. If they are the same, then the ground-state electron density has been found and can be used to calculate the total energy and other properties. If those two electron densities are different, the initial input electron density will be updated and this process repeats from the second step.

As a result, the solution to the Kohn-Sham equations from this iterative method is self-consistent.

Once the electronic wave functions or the electron density have been solved, a lot of physical properties can be obtained by:

$$O = \langle \Psi(\vec{r})|\hat{O}|\Psi(\vec{r})\rangle$$  

(2.8)

where $O$ is the expectation value of the Hermitian operator $\hat{O}$, relates to a quantum mechanical observable.

### 2.3 Exchange-Correlation Functionals

Now we have found an iterative way to solve the Kohn-Sham single-electron equations. Another complication is specifying the exchange-correlation functional, $E_{XC}[\Psi_i]$, which is very difficult as also indicated by the definition. The exact form of the exchange-correlation functional is not known. And it is still an important and active area of research in quantum chemistry. There are several widely used functionals: 1) local density approximation (LDA) that derives the functional from the uniform electron gas and
uses only local electron density. Thus in this case, the electron density is a constant at any spatial position, \( n(r) = \text{constant} \). The exchange-correlation potential is set as:

\[
V_{XC}(r) = V_{XC}^{\text{electron gas}}[n(r)]
\]

where \( V_{XC}^{\text{electron gas}} \) is the known exchange-correlation potential of the uniform electron gas. However, this is not the true exchange-correlation functional that describes the nature of materials. Thus the solution to Kohn-Sham equations using this functional is not the true solution of Schrödinger equation.

2) Generalized gradient approximation (GGA). GGA includes more physical information than the LDA because it includes information about the local electron density and also the local gradient in the electron density. There are many distinct GGA functionals that use different ways to include information from gradient of the electron density, e.g. the Perdew-Wang functional (PW91) and the Perdew-Burke-Ernzerhof functional (PBE). A number of those GGA functionals have been widely used and produce very good results for various physical problems.

For a specific configuration of atoms or physical problems, the results from using different functionals will be somewhat different. Especially in the area of quantum chemistry for organic molecular systems, the results from different functionals can be very different. And the most suitable exchange-correlation functionals for a specific system have to be found by comparing the results from different functionals with experimental results. There are a number of hybrid functionals available in quantum chemistry that are a mixture of Hartree-Fock exchange and DFT or other exchange-correlation functionals, such as the Becke three parameter hybrid functionals (B3LYP)[80], wB97XD[81] that includes long range corrections for electron excitations to high orbitals, MP2 method that include the HF exchange functionals and
Møller-Plesset correlation correction[82]. Thus for DFT and other first-principles calculations, it is necessary and sometimes really important to specify the exact exchange-correlation functionals being used.

2.4 Bloch Theorem

For periodic systems (the arrangements of atoms are periodic in space), e.g. crystalline materials, the solution of Schrödinger equation must satisfy the Bloch’s theorem, having the form of

$$\Psi(\mathbf{r}) = \sum_i c_i \psi_{ik}(\mathbf{r})$$  \hspace{1cm} (2.10)

and

$$\psi_k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_k(\mathbf{r})$$  \hspace{1cm} (2.11)

where $\mathbf{k}$ is k-points in reciprocal space (or $\mathbf{k}$ space) and $\mathbf{r}$ is real space vector, respectively; $u_k(\mathbf{r})$ has the same periodicity as the supercell lattice, thus $u_k(\mathbf{r} + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3) = u_k(\mathbf{r})$ where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the lattice vectors and $n_1$, $n_2$, $n_3$ can be any integer. Functions $\exp(i\mathbf{k} \cdot \mathbf{r})$ are called plane wave functions. Thus the Bloch’s wave function theory is also called plane-wave function theory.

It is much more convenient to solve the Schrödinger equation and many other mathematical problems in terms of $\mathbf{k}$ rather than in terms of $\mathbf{r}$. First because the $\mathbf{k}$ points can be reduced to a finite region in reciprocal space, the Brillouin zone. Then most of the properties can be studied by taking the integral in the first Brillouin zone (BZ):

$$g = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{BZ} g(\mathbf{k}) d\mathbf{k}$$  \hspace{1cm} (2.12)

Second, it is possible to obtain a sufficiently accurate electron density from the wave functions evaluated only from a subset of these $\mathbf{k}$-points. According to Eq. 2.12, larger
number of \( k \) points could result in more accurate calculations, but also a lot more computational effort. Monkhorst and Pack\cite{83} have described a method to generate uniform set of \( k \)-points, usually called Monkhorst-Pack mesh.

With Bloch’s theorem and simplification on \( k \)-points, solving Eq. 2.5 reduces to specifying \( u_k(r) \), which can be expanded using a set of plane-waves because of the periodic nature:

\[
u_k(r) = \sum_G c_G \exp[iG \cdot r]
\] (2.13)

Here \( c_G \) is the expansion coefficient and \( G \) represents reciprocal space vectors, \( G = m_1 b_1 + m_2 b_2 + m_3 b_3 \), where \( b_1, b_2, b_3 \) are the reciprocal lattice vectors. Combining Eq. 2.11 and Eq. 2.13:

\[
\psi_k(r) = \sum_G c_{(k+G)} \exp[i(k + G) \cdot r]
\] (2.14)

This expression indicates that even at a single point \( k \) in reciprocal space, evaluation of the wave functions involves the summation over infinite possible values of \( G \). This doesn’t seem promising. However, according to Eq. 2.13, the magnitude of \( k \) and \( G \) represents the kinetic energy of the plane-wave:

\[
E = \frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2
\] (2.15)

According to Hohenberg-Kohn theorem described in section 2.2, the Schrödinger equation can be solved by finding the right electron density that minimizes the total energy. Thus solutions with very high energies are physically much less important than solutions with lower energies. And calculations with infinite plane wave sets (usually called basis set) are impossible or too time-consuming. So a cut-off energy \( (E_{cut}) \) is
utilized to include solutions with energies less than \( E_{\text{cut}} \):

\[
E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2 \tag{2.16}
\]

which largely improves the calculation efficiency.

According to the discussions above, increasing the number of \( k \)-points and energy cut-off \( E_{\text{cut}} \) will result in solutions closer to the true solution but also increase the computational burden. However, it is possible to truncate the plane-wave expansion by using optimized \( E_{\text{cut}} \) and choosing a subset of the \( k \)-points to ensure sufficient accuracy while reducing the computational burden. In this study, the number of \( k \)-points and value of \( E_{\text{cut}} \) are tested and carefully selected for the W-Os systems. This will be discussed in Section 4.1.

### 2.5 Pseudopotentials

As discussed in previous section, the use of energy cut-off \( E_{\text{cut}} \) can largely reduce the number of plane-waves. There is another challenge that the wave functions of electrons in regions near the atomic nuclei varies significantly. From a physical aspect, the properties and physical characteristics are mainly attributed to the less tightly bound valence electrons. While the tightly bound core-electrons (in regions near the atomic nuclei) stays in a deep potential well and insensitive to external perturbations. Thus the core-electrons are especially challenging to solve but of much less physical interest. As a result, a chosen set of core-electrons can be regarded as frozen cores and a pseudo-potential that includes this set of core-electron structures and the atomic nucleus is used to replace the full potential of the atomic nucleus. Therefore the deep potential well of the core-electrons is replaced by a smoothed pseudo-potential. In this way, the number of electrons to solve and plane-wave expansion can be significantly reduced. This
is called frozen core method, which is much more widely used than the all-electron calculations that do not include a frozen core of electrons.

Currently, there is a library of pseudopotentials that has been developed and carefully tested for almost every elements in the periodic table for DFT codes. For a particular pseudopotential, a minimum energy cutoff is defined to include atoms associated with that pseudopotential. The ‘softness’ of a pseudopotential represents how smoothly the potential varies in the region of atomic core. Softer pseudopotentials are more computationally efficient requiring low energy cutoff because smaller number of plane-waves is necessary for accurate expansion of eigenfunctions. One of the most widely used pseudopotential is the ultrasoft pseudopotentials (USPPs) that are based on the work of Vanderbilt[84]. One disadvantage of this USPPs is the requirement to specify a number of empirical parameters for each atom. Another forzen core method is the projector augmented-wave (PAW) method[85, 86], which overcomes the disadvantages of USPPs. Kresse and Joubert[86] has compared the USPP and PAW method with the all-electron calculations for various materials including small molecules and extended solids. And they found that the results from well-constructed USPPs and the PAW method are, in many cases, essentially identical and consistent with the all-electron calculations.

2.6 Maximally Localized Wannier Functions

In the above, we have introduced the representation of electronic ground state by using a set of the Bloch wave, or plane-wave functions $\Psi_{nk}(r)$ where $n$ is the band index. An alternative representation is the Wannier functions[87] that transforms the extended Bloch waves calculated by, e.g. DFT calculations, to localized functions. The Wannier
functions can be described as [87]:

\[ w_{n\mathbf{R}}(\mathbf{r}) = \frac{V}{(2\pi)^3} \int_{BZ} \left[ \sum_m U^{(k)}_{mn} \psi_{mnk}(\vec{r}) \right] e^{-i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k} \]  

(2.17)

where \( w_{n\mathbf{R}}(\mathbf{r}) \) represents the \( n \)th Wannier functions \((n \in [1,N])\) centered on a Bravais lattice site \( \mathbf{R} \) in real space; \( V \) is volume of the unit cell; \( U^{(k)}_{mn} \) is a unitary transformation matrix mixing the bands at each \( k \). \( U^{(k)}_{mn} \) is non-unique but always represent the same manifold. \( U^{(k)} \) is chosen so that the sum of the spreads \( \Omega \) (Eq. 2.18) of the Wannier functions about their centers are minimized (Wannier functions as localized as possible). The The Wannier functions are not the eigenstates of the Hamiltonian as the Bloch functions \( \psi_{nk}(\mathbf{r}) \) because localization in space instead of localization in energy is optimized [87].

\[ \Omega = \sum_n \left[ \langle w_{n0}(\mathbf{r}) | \mathbf{r}^2 | w_{n0}(\vec{r}) \rangle - |\langle w_{n0}(\mathbf{r}) | \mathbf{r} | w_{n0}(\mathbf{r}) \rangle|^2 \right] \]  

(2.18)

And the total spread can be represented by two terms:

\[ \Omega = \Omega_I + \tilde{\Omega} \]  

(2.19)

where

\[ \Omega_I = \sum_n \left[ \langle w_{n0}(\mathbf{r}) | \mathbf{r}^2 | w_{n0}(\mathbf{r}) \rangle - \sum_{\mathbf{R}m} |\langle w_{m\mathbf{R}}(\mathbf{r}) | \mathbf{r} | w_{n0}(\mathbf{r}) \rangle|^2 \right] \]  

(2.20)

\[ \tilde{\Omega} = \sum_n \sum_{\mathbf{R} \neq 0} |\langle w_{n\mathbf{R}}(\mathbf{r}) | \mathbf{r} | w_{n0}(\mathbf{r}) \rangle|^2 + \sum_m \sum_{n \neq m} \sum_{\mathbf{R}} |\langle w_{m\mathbf{R}}(\mathbf{r}) | \mathbf{r} | w_{n0}(\mathbf{r}) \rangle|^2 \]  

(2.21)

where \( \Omega_I \) is a gauge invariant term insensitive to the change of \( U^{(k)} \). Thus the minimum of \( U^{(k)} \) is achieved when \( \tilde{\Omega} \) is minimized.

For isolated set of bands, it is sufficient to obtain maximally localized Wannier functions using the above descriptions. But for entangled energy bands at a given \( k \), a
set of Bloch states need to be generated at a energy window containing $N_{win}^{(k)}$ states by a unitary transformations:

$$ |u_{nk}^{opt} \rangle = \sum_{m \in N_{win}^{(k)}} U_{mn}^{dis(k)} |u_{mk} \rangle \quad (2.22) $$

where $u_{mk}$ is the Bloch states fall within the energy window and $U_{mn}^{dis(k)}$ is a $N \times N_{win}^{(k)}$ matrix. In this case, the energy bands in this defined energy window (outer energy window) are mixing states, not the original energy bands. A second energy window need to be specified inside the outer energy window where the states are unchanged, in order to preserve the properties of the system.

Wannier functions characterize the electronic structure of a system in real space, and give useful understanding on the nature of chemical bonds. It plays a important role in electronic-structure calculations, in dealing with more details and exploring more information from the electronic-structure with high computational efficiency because it calculates the electronic structures linearly scaling[88] so that the computational time is proportional to the first power instead of the third power (conventional Bloch states calculations) of the system size. This is achieved by a forward Fourier transformation of Bloch wave functions obtained in a more coarse k-points grid in reciprocal space, resulting in a set of Wannier functions in real space with the same grid size, followed by a inverse Fourier transformation of the Wannier functions which results in a finer grid in reciprocal space. Thus the forward and inverse Fourier transformation makes it possible to refining the band structure and deal with entangled bands which would be very difficult by Bloch wave functions calculations. The Wannier Functions are also of broad interest in constructing effectively the Green’s function and self-energies in the theory of ballistic, or Landauer transport that will be discussed in section 3.1.2.3.

In this work, we used MLWFs for calculations of first-derivative of energy band to obtain the group velocities of electrons for the quantitative calculation of thermionic
emission current densities to be discussed in section 4.4.

### 2.7 Orbital Wave Expansions

In the Bloch theorem, the electronic wave function $\Psi$ is represented as Bloch wave functions which can be expanded using plane-wave functions, see Eq. 2.11 and Eq. 2.13, for periodic crystal systems. Unlike crystal materials, the valence electrons in molecules are more localized and more strongly interacted with the parent ion. Thus the plane-wave approximation used in molecules have been questioned since it was proposed\[89\]. In quantum chemistry, the wave functions of electrons are described by molecular orbitals where the electrons are assigned to molecular orbitals represented by a linear combination of atomic orbitals (LCAO)[90]:

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu}$$  \hspace{1cm} (2.23)

where $\psi_i$ is the orbital wave function of molecular orbital $i$, $\phi_{\mu}$ is the basis function of atomic orbital $\mu$ and $c_{\mu i}$ is the variational coefficient. The basis sets $\phi_{\mu}$ are often represented as linear combinations of contracted Gaussian functions\[91, 92\]:

$$g_s(\alpha, \vec{r}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{\alpha \vec{r}^2}$$  \hspace{1cm} (2.24)

$$g_{pz}(\alpha, \vec{r}) = \left(\frac{128(\alpha^5)}{\pi^3}\right)^{1/4} x e^{\alpha \vec{r}^2}$$  \hspace{1cm} (2.25)

where the exponent $\alpha$ changes with different atomic orbitals. Small basis sets $\phi_{\mu}$ used for quantum chemistry calculations usually includes only 1s function for the first-row atoms and 1s, 2s, 2p functions for heavier atoms. For example, the minimal basis set is STO-nG where $n$ is an integer usually taking the value of 2~6 which represents the number of Gaussian functions fitting into a single Slater-type orbital (STO)[93]. There are also a series of larger basis sets which usually allowing extra feature description
such as the angular distortion, anisotropic atomic shape and even diffusion functions, for example, the split-valence Pople basis sets in the form of X-YZG[92] such as 3-21G, 6-31G, 6-31G*. X, Y, Z are integers where X represents the number of Gaussian functions comprising each atomic orbital basis function. Y and Z indicates that each valence orbital are comprised of two basis functions with the number of Gaussian functions as Y and Z for each basis function. 6-31G* basis set indicates six Gaussian polarization functions for each of the atoms. The two numbers after the hyphens indicates the basis set is a split-valence double-zeta basis set while three or four numbers represents triple- or quadruple-zeta basis set[94, 95].

In section 2.3, several exchange-correlation functionals have been introduced for the approximation of the electron exchange-correlation energy, see Eq. 2.7, used in the Kohn-Sham equation (Eq. 2.5). In quantum chemical calculations for molecules based on DFT, those functionals can also be used but usually in hybrid functionals with the Hartree-Fock exact exchange functional[96]. The most commonly used hybrid functional is B3LYP (Becke, 3-parameter, Lee-Yang-Parr)[97] exchange-correlation functional:

\[
E_{XC}^{B3LYP} = E^{LDA}_X + a_0(E^{HF}_X - E^{LDA}_X) + a_X(E^{GGA}_X - E^{LDA}_X) + E^{LDA}_C + a_C(E^{GGA}_C - E^{LDA}_C)
\]

(2.26)

where \(a_0\) is 0.2. \(a_X\) and \(a_C\) are 0.72 and 0.81, respectively. LDA and GGA are local-density approximation and generalized gradient approximation as introduced in section 2.3.

For quantum mechanical calculations based on DFT, the choice of functionals and basis sets are essentially important in determining the accuracy of calculation results. For calculations on azobenzene and azobenzene-containing molecules, the B3LYP functional with 6-31G* basis set are used in previous reports that demonstrated good agreements with experimental results[18, 98, 99].
2.8 Time-Dependent Density Functional Theory (TD-DFT)

As introduced in section 2.2, DFT is a ground-state theory used to study ground-state geometries and properties. Since the photoisomerization of azobenzene and its derivatives takes place at excited states, the electronic excited state structure and properties are of great interest in this work. Time-dependent density functional theory (TDDFT) is a practical and convenient method in calculating electronic excitations[100]. The basic ideas and theories of TDDFT are similar to DFT except that the time-dependent Schrödinger equation is used and all the corresponding terms like the Hamiltonian, potential, wave functions all have a new variable, time.

For a N-particle three-dimensional system, the time-dependent Schrödinger equation is:

\[ i \frac{\partial}{\partial t} \Psi_j(\vec{r}_1, ..., \vec{r}_N, t) = \hat{H}(t) \Psi_j(\vec{r}_1, ..., \vec{r}_N, t) \]  \hspace{1cm} (2.27)

where the time-dependent Hamiltonian \( \hat{H}(t) \) has the same kinetic energy and electron-electron interactions as the static Hamiltonian as described in Eq. 2.5, except that the potential term is time-dependent[100]:

\[ \hat{T}(t) = \sum_i^N V(\vec{r}_i, t) \]  \hspace{1cm} (2.28)

Time-dependent Schrödinger equation can be obtained by representing the wave function as a product of spatical and temporal terms:

\[ \Psi(\vec{r}_1, ..., \vec{r}_N, t) = \Psi(\vec{r}_1, ..., \vec{r}_N) f(t) \]  \hspace{1cm} (2.29)

thus Eq. 2.27 becomes:

\[ i\hbar \frac{df(t)}{dt} \Psi(\vec{r}_1, ..., \vec{r}_N) = f(t) \hat{H} \Psi(\vec{r}_1, ..., \vec{r}_N) \]  \hspace{1cm} (2.30)
The left-hand side is a function of time \( t \) only and the right-hand side is a function of coordinates only. Thus the two sides must be a constant, \( E \), for instance. As a result, two equations can be obtained:

\[
\frac{1}{f(t)} \frac{df(t)}{dt} = -i \frac{E}{\hbar}
\]  \hspace{1cm} (2.32)

\[
\hat{H}\Psi(\vec{r}_1, ..., \vec{r}_N) = E\Psi(\vec{r}_1, ..., \vec{r}_N)
\]  \hspace{1cm} (2.33)

where Eq. 2.33 is the time-independent Schrödinger equation. The general solution to Eq. 2.27 becomes:

\[
\Psi(\vec{r}_1, ..., \vec{r}_N, t) = \sum_i c_i e^{-iE_i t/\hbar}\Psi(\vec{r}_1, ..., \vec{r}_N)
\]  \hspace{1cm} (2.34)

where the wave functions \( \Psi(\vec{r}_1, ..., \vec{r}_N) \) can be solved follow the same approach as the wave functions for time-independent Schrödinger equation. In order to solve the time-dependent Schrödinger equation 2.27, a initial state has to be specified. In most cases, though not required, the starting point at the initial time \( t_0 \) is the ground state obtained from stationary DFT. Then the evolution of the wave functions influenced by the time-dependent potential can be described and properties can be derived from the time-dependent wave functions, the same as for time-independent DFT, Eq. 2.8.

### 2.9 Cluster Expansion

Quantum mechanical techniques based on DFT allow the calculations of stable crystal structures without any experimental input[101, 102]. But considering all possible
atomic configurations is computationally time-consuming and expensive. Thus cluster expansion (CE)[103] is combined with DFT calculations in this study for the stable structures search in the W-Os system, which allows the prediction of stable structures at 0 K, the ground states, by DFT calculating only a small amount of configurations. Cluster expansion considers a configuration as the sum of configurational subunits (α, configurational "clusters" of atoms such as points, pairs, triplets, quadruplets of atoms), whose contributions to the total energy of a solid (effective interaction coefficients, $J_\alpha$) are fitted from DFT calculations of the energy of a subset of structures. Eq. 2.35 shows the energy of a configuration $\sigma$ given by cluster expansion.

$$E(\sigma) = \sum_\alpha m_\alpha J_\alpha \left\langle \prod_{i \in \alpha'} \sigma_i \right\rangle$$

(2.35)

Where $\sigma_i$ is the occupation variable of site $i$ in the parent lattice, which has the value of -1 or +1 according to the type of atom occupying the site. $\alpha$ is a cluster. The energy of configuration $\sigma$ is given by taking the sum of all the clusters $\alpha$ that are not equivalent by symmetry. $m_\alpha$ is the multiplicities which indicates the number of clusters $\alpha'$ that are equivalent by symmetry to $\alpha$. $J_\alpha$ is the effective cluster interaction (ECI) of cluster $\alpha$. The ECI and clusters to include in the cluster expansion are determined by using the energies of a relatively small number of configurations obtained through DFT calculations, according to the Structure Inversion Method[16]. A cross-validation (CV) value, see Eq. 2.36, is used to determine the accuracy of the cluster expansion by comparing the energy of structure $i$ from DFT ($E_i$) and that from predicted from cluster expansion ($\hat{E}_i$):

$$CV = \left( n^{-1} \sum_{i=1}^n (E_i - \hat{E}_{(i)})^2 \right)^{1/2}$$

(2.36)

When CV value is very small, typically smaller than 0.025 eV/atom[104], it means that sufficiently accurate cluster expansion has been determined.
Chapter 3  Background

3.1  Thermionic Dispenser Cathodes

The historical evolution of thermionic cathodes for the pursuit of higher current density at lower possible temperature has been explicitly reviewed by Dr. P. D. Swartzentruber in his dissertation[105]. Here we are going to focus on the general concepts and previous experimental, computational findings on tungsten thermionic dispenser cathodes.

3.1.1  Thermionic Emission and Dispenser Cathodes

Thermionic emission describes the emitting of electrons from hot bodies, which was probably first discovered by Thomas A. Edison in 1883 and has become interesting since 1899 when Thomson discovered the electron emission associated with hot carbon filament and electron emission[106]. Thereafter researchers have made a lot of efforts to try to understand the thermionic emission phenomena, using advanced experimental techniques and theoretical interpretations. Though mechanism of thermionic emission has not yet been fully understood, thermionic cathodes have already been widely applied on a variety of electronic devices, e.g. thermionic converters and vacuum tube devices that make use of the electron beams generated by a hot body to, for example rectify, magnify or switching the input radio wave signal. These cathodes are essential components in high-power vacuum electron devices.

Tungsten dispenser cathode is one of the most widely used thermionic cathodes, with applications in various electron devices such as travelling wave tubes used in communication satellites, microwave devices used in everyday life or medical applications, gyrotrons and so on[107]. One of the most common types of dispenser cathodes used
currently is coated-tungsten dispenser cathode, which consists of porous tungsten matrix with barium-calcium-aluminate compound embedded in the pores and noble metals, such as Os, Ru, Re or their alloys as coatings. There’s also a filament associated to heat the cathode, see Figure 3.1. Before operation, the cathode will be activated at temperatures a little higher than the operating temperature to allow for the flow of Ba or Barium oxide on to the surface which has found to be essential for the high electron emission of the cathode[29]. Those cathodes are called ‘M-type’ cathodes where ‘M’ stands for ‘magic’ because those cathodes have much higher thermionic emission current density than non-coated tungsten cathodes[31] but the underlying mechanism has not yet been fully understood.

For current vacuum tubes, e.g. traveling wave tube that uses thermionic emitting electron beams to amplify radio frequency signals to be transmitted over very long distances without being disrupted. This requires cathodes to generate electron beams with higher current density. As a result, understanding the mechanism of thermionic emission and discovering better cathode materials for the design of next-generation
thermionic cathodes have become extremely important.

3.1.2 Thermionic Emission Theories

3.1.2.1 Richardson Equation

The Richardson equation is named after Owen Willans Richardson who was awarded Nobel prize in physics 1928 for his discovery of the relationships of thermionic current density $J$, temperature $T$ and work function $\Phi$. The equation was then modified by Richardson and Von Laue[108, 109] to:

$$J = A_R T^2 \exp\left(-\frac{\Phi}{k_B T}\right)$$  \hspace{1cm} (3.1)

where $k_B$ is the Boltzmann constant and $A_R$ is called Richardson constant. The discovery of this equation by Richardson was based on the classical free electron theory of electronic conduction in metals. Dushman[110] was one of the first researchers to give quantum mechanical deduction of Eq. 3.1. Thus Eq. 3.1 is usually called Richardson-Laue-Dushman equation. They specify $A_R$ to be a universal constant, by using the density of states of the free electron gas, having the value of[111]:

$$A_R = \frac{4\pi e m k_B^2}{\hbar^3} = 120 \, A \cdot cm^{-2}K^{-2}$$ \hspace{1cm} (3.2)

where $e$ is electron charge and $m$ is mass of free electrons. $\hbar$ is Plank constant.

Richardson equation gives the relationship between $J$, $T$ and $\Phi$ that has been proved by various experimental results. According to Eq. 3.1, higher $J$ can be achieved by increasing the temperature or lowering the work function. However, increasing the operating temperature leads to deterioration of cathode materials that largely reduces cathode lifetime. Thus Richardson equation has lead most thermionic cathodes design to finding new materials with as low work functions as possible.
However, the key assumptions made in Eq. 3.1 described as follows have limited its applications for understanding thermionic emission[109]: a) it is based on the theory of free electrons, using density of states (distribution of number of states available for electrons to be occupied at each energy) of free electron gas, independent of real materials structures. b) the definition of work function $\Phi$ is ambiguous. In solid state physics, work function $\Phi$ is defined as the minimum energy required for an electron to escape from interior of a material to field-free (vacuum) region just outside the surface. As a result:

$$\Phi = E_{\text{vac}} - E_F$$  \hspace{1cm} (3.3)

where $E_{\text{vac}}$ is the electron vacuum level and $E_F$ is the Fermi level of the material. However, in experimental studies, the work function of the dispenser cathode measured before operation at room/low temperatures are different from that during operation. The work function for operating cathodes, called effective work function, is usually obtained by fitting measured $J$ and $T$ with $A_R$ the value as in Eq. 3.2 to Richardson Equation, Eq. 3.1. Effective work function is challenging to be measured in experiment because of the very high operating temperature.

### 3.1.2.2 Fowler-Nordheim Based Theories

Fowler-Nordheim theory (FN)[112] was developed by R. H. Fowler and L. Nordheim to evaluate the field-emission and tunneling phenomena. Based on FN formalism, Murphy and Good[37] developed a numerical model to quantitatively evaluate field to thermoelectric current density by including the work function. According to Murphy-Good theory, the current density $J$ can be described as an integral of the product of electron charge $e$, a supply function $N(T, E_q, \Phi)$ and tunneling probability $D(F, E_q)$:

$$J = e \int_{-\infty}^{\infty} N(T, E_q, \Phi)D(F, E_q)dE_q$$  \hspace{1cm} (3.4)
where $T$, $F$ are the temperature of the surface and electric field at the cathode surface, respectively. $E_q$ describes the part of electron energy for the motion along the emitting direction (normal to the surface) using the energy of a free electron outside the metal as reference. Eq. 3.4 looks very simple, however, fast and accurate evaluation of the terms in the framework of Eq. 3.4 is not trivial. A lot of studies [38, 113–118] have developed different models to improve the Murphy-Good method in evaluating the electron emission, especially the term $D(F, E_q)$, in order to make it computationaly more efficient and applicable in the whole range of cathode operating temperatures and for both uniform and nonuniform surfaces, with also the objective to combine the theories of field, thermionic and photo-emission. However, those approaches relies on complex analytical or numerical models based on semi-classical approximations that neglect the material/structure-depended properties. The quantitative evaluation of thermionic emission is illusive therefore.

### 3.1.2.3 Non-Equilibrium Green’s Function (NEGF) approach

Another theory on current density calculation is the Landauer-Büttiker formalism[119, 120]. Landauer-Büttiker formalism is an approach to solve the quantum transport of typically metal-junction-metal system as shown in Figure 3.2, where $q$ and $p$ are treated as semi-infinite reservoirs. The total current as a result of electron flow from $p$ to $q$ under electric bias $V$ is:

$$I = \frac{e}{\pi \hbar} \int_{-\infty}^{\infty} dE [f_p(E) - f_q(E)] T(E)$$

(3.5)

where $e$ is electron charge. $f_p(E)$ and $f_q(E)$ are the Fermi-Dirac distribution function of electron in $p$ and $q$. $T(E)$ is the transmission function.

As seen in Eq. 3.5, the calculation of total current relies mainly on the calculation of transmission function $T(E)$, which has developed from semi-classically using Boltzmann
Figure 3.2: General model for electron transport

transport equation to quantum transport by using non-equilibrium Green’s function[121, 122].

Here we are going to introduce some basics of non-equilibrium Green’s function theory[123, 124] on the evaluation of \( T \) and examples of applications on thermionic cathodes. NEGF allows for the description of current and charge densities for systems not in thermodynamic equilibrium, e.g., the two reservoirs p and q in Figure 3.2 are at different chemical potentials, or temperatures, as for thermionic cathodes. The reservoir p acts as source and q is the drain. Both of them are semi-infinite and in their thermodynamic equilibrium, respectively. The electrons traveling inside the channel is ballistic or energy-conserving, which can be solved using the general Schrödinger equation. Whereas electrons traveling through the interface of the two-end p/q and the channel (conductor) are entropy-driven processes, with interactions between electrons and the lattice accounted for via self-energy \( \Sigma \). As a result, Schrödinger equation becomes:

\[
\hat{H} \Psi + \Sigma \Psi + S = E \Psi \tag{3.6}
\]

\[
\Psi = [E \hat{I} - \hat{H} - \Sigma]^{-1} S \tag{3.7}
\]
where S represents the overlap matrix between p/q and channel region. \( \hat{I} \) is unit matrix. And the Green’s function is defined as:

\[
[G] = [E \hat{I} - \hat{H} - \Sigma]^{-1}
\] (3.8)

**Figure 3.3:** An example of W(110) supercell slab used in DFT calculations for NEGF\[39\]. The bulk lead (tungsten, periodic) is on the left and vacuum on the right. The scattering region consists of two principal lead layers, one coupling with lead on the left and the other coupling with vacuum on the right, and a principal vacuum layer.

Johannes Voss, et al.\[39\] has reported the their work on thermionic emission using NEGF approach. In their model, the thermionic cathodes are represented by three separate subsystems analogous to Figure 3.2 but with different components: bulk lead on the left and vacuum on the right separated by scattering region, as shown in Figure 3.3. The bulk lead and vacuum are periodically continued along the transport direction and subdivided into principal layers. A principal lead layer contains four atomic layers and a principal vacuum layer spanned about 10 Å. Only interactions between adjacent principal layers were considered. While interactions beyond adjacent principal layers were neglected. Thus the scattering region has two principal lead layers, one coupling to lead and the other coupling to vacuum, and one principal vacuum layer. The subsystems were treated separately using non-interacting Kohn-Sham theory in DFT calculations. The Green’s functions for principal layers of the separated, periodic subsystem of bulk
lead and vacuum were calculated iteratively[125] that relates Green’s function of a principal layer $g_n$ and its adjacent principal layer $g_{n+1}$ using transfer matrices $T$ and $\bar{T}$:

$$g_{n+1} = T g_n \text{ and } g_n = \bar{T} g_{n+1}$$ (3.9)

Since there are no interaction between the bulk lead and vacuum subsystems, the Hamiltonian is:

$$H = \begin{pmatrix} H_L & \tau_{LS} & 0 \\ \tau_{LS}^\dagger & H_S & \tau_{SV}^\dagger \\ 0 & \tau_{SV} & H_V \end{pmatrix}$$ (3.10)

where the Hamiltonians $H_L$, $H_S$, $H_V$ are for the bulk lead, scattering region and vacuum region, respectively. $\tau_{LS}$ and $\tau_{SV}$ represent the interactions between the lead and scattering regions, the scattering and vacuum regions, respectively. Then the Green’s function of the scattering region can be expressed, analogous to Eq. 3.8 as:

$$G_S(E) = [E - H_s - \Sigma_L(E) - \Sigma_V(E)]^{-1}$$ (3.11)

where $\Sigma_L$ and $\Sigma_V$ are the self-energies of the lead and vacuum regions, respectively, which were calculated from the Green’s functions of the lead and vacuum principal layers, $g_L$ and $g_V$, respectively,

$$\Sigma_L(E) = \tau_{LS}^\dagger g_L(E) \tau_{LS}$$ (3.12)

$$\Sigma_V(E) = (\tau_{SV} - E S_V)^\dagger g_V(E) (\tau_{SV} - E S_V)$$ (3.13)

Here $S_V$ describes the overlap of the basis functions for the vacuum region and the slab shown in Figure 3.3. The Green’s functions $g_L$ and $g_V$ were obtained from the separate DFT calculations of lead and vacuum subsystems. The interaction $\tau_{SV}$ was calculated by projecting the Hamiltonian (represented by Wannier function) of the scattering region
onto the basis functions of the vacuum principal layer.

The work function of the surface slab from DFT calculations was added to the Hamiltonian of the vacuum region in order to align the subsystem Hamiltonians in Eq. 3.10.

$$H_V = \frac{1}{2}(q_x^2 + q_y^2) + \frac{1}{2\hbar^2}(2\delta_{z,z'} - \delta_{z,z'-1})|z\rangle\langle z'| + \phi$$  \hspace{1cm} (3.14)

Once the Green’s function of the scattering region has been determined for the system, the transmission function at discrete energy levels can be obtained, for fixed values of in-plane momenta, via[121, 122]:

$$T(E) = Tr[\Gamma_p(E)G^\dagger_S(E)\Gamma_V(E)G_S(E)]$$  \hspace{1cm} (3.15)

where $$\Gamma_{L/V}(E)$$ are broadening functions equal $$i[\Sigma_{L/V}(E) - \Sigma_{L/V}^\dagger(E)]$$. Then the total current density through surface area A can be calculated according to Eq. 3.5:

$$J(T) = \frac{1}{\pi A} \int dEf[E - \mu(T), T]T(E)$$  \hspace{1cm} (3.16)

where $$f[E - \mu(T), T]$$ is the Fermi-Dirac distribution function. In those calculations, the basis functions of the principal layers were represented using Maximally-localized Wannier functions (MLWF)[87] transformed from Bloch states using ASE software suite[126].

In summary, the NEGF approach reported by Johannes Voss, et al. as introduced above provides quantitative prediction of thermionic emission from quantum mechanics without any semi-classical approximations. The assumptions and approximations made in this approach are:

- The bulk metal (electron source) and vacuum region (drain of electrons) are semi-infinite.
The system is divided into separate subsystems that are subdivided into principal layers. And Interactions beyond adjacent principal layers are neglected.

This NEGF approach can be used for calculation of current density for composite and multi-layer electrodes like hexaboride heterostructure[39, 127]. However, the structure-property relationship of the electron emitter governing thermionic emission remains unclear. And the criterion for screening or discovering novel/better electron emitters is purely lower work function, which is computationally possible by using DFT. But it requires firstly not only the determination of composition and structure of bulk cathode material but also the component, composition and structure of surface adsorbates, which are computationally expensive. As a result, elucidation of structure-property relationships governing thermionic emission from materials science perspective is still needed for the understanding of underlying operating mechanism of thermionic cathodes. And more simple and efficient methods/criteria for discovering next-generation thermionic emitters are still needed. However, this NEGF approach can be used for final verification of the screening results.

3.1.3 Experimental Findings on Thermionic Dispenser Cathodes

Previous studies have mainly focused on the effects of surface Ba/BaO adsorptions and evaluation of coating-metal/alloys, especially after P. Zalm[31] discovered that the coatings of noble metals like Os, Ru, Re improve remarkably the thermionic emission comparing to the non-coated tungsten dispenser cathodes.

Work function has been an important point of research in experiments, whether it is the work function directly measured from advanced techniques or that indirectly predicted from fitting the measured current density into Richardson equation. According to Richardson equation, Eq. 3.1, even a decrease of 0.2 eV in $\Phi$ could lead to a increase of the current density by a factor of 6 at the temperature of 1300 K.
There are several factors that affect the work function. First, work function is material-dependent. Most of the noble metals, such as Os, Ru, Ir and Pt all have high work functions over 5.0 eV. While the work function of tungsten is around 4.5 eV. P. Swartzentruber, et al.[128] has measured the work functions of the substrate W-Os-Ru alloys with various compositions by using Kelvin Probe and discovered that work function varies with the composition of W-Os-Ru alloys. A maximum work function was observed at a transition point of about 30∼40 at.% W. When W concentration is smaller or larger than this transition point, the work function increases or decreases, respectively, almost linearly with increase of W concentration. This change of work function of the substrate alloys with composition is opposite to the change of effective work function of the cathodes[32–34]. The effective work function of Os, Ru, Re or their alloys coated tungsten cathodes, which is obtained by fitting the thermionic current density according to the Richardson-Laue-Dushman equation[108, 109, 129], reduced to about 1.8 eV, 0.2 eV lower than that of the non-coated cathodes, 2.0 eV[130, 131]. Second, work function is surface orientation-dependent[132]. For example, the work function of W along \{100\}, \{110\}, \{111\} are 4.63 eV, 5.22 eV and 4.45 eV, respectively[133]. Third, surface adsorptions are able to remarkably modify the work function. The substrate work function of W (100) is about 4.63 eV, while the effective work function of tungsten cathodes (with Ba or BaO adsorption on surface during operation) is only about 2.0 eV, with a work function decrease of more than 2.0 eV[130, 134]. R. Cortenraad, et al.[29] reported that the effective work function of the cathodes also varies with the coverage density of the Ba-O dipoles on the surface, and that the high-work function elements, e.g., Ir, Os and Re, all have two vacant d-orbitals available for bonding with O orbitals while W atoms only have one, which enhances the stability of Ba-O coverage on coated-tungsten cathodes. However, A. P. Makarov[135] found that substrate work functions, coverage and adsorption energy of Ba/O for the W-Os alloys with Os concentrations in the range of 35 at.% ∼ 80 at.% are different,
but their effective work functions are the same (1.95 eV). Studies have also found other alkaline-metals or metal-oxides that could largely modify (either increase or decrease) the work function of metals/metal-alloys\cite{136–138}. Finally, work function is also affected by temperature. For metals and binary alloys, the change of work function with temperature was found to be in the order of $10^{-4}$ eV/K.

On the coating-alloys, it has been found that during operation at high temperatures, tungsten in the matrix will diffuse into the coatings and form, e.g. W-Os alloys, which has been found to contribute to the increased thermionic emission. Several different groups\cite{32–34} have all found the same interesting phenomena that thermionic emission various significantly with W-Os alloy composition, as shown in Figure 1.1. The specific compositions correlated with the maximum current density (or minimum effective work function) were slightly different in different studies probably due to differences in temperatures or activating/operating conditions. It was also found that the thermionic emission was significantly decreased by the formation of W-Os $\sigma$ phase\cite{32, 35, 36}, see Figure 3.4. P. Swartzentruber, et al.\cite{139} have also studied the influence of surface microstructures (grain sizes), thickness of coatings and surface orientations on thermionic emission.

The phase diagram of W-Os alloys have been explicitly studied by A. Taylor, et al.\cite{140, 141} at temperatures above 1000 K. As shown in Figure 3.4, there are three single-phases, $\theta$ (Os) phase, $\sigma$ phase and $\alpha$ (W) phase. The $\theta$ phase has the same lattice structure as Os of closed packed hexagonal (HCP) and likewise $\alpha$ phase the lattice structure of body-centered cubic (BCC) as for W. Thus the previous experimental phenomena shows that the highest thermionic emission was achieved at the HCP phase. The crystal structure of the $\sigma$ phase, with W atomic concentration from 64% to 80%, was found to be tetragonal, tP30 with space group of P4$_2$/mmn\cite{141}. The formation of the $\sigma$ phase was found to significantly reduce the thermionic electron emission of
the tungsten cathodes[33]. A. Taylor, et al.[140] also provided the information of lattice constants of various W-Os alloys and some mechanical properties, however, to the knowledge of the authors, no information on electronic properties of W-Os alloys related to thermionic emission have been reported previously.

3.1.4 Computational Studies on/Related to Thermionic Dispenser Cathodes

Computational studies using first-principles methods have been widely used in various materials and systems, including non-coated and coated thermionic tungsten dispenser cathodes. The stability of structures, surface adsorption energies, work function, current density calculations have all been studied by first-principles calculations for understanding the physics fundamentals.

First-principles calculations based on Density-functional theory are powerful in determining stable structures. D. R. Jennison[142] found that the stable atomic configuration of the surface W, Ba, O atoms with different BaO coverage was that an upfront Ba-O dipole with O atoms bonding to the surface W atoms. The most thermodynamically stable surface in operating temperature of 1200 K was found to be Ba$_{0.25}$O with

![Os-W phase diagram at temperatures above 1000 °C, reproduced from the results of A. Taylor, et al. [140].](attachment:phase_diagram.png)
a lowest work function of about 1.9 eV for B-type (Ba-O adsorbents on tungsten) and 
\( \text{Ba}_{0.25}\text{Sc}_{0.25}\text{O} \) for scandate cathodes with a lowest work function of 1.16 eV\[143, 144\].
The optimum coverage (with highest stability) of Ba-O on tungsten surface is about 0.25 monolayer. But it was also found that the addition of Sc actually reduces the stability of Ba_{0.25}O on the cathode surface[143].

A number of previous studies have also used DFT calculations to predict the work function of surfaces with or without adsorptions that produced results comparable to experimental findings. M. Lin, et al.[28] has calculated the work function of pure W(001) surface and that with Ba and Ni adsorbed on top. G. Pacchioni[145] have calculated the work function of LiF, CaS, NaCl, MgO and BaO on various metal surfaces and attributed the increased or decrease work function after adsorption to various effects, such as electrostatic “compression” effect, charge-transfer effect and the lattice mismatch between adsorbate and metal, or in sum, the relative energies between the Fermi level of the metal and top valence band of the adsorbate. Johannes Voss, et al.[146, 147] have reported coverage-dependence of work function and efficient screening of low work function alkali-earth oxide films on W(100) by using virtual crystal approximation. They discovered that films with Sc/Li and Ca-contained alloys have low work functions.

Apart from structure stability and work function, DFT calculations have also been used for the calculation of surface density of states of W surfaces with and without Ba adsorption[134, 148], which led to the conclusion that the substrate-adsorbate interaction was mainly from the d-states of both W and Ba.

In summary, first-principles calculations are powerful and reliable for the determination of structure stability, for both known and unknown systems, and properties related to thermionic dispenser cathodes.
3.2 Azobenzene-Containing Photoresponsive Materials

3.2.1 Azobenzene and Azobenzene-Containing Polymer Films

Azobenzene, \((C_6H_5)-N=N-(C_6H_5)\), consists of two benzene rings connected by an azo-group (-N=N-) in trans and cis conformations, as shown in Figure 1.2. The reversible cis-to-trans isomerization can be easily achieved photochemically or thermally[18, 149, 150]. In the electronic ground state, the planar trans isomer with a symmetry of \(C_{2h}\) is more thermodynamically stable and is about 1.6 eV lower in energy than the metastable cis isomer, which has a rotated azo-group with \(C_2\) symmetry[151]. The trans-to-cis isomerization takes place under ultraviolet light (UV) with a wavelength of about 365 nm (3.40 eV) and the cis-to-trans isomerization can occur photochemically under visible light of about 420 nm (2.95 eV)[152, 153] or by thermal relaxation[154]. By isomerization, the structural change can considerably alter the optical and electronic properties of azobenzene-containing materials.

In application, the azobenzene derivatives, which are azobenzene molecules modified with functional groups, are more widely used[54, 155]. Because the functional group makes it easier for the formation of a variety of azobenzene-containing molecules or polymers with similar properties as azobenzene and the light wavelength required for triggering the reversible cis-to-trans transformation can be tailored by modifying the functional group while following the same mechanism[18, 156]. Thus in many circumstances, the word azobenzene often represents the azobenzene-containing molecules.

The incorporation of AB into polymers results in light-responsive macroscale properties that are of interest for a range of applications in optical devices, sensors, information displays and storage systems[20, 157, 158]. Although the structural change of one azobenzene from cis-to-trans or vice versa seems small, the polymer films with reasonable amount of azobenzene moieties could undergo structure or property changes significantly enough to be detected or observed. For example, the wettibility of polymer films
can be modulated through the reversible changes of dipole moment and surface alignment of functional groups, forming surface grafts that induced by photoisomerization of trans and cis AB[159–162]. A azobenzene-containing polymer ribbon underwent helical motion that turn the ribbon into helix and springs by exposing different regions of the ribbon under UV light[163]. Mass migration of AB-containing polymer films was also observed by non-uniform illumination of light, which has promising applications in optical-field nanoimaging and optical nanolithography[164]. The photo-induced dynamical properties of AB-containing liquid crystal polymers suggest that they may be used as artificial muscles[70, 163, 165, 166].

However, previous studied responsive polymer materials are usually limited to two-dimensional films with defect-free thickness that are usually beyond the penetration length of UV light[70, 71], which is not applicable in cases where 3D manipulation of the polymers is needed.

3.2.2 Ring-Opening Metathesis Polymerization (ROMP)

Ring-opening Metathesis Polymerization (ROMP) is a type of chain-growth polymerization based on cyclic olefin metathesis[167, 168], having been developed to produce a variety of functionalized polymers[72]. ROMP involves a unique carbon-carbon double bonds rearrange process mediated by the presence of metal carbene catalysts, e.g. Grubbs catalyst (PCy$_3$)$_2$Cl$_2$Ru[169], which opens the carbon-carbon double bond and then link with the open double bond of another molecule to form growing chains. Thus an very important feature of ROMP is the conservation of the carbon-carbon double bond of the monomers during polymerization. Polymerization, as opposed to reclosing of the ring monomer, is driven by the existence of a non-zero ring strain energy (RSE)[75, 77], as shown in Figure 1.3. For large enough RSE, ROMP is preferential to reclosing in the presence of a catalyst, as an open configuration allows the release of
RSE present in a closed ring. Too small RSEs limit polymerization, as open configuration are increasingly likely to re-close instead of polymerizing (see Eq. Figure 1.3).

\[ \Delta G = \Delta H - T \Delta S \]  

45
where $\Delta G$ is the Gibbs free energy, $\Delta H$ and $\Delta S$ are the enthalpy and entropy of ROMP processes. $T$ is the absolute temperature. If $\Delta G<0$, the forward ROMP processes takes place and the reverse processes occur if $\Delta G>0$. When $\Delta G=0$, the ROMP reaction are at equilibrium which can also be viewed as the termination of ROMP reaction. The Gibbs energy $\Delta G$ is closely related to temperature and monomer concentration. In general, successful ROMP reaction can be achieved by using the highest monomer concentration at the lowest possible temperature[72, 172]. The driving force for the monomer to polymer ROMP reaction is the release of the ring (cyclic olefin) strain, which is included in the enthalpic term $\Delta H$[172]. Thus by controlling the ring strain of the monomer, the forward and reverse ROMP reaction can be mediated[173].

Surface-initiated ring-opening metathesis polymerization (SIROMP) is a currently widely ROMP process taking place on the surface which can be used to construct surface-grafted polymer films[48]. It involves the immobilization of a catalyst or initiator on the surface and the ROMP process by adding strained monomers[174]. Comparing with other polymer films depositing methods, SIROMP has several advantages: the surface-grafted films are more stable and more tightly bonded to the surface[175]; more uniform films with controllable thickness can be achieved[46, 176]; the grafting densities can be adjusted by the surface initiator coverage[177]; good control of depth-dependent composition[178].

There are different approaches on immobilizing catalysts or initiators on the surface for surface-initiate ROMP to take place. One of the approaches is forming a self-assembled monolayer terminated by alcohol followed by the reaction with a norbornene-diacid chloride on the norbornene-decorated gold surface. In this way, a stable monolayer support is created for further functionalization and ROMP reaction with Grubbs catalyst by adding ring-strained monomers[173]. The strain of the monomer is found to have significant influence on the probability of forming coating by SI-ROMP[174]:
when the monomers have low strain energy of about 2.5 kcal/mol, no measurable coatings were formed on the surface, while thick coatings excess of 5 µm can be formed by using monomers with high ring strain energy of about 13 kcal/mol. Thus a relatively high-strained monomer has to be selected in order for the formation of films by surface-initiated ROMP.

### 3.2.3 Photoisomerization Mechanism of Azobenzene

For the mechanism of photoisomerization of azobenzene, considerable experimental[70, 179, 180] and computational[151, 156] studies have been reported. There are mainly two pathways proposed for the mechanism of the isomerization of azobenzene[99, 181, 182], an inversion pathway that the NNC angle undergoes an in-plane inversion and a rotational pathway which involves the change of the CNNC dihedral angle. It is also found that the mechanisms of the isomerization at different states are different[151, 156, 183]. In the ground state (S\(_0\)), it is widely accepted that the inversion mechanism dominates[99, 156], and the isomerization barrier can be increased by electron donating substituent or decreased by electron withdrawing substituents[99]. For excite states, the mechanism was first believed to be different for trans and cis transformation after exciting to the first excited state S\(_1\) (n \(\rightarrow\) \(\pi^*\)) and the second excited state S\(_2\) (\(\pi \rightarrow\) \(\pi^*\)), due to the different quantum yield observed[99]. As a result, it was reported that the transformation via inversion pathway dominates after excited to S\(_1\) while the rotation pathway dominates after excited to S\(_2\)[153, 184]. However, most recent studies[98, 99, 151, 185] all disagree with the previous conclusions and believe that the rotational pathway is dominate for trans-to-cis isomerization at both excited state S\(_1\) and S\(_2\).

The energy barrier between the cis and trans local minimum is about 1.6 eV in ground state. But in excited states S\(_1\), there is no energy barrier for the isomerization along the rotation pathway and a excited-state minimum half-way between the cis and trans conformations is stabilized and can be easily relaxed to either cis or
trans azobenzene\[99\]. And the cis-to-trans isomerization takes much less time than the trans-to-cis relaxation\[151\]. At excited state S\(_2\), the isomerization energy barrier is very high, about 1.28 eV along the rotation pathway, result in unlikely occurrence of isomerization. However, the relaxation of S\(_2\) state to S\(_1\) state is energetically favorable and occurs rapidly\[99\]. Since the S\(_0\)-to-S\(_1\) is forbidden by symmetry with zero oscillator strength for trans AB, trans-to-cis photoisomerization can only occur after trans AB being excited to S\(_2\), following a fast S\(_2\)-to-S\(_1\) relaxation, and further relaxation along S\(_1\) to ground state of cis AB. While cis-to-trans isomerization can occur after being excited to S\(_1\) for cis AB. The electron excitation can be achieved photochemically and the wavelengths of light depend on the energy difference between ground state and corresponding excited states. It was reported that vertical excitation (S\(_0\) to S\(_1\)) energies for trans azobenzene (same for trans|cis transformation) is about 2.8 eV and 2.87 eV for cis azobenzene (cis to trans transformation)\[180, 186\] in solution.

3.2.4 First-Principles Calculations on Azobenzene

First-principles calculations based on DFT have been widely used to investigate the geometry, energetics and properties\[98, 151, 187\] of azobenzene and its derivatives to help understand the mechanism of the reversible cis and trans transformation and their dependence on solvent effects, substitution (functional groups)\[18, 99\] and surface effects\[19\], as well as predict materials properties such as vibrational frequency, UV/Visible spectra, Raman spectra, etc\[188, 189\]. Conformations and formation energies of azobenzene and azobenzene-containing molecules have been successfully calculated by static, ground-state calculations, with results comparable to experiments\[19, 187\]. Since the photoisomerization of AB is associated with electron excitation, non-ground-state calculations are also required to study the azobenzene trans and cis conformational change and corresponding properties. Time-dependent density functional theory (TD-DFT)\[190\] calculations have been used for electronic excited state S\(_1\) (n→ π\(^*\))
and $S_2 (\pi \rightarrow \pi^*)$ calculations on azobenzene which give reliable results compared with experiments[99, 191, 192]. All those techniques are available in the quantum chemistry code Gaussian03 or Gaussian09[188] with the expansion of electronic wave functions based on orbital approximation[187]. The expansion of electronic wave functions based on plane waves has also been used to successfully model azobenzene[66].

In summary, first-principles methods are available and reliable on the study of azobenzene and azobenzene-containing materials.
Chapter 4  Thermionic Mechanism of Os-Coated Tungsten Dispenser cathodes

4.1 Computational Details

In order to perform the self-consistent calculations as introduced in Section 2.2, a series of computational settings have been carefully chosen to produce reliable results while at the same time improve the computation efficiency. Here in this section, we will show how the number of $k$-points and value of cutoff energies are tested and chosen, and the reason for using certain exchange-correlation functionals for treating the W-Os system.

For the calculation of ground-state structures and energies, we have introduced in Chapter 2 the theoretical processes as two sets of circular steps: 1) first fix the positions of atomic nuclei in the system and allowing electrons to redistribute into a lowest energy electronic configuration. And the associated total electron density $n(r)$ is obtained; 2) based on this total electron density, the atomic nuclei are allowed to rearrange according to Coulomb forces, until a minimum energy configuration is achieved. This process is also called the relaxation of atomic structures. Here we will introduce in detail how ground-state structures and energies are determined in practical.

The calculations of properties for W-Os system, such as electron density of states, work function and surface adsorption will also be introduced. In this work, all the DFT calculations of W-Os system are performed in the Vienna Ab-Initio Simulation Package (VASP)[193–196], a commercially available first-principles code using the plane-wave expansions as introduced in section 2.4. VASP code is available in the high-performance supercomputer in University of Kentucky. Other computational codes will be introduced in the following sections.
4.1.1 Convergence Testing–k-Points and Cutoff Energy

In order to choose the appropriate values of \( k \)-points density and cutoff energy, we need to find out how the ground-state energy evolves with different settings. The criterion of convergence is that the ground-state energy does not vary beyond a small scale of value with the change of these settings, in which case we call the calculation is converged. And this small scale of value represents the convergence precision and is used as the criterion for choosing calculation input parameters like \( k \)-point density and cutoff energy. In VASP, high calculation precision will ensure the convergence of ground-state energies to a few meV.

4.1.1.1 Choosing k-Points

As introduced in section 2.4, for periodic systems, the electronic wave function can be expressed as an expansion of a set of plane-wave functions, and sum over or integrated over a set of special \( k \)-points in the first Brillouin zone. Thus the accuracy and efficiency of the calculations are directly related to how many \( k \)-points are included to integrate the Brillouin zone. And we choose the smallest possible number of \( k \)-points necessary to produce accurate results in order to improve computation efficiency. A series of tests have been carried out in order to choose optimal \( k \)-point density. Here we are going to introduce the test calculations for choosing \( k \)-point density using the example of body-centered cubic (BCC) W.

To specify the \( k \)-points densities, there is a file named ‘KPOINTS’ as input for VASP calculations. In this file, we will specify a uniform density of \( k \)-points along the three reciprocal vectors. Here for BCC W, the unit cell contains two W atoms and is cubic. Thus the number of \( k \)-points along the three lattice vectors are kept the same. The example ‘KPOINTS’ file is shown in Table 4.1, where \( N_{k1}, N_{k2}, N_{k3} \) represent the number of \( k \)-points along the three reciprocal lattice vectors and \( N_{k1}=N_{k2}=N_{k3} \) in this case for BCC W. And ‘Gamma’ in the third line indicate the origin of the \( k \)-point
meshes is at the $\Gamma$ point. It can also be replaced by ‘Monkhorst-Pack’ which represents the generation of $k$-mesh according to the Monkhorst-Pack scheme[83]. The resulted variation of energy with different $k$-points $N_k$ are shown in Figure 4.1.

<table>
<thead>
<tr>
<th>Automatic mesh</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma</td>
<td>$N_{k1}$ $N_{k2}$ $N_{k3}$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.1: KPOINTS file

As shown in Figure 4.1, with the increase of $N_k$, the calculated ground-state energies converge rapidly to variation of a small value of a few meV. The smallest $N_k$ for achieving this small variation is 15. In calculations for super-cells or surface slabs, the densities of $k$-points are kept consistent with smaller $N_k$ for larger cells (smaller reciprocal cell).

4.1.1.2 Choosing Cutoff Energy

As discussed in section 2.4, we would like to truncate the plane-wave expansion by cutting off very high energies that are of much less physical interest. Choosing the appropriate cutoff energy requires convergence tests same as for choosing $k$-points as discussed above. Meanwhile, according to section 2.5, a minimum cutoff energy is defined for a particular pseudopotentials. Here, we introduce the test calculations for BCC W unit cell that contains two W atoms, and the PAW pseudopotentials[85, 86]
which defines a cutoff energy of ‘ENMAX=223.057 eV’. In the input file, we specify the keyword ‘ENCUT’ and here we give it the values of ‘$n \times ENMAX$’ where $n$ has the value of 1.1, 1.2, 1.4, 1.6,..., 3.4. The calculated ground-state energies with those ‘ENCUT’ values are shown in Figure 4.2

As seen in Figure 4.2, the variation of ground-state energy decreases to only a few meV when ‘ENCUT’ is larger than 357 eV, which is chosen as the cutoff energy for BCC W. For W-Os alloys, the pseudopotentials of the two elements, W and Os, have to be combined in the same order as in the POSCAR that specifies the unit cell vectors, atomic species and coordinates of the atoms. The larger ‘ENMAX’ in the two pseudopotentials is used for the test calculations to choose appropriate ‘ENCUT’ for W-Os alloy system. The final result of cutoff energy for W-Os and W-Os-Ru systems are 387 eV and 390 eV, respectively.

### 4.1.2 Determining Lattice Constant

Before studying the W-Os alloys, we first need to calculate the structure for pure BCC W and HCP Os. These two structures have been well studied, both experimentally
and computationally. In generating initial structures for ground-state calculations, we adopted the structures from the MaterialsProject database[197] and tested the variation of ground-state energy with lattice constant. The result for, e.g., BCC W, is shown in Figure 4.3.

![Figure 4.3: Total energy of BCC W unit cell as a function of lattice constant.](image)

As introduced in section 2.4, the ground-state calculations are to minimize the total energies. Thus the minimum-energy corresponded lattice constant, which is 3.18 Å in this case for BCC W, is that for the ground-state structure. The final lattice constants for HCP Os are $2.75 \times 2.75 \times 4.35$ Å.

### 4.1.3 Calculations of Ground-State Structures of W-Os/OsRu Alloys

The ground-state structures are the atomic configurations with minimum total energy of the system. Here in this work, we are focusing on finding the ground-state structures for W-Os and W-OsRu alloys with various compositions. According to section 2.2 and section 2.4, we can predict the ground-state structures and energies using DFT calculations. However, there are too many possible atomic arrangements even for W-Os
binary alloy at a specific composition. Thus it is not computationally tractable to survey all those configurations using only DFT calculations. To address this limitation, we used an approach based on the cluster expansion (section 2.9)[102, 103]—parameterized with energies from DFT calculations performed in VASP—to screen possible W-Os and W-Os-Ru alloy atomic configurations at compositions ranging from pure W to pure Os/Ru. This combination of cluster expansion and DFT calculations are fulfilled by the MIT Ab-initio Phase Stability (MAPS) code that is implemented in the Alloy Theoretic Automated Toolkit (ATAT)[104, 198], which allows efficient screening for ground state (minimum energy) atomic configurations of multicomponent alloys[14, 101]. A number of studies using this methods of combined cluster expansion and DFT calculations in determining structures have reported results comparable to experiments, proving its accuracy and stability for a range of different material systems, e.g. metals[14, 101, 199], semiconductors[200, 201], layered-structures[202].

As introduced in section 2.9, Eq. 2.35, cluster expansion describes the energy of a configuration as the sum over a set of small clusters (configurational subunits), each has a effective interaction energy—fitted from DFT calculations— that contributes to the total energy. Thus we first need to specify a lattice geometry as input for ATAT, which then will construct possible atomic configurations at give compositions by assigning different atomic species to different lattice sites. For W-Os/OsRu system, both Os and Ru are HCP structures while W is BCC. Thus we did two ground-state structure calculations using combined DFT and cluster expansion in HCP and BCC parent lattices. The cluster expansion is automatically constructed in ATAT using the MAPS code that also reads the DFT calculated energies from VASP.

For the DFT calculations of energies of the configurations constructed by ATAT for fitting the cluster expansion parameters, two steps of calculations are carried out: a)
formation enthalpies were obtained from static calculations using the Perdew-Burke-Ernzerhof (PBE) formalism of GGA[203] exchange-correlation functional. b) Low-energy structures used as inputs to calculations of formation enthalpies were obtained from relaxation calculations using LDA[204] exchange-correlation functional. The value of the plane-wave energy cutoff and \(k\)-points density have been tested to give numerical convergence of DFT results to 1 meV/atom, following the same processes as introduced in section 4.1.1.1 and 4.1.1.2. The density of special \(k\)-points used to compute electronic wave functions was specified in terms of the number of \(k\)-points per reciprocal atom (KPPRA)[104]. For W-Os binary system, the KPPRA were 1500 and 4100 for calculations on HCP- and BCC-based structures, respectively. And the plane-wave energy cutoff was 334 eV and 387 eV for, again, HCP- and BCC-based structures, respectively. For W-Os-Ru ternary system, the KPPRA were 7000 and 2000 for calculations on HCP- and BCC-based structures, respectively. And the plane-wave energy cutoff was 390 eV for both HCP- and BCC-based structures.

The criterion for determining whether the right cluster expansion has been constructed and ground-state structures have been determined accurately is the CV score (Eq. 2.36) be smaller than 0.025 eV/atom[104]. For both W-Os binary system and W-Os-Ru ternary system, the range of W concentrations for ground-state search is [0,1]. However, the convergence of calculation in BCC lattice with W concentration in the range of [0,1] is really difficult (high CV score, Eq.2.36), indicating the difficulty of rich Os or Ru atoms fitting into the BCC lattice (with very high energy). This also implies that W atoms are more likely to diffuse into the HCP Os/OsRu coatings than Os or Ru atoms diffusing into BCC W structure, which is in well agreement with the experimental phenomena that W atoms from the cathode matrix diffuse rapidly into the Os/OsRu coatings. Thus for calculations in BCC lattice, the range of W concentration is reduced to [0.5,1].
In ATAT, the formation energy of a configuration was given by subtracting the energies of pure HCP Os, W (for W-Os from HCP lattice, Eq. 4.1) and BCC Os, W (for W-Os from BCC lattice, Eq. 4.2) from the energies of the considered configurations.

$$\Delta E_{W_xO_{1-x}}^{HCP} = E_{W_xO_{1-x}} - xE_{W}^{HCP} - (1 - x)E_{Os}^{HCP}$$ (4.1)

$$\Delta E_{W_xO_{1-x}}^{BCC} = E_{W_xO_{1-x}} - xE_{W}^{BCC} - (1 - x)E_{Os}^{BCC}$$ (4.2)

Here $\Delta E_{W_xO_{1-x}}^{HCP}$ and $\Delta E_{W_xO_{1-x}}^{BCC}$ are the formation energies of $W_xO_{1-x}$ from hcp and bcc lattice, respectively. $E_{W_xO_{1-x}}$ is the energy of $W_xO_{1-x}$, $E_{Os}^{HCP}$, $E_{W}^{HCP}$, $E_{Os}^{BCC}$ and $E_{W}^{BCC}$ are the energies of the HCP Os, W and BCC Os, W, respectively.

After calculations in HCP and BCC lattices separately, the formation energies of the configurations from these two lattices have to be rescaled by using the same reference energies in order for direct comparison to find the absolute minimum formation energies. In this work, we rescaled all the formation energies using the energies of BCC W and HCP Os as references, see Eq. 4.3 for rescaling the formation energies of configurations from HCP lattice and Eq. 4.4 for configurations from BCC lattice.

$$\Delta E_{W_xO_{1-x}}^* = \Delta E_{W_xO_{1-x}}^{HCP} + x(E_{W}^{HCP} - E_{W}^{BCC})$$ (4.3)

and that from BCC lattice are rescaled as:

$$\Delta E_{W_xO_{1-x}}^* = \Delta E_{W_xO_{1-x}}^{BCC} + (1 - x)(E_{Os}^{BCC} - E_{Os}^{HCP})$$ (4.4)

The formation energies for W-Os-Ru ternary system were also calculated in the same way, except that the energies of HCP Ru and BCC Ru have to be subtracted in Eq. 4.1 and Eq. 4.2, respectively. And the energies of Ru used as references also need to be rescaled the same way as that for W and Os in Eq. 4.3 and Eq. 4.4. In this way, the absolute minimum energy configurations at a specific composition can be determined.
However, determination of the final ground-state structures involves the construction of a convex hull following the same process of constructing a phase diagram, which will be discussed in section 4.2.1.1.

4.1.4 Constructing Surface Slabs and Calculation Settings

In order to study the surface properties of the W-Os alloys, first we need to construct cell geometries with surfaces, usually called surface slab, which is a unit slab, like the unit cell, that repeated to form a periodic structures. The surface slab is constructed from the bulk unit cells and vacuum layers that separate the bulk unit cells creating two terminating surfaces, one at the top and one at the bottom, see Figure 4.4 of the surface slab of W(001).

![Figure 4.4: A description of the W(001) surface slab, where $t_b$ and $t_v$ represents the thickness of bulk cells and vacuum, respectively.]

According to Figure 4.4, we need to specify the following parameters that constitute the surface slab: bulk unit cell (with unit cell vectors $x$, $y$ and $z$), $M$ (number of atoms in the slab), $t_x$, $t_y$ and $t_z$ (the thickness of the slab along the $x$, $y$ and $z$) directions). In the case of W(001), $t_z$ includes the thicknesses of the bulk cells ($t_b$) and vacuum ($t_v$): $t_z=t_b + t_v$. Here in this study, the bulk unit cells of W-Os alloys are from the ground-state
structure calculations as introduced in section 4.1.3. The bulk unit cells of pure BCC W and HCP Os are from DFT calculations. The size of the surface slabs are described in number of bulk unit cells. For example, the in-plane slab size $t_x$ and $t_y$ in Figure 4.4 are chosen as: $t_x=2|\vec{x}|$ and $t_y=2|\vec{y}|$, then the surface cell size can be described as 2x2. And if $t_z=\vec{c}$, then the size of the surface slab can be described as 2x2x$c$.

The slab thicknesses, including that of vacuum, $t_v$, and bulk cells, $t_b$ need to be chosen carefully. In order to improve computational efficiency, we will select the minimum thickness required to avoid interactions through the vacuum and bulk cells. A large enough $t_v$ is necessary to give calculated surface energies independent of vacuum thickness. If $t_v$ is too small, the top and bottom surfaces (see Figure 4.4) will interact through the vacuum under periodic boundary conditions. These are electronic interactions and expected to decay exponentially with vacuum thickness.

There are several different methods for the evaluation of surface energies from slab calculations as introduced by Vincenzo Fiorentini and M. Methfessel. The convergence of surface energies from different methods is somewhat different due to the choice of bulk energy. In this work, for studying the variation of surface energy with vacuum thickness, we use the expression for surface energy $\gamma_s$ as:

\[
\gamma_s = \frac{1}{2}(E_{\text{slab}} - M \cdot E_{\text{bulk}})
\]

Here the $E_{\text{slab}}$ is the total energy of the surface slab. $M$ is the number of atoms in the slab. $E_{\text{bulk}}$ is the atomic energy of the bulk unit cell. Since $M \cdot E_{\text{bulk}}$ is used as a reference energy and same for each surface slab with different vacuum thickness, the convergence of surface energy is independent on the absolute energy of $E_{\text{bulk}}$. The result of surface energies calculated according to Eq. 4.5 with $t_v$ by fixing $t_b=3|\vec{z}|$, is shown in Figure 4.5.

In general, the variation of surface energy with vacuum thickness is exponential.
while Figure 4.5 does not show a perfect exponential curve probably due to the difference in \( k \)-point density for the slab calculations. As shown in Figure 4.5, the surface energy differs less than 0.05 meV/Å\(^2\) when \( t_v \) increases from 8 (\( \sim 25 \) Å) to 9 (\( \sim 28 \) Å) and the variation tends to decrease. Thus a vacuum thickness of about 25 Å is sufficient for the slab calculations.

Similarly, the surface energies also need to be converged with thickness of bulk cells \( t_b \). The dependence of surface energy on \( t_b \) arises from some non-trivial interactions through the bulk cells themselves, or more specifically, the interaction of atoms at the two surfaces interacting through not the vacuum but the bulk cells. These interactions can be: 1) the interactions between the strain fields of the two slab surfaces, which decay slowly, or exponentially for periodic structures, into the bulk[206]. This one has found to be dominant; 2) electronic interactions resulting from Coulomb interactions of charge density variations induced by the surface, which is expected to decay more rapidly than the first strain field interactions.
For evaluating the surface energy with different thickness of bulk cells, $t_b$, we used a different expression:

$$\gamma_s = \frac{1}{2}(E_{slab}^N - N\Delta E_N)$$  \hspace{1cm} (4.6)

where $N$ is the number of atomic layers in the slab and $\delta E_N = E_{slab}^N - E_{slab}^{N-1}$. Eq. 4.6 is used to minimize the effect of different $k$-point density used for the slab and bulk calculations. The surface energy evaluated according to Eq. 4.6 varies about 0.3 meV/Å$^2$ when $t_b$ was increased from 6 to 7 (or $N$ increased from 13 to 15). Thus we adopted $t_b=6$ for W surface slab calculations.

In this work, we have studied the surface properties of four structures: HCP Os, HCP WOs$_3$, tetragonal W$_8$Os and BCC W, that feature the highest and significantly reduced thermionic emission for Os-coated tungsten dispenser cathodes. The ground-state structures of the surface slabs are all calculated using DFT in VASP. After convergence testing as described above, the final size of the surface slab, $t_x \times t_y \times t_z$, in Å, in the order of HCP Os, HCP WOs$_3$, tetragonal W$_8$Os and BCC W, were about $5.49 \times 5.49 \times 60(45)$, $5.54 \times 5.54 \times 62(44)$, $6.3 \times 6.3 \times 75(50)$ and $6.32 \times 6.32 \times 62(43)$, respectively, where in the brackets are the thicknesses of the vacuum region. Monkhorst-Pack mesh grids were used to sample the $k$ points density in the Brillouin zone and were $11 \times 11 \times 1$, $12 \times 12 \times 1$, $12 \times 12 \times 1$, $10 \times 10 \times 1$ for the four structures in the same order. The $k$-point in the $z$ direction are all 1 because the surface slab are large in that direction. In this case, the $k$-point density were kept as similar as possible in different directions for all the four supercells. For Ba adsorbed surfaces, irreducible $k$-points from the substrate surface slab calculations were used. The cut-off energies were 387 eV for all the supercells, with and without Ba adsorption. The PAW pseudopotentials were used for each element with the electronic configurations of Os($5p^66s^25d^6$), W($5P^66s^25d^4$) and Ba($5s^25p^66s^2$). No spin polarization was considered. PBE exchange-correlation functionals were used for all surface slab calculations.
With those calculated surface slab structures, surface properties, e.g. work function and surface adsorption can be predicted from DFT calculations.

### 4.1.5 Surface Adsorption—Geometries and Stability

Ba adsorption at the cathode surface is essential for thermionic cathodes because it could lower the work function of the substrate by about 2 eV \cite{29, 143}. It has been found for B-type (non-coated) tungsten dispenser cathode that Ba desorption/depletion at high temperature leads to degradation of thermionic cathodes \cite{207, 208}. In order to explore whether Ba desorption is the reason for significantly reduced thermionic emission for tetragonal phase, we have studied the relative stability of Ba adsorption on (001) surfaces of W-Os alloys by calculating the formation energy $\Delta E_f[W_xOs_y(001)/Ba]$ of Ba-adsorbed $W_xOs_y(001)$ surfaces, see Eq. 4.7:

$$
\Delta E_f[W_xOs_y(001)/Ba] = \frac{1}{n} \{ E[W_xOs_y(001)/nBa] - E[W_xOs_y(001)] - nE(Ba) \}
$$

where the reference energies for the surface formation energy $\Delta E_f[W_xOs_y(001)/Ba]$ calculation are the energies of bare substrate (001) surface $E[W_xOs_y(001)]$ and the atomic energy of bulk Ba $E(Ba)$. $E[W_xOs_y(001)/nBa]$ is the energy of Ba-adsorbed (001) surfaces. $n$ in Eq. 4.7 is the number of Ba atoms on the $W_xOs_y(001)$ surface. Thus Eq. 4.7 gives the surface formation energy per slab surface. Note that solid bulk Ba may not be the exact phase of Ba in the cathode before/after adsorbing to the substrate surface. However, this reference should be the same for all of the four structures. Thus although the exact energy of Ba adsorption may not be calculated using Eq. 4.7, it gives a reasonable evaluation of the relative stability of Ba adsorption on those four structures for determining whether Ba-desorption is the reason for largely reduced thermionic emission associated with tetragonal W$_3$Os.
4.1.6 Work Function Calculations

According to Eq. 3.3, work function can be expressed as the energy difference between the vacuum level and Fermi level. Thus we don’t need to know exactly what the vacuum level is but this energy difference to obtain the value of work function. Since there are no electron-electron interactions in vacuum, the vacuum level can be determined by the electro-static potential energy, which can be obtained from DFT calculations in VASP by specifying the keyword ‘LVTOT=.True.’ in the input (INCAR) file.

The electro-static potential energy, \( V(x, y, z) \), from DFT calculations in VASP are three-dimensional in real space. In order to determine the vacuum level, one-dimensional electrostatic potential along the surface normal, \( z \)-axis, for example, needs to be obtained by taking the average of the integrated planar potential in the xy plane[209]:

\[
\bar{V}(z) = \frac{1}{A} \int \int_{cell} V(x, y, z) \, dx \, dy
\]  

(4.8)

This projection of electro-static potential energy into one-dimensional can be achieved by using the free FORTRAN code provided by Aron Walsh[210].

4.1.7 Wannier Interpretation

The projection of DFT calculated Bloch wave functions into Wannier functions is achieved by using the free WANNIER90 package[87, 211, 212] in combination with DFT calculations. The entangled energy bands (two or more Bloch wave functions having the same energy at one \( k \)-point) are treated with the Maximally-Localized Wannier Functions (MLWF)[87, 212] to disentangle them in order to obtain properties related to band derivatives. There are two codes in the package of WANNIER90: wannier90.x for calculating the MLWFs, and postw90.x that includes a series of modules to calculate different properties using the Wannier functions calculated by wannier90.x.
In order to obtain Bloch wave functions that can be recognized by WANNIER90, we need to first carry out regular band structure calculations using DFT in VASP and adding the keyword ‘LWANNIER90=.TRUE.’ in INCAR file to produce input files for Wannier functions calculations. The Bloch wave functions from DFT calculations are usually described as \( \psi_{nk}(r) \) where \( n \) is called the band index. For a specific band \( n \), \( \psi_{nk}(r) \) varies continuously with \( k \). And the wave energy \( E_{nk} \) is solved in each \( k \). This calculation of band structure is performed after the ground-state structure calculations as described in section 4.1.3. The number of bands to include in the DFT calculations is specified using the keyword ‘NBANDS’ in INCAR file, which has been increased much more than the default (NBANDS=NELECT/2+NIONS/2, NELECT: number of valence electrons, NIONS: number of ions). The \( k \)-point density has also been largely increased as compared to the ground-state structure calculations for accurate density of states and band structure calculations. For the DFT band-structure calculations of the four structures of interest, HCP Os, HCP W\textsubscript{2}Os\textsubscript{6}, tetragonal W\textsubscript{3}Os and BCC W, the number of bands were 16, 64, 32, 16, respectively. And the \( k \)-mesh for those four structures in the same order are: 19x19x12, 17x17x19, 25x25x13, 19x19x19, respectively.

After this DFT band-structure calculations, there will be three output files to be used as input for wannier90.x and one output file indicating whether the input file generation is successful. With these input files, we can then perform Wannier function calculations using the wannier90.x code. The number of Wannier functions to be included in the calculations was set to be the same as ‘NBANDS’ from the DFT calculations. Based on those calculated Wannier functions, we can calculate various properties using the post-processing code, postw90.x. Here in this work, we are interested in the group velocity of electrons, which can be calculated based on how the eigenvalues of the wave functions varies with \( k \):

\[
\mathbf{v}_g = \frac{1}{\hbar} \frac{\partial E(k)}{\partial k} \quad (4.9)
\]

This is achieved by specifying the keywords: ‘geninterp=.True’ and ‘geninterp_alsofirstder
= .True’ in the input file, which means calculating the band energies (and first derivatives) on a generic list of \( k \) points. Another input file required is the \textit{filename.kpt} file that includes the coordinates of all \( k \) points, which can be obtained by specifying the keyword ‘bands_plot=.TRUE’ in the input file or extract from the ‘IBZKPT’ file output from DFT calculations that contains all the information of \( k \) points.

\section*{4.2 Composition-Structure-Properties of Bulk W-Os/OsRu Alloys}

The current widely commercially available tungsten dispenser cathode is that with OsRu-alloy coatings. The original M-type cathode is Os-coated while the alloying with Ru stabilizes Os from being oxidized to volatile and toxic OsO\(_4\). While the thermionic current densities from Os-coated and OsRu-coated tungsten dispenser cathodes are about the same\cite{213}. In this work we studied first the atomic structures and bulk electronic properties of both W-Os binary and W-Os-Ru ternary alloys. Although the W-Os phase diagram gives the expected phases of W-Os alloys as a function of composition, calculating properties of W-Os alloys and exploring their relationships with structures requires specific atomic arrangements within each phase of W-Os alloys, which will be the mainly discussed in this section.

\subsection*{4.2.1 Ground States of W-Os Binary Alloys}

The ground states (minimum-energy configurations) calculations were performed using the MAPS code in ATAT. The steps for determining ground states can be summarized as follows:

\begin{itemize}
  \item MAPS code generated a number of configurations according to the symmetry of parent lattices (HCP and BCC, e.g., for W-Os alloys) by assigning different atoms (in our case, Os and W atoms) at different lattice sites.
\end{itemize}
• Those configurations were relaxed (that is, there atomic positions are allowed to rearrange to find a local energy minimum) and their total energies were calculated using DFT in VASP.

• Cluster expansion was constructed in MAPS code by using the energies and configurations from DFT calculations to determine the clusters (pairs, triplets, and/or quadruplets) and their ECI contribution to the total energy. More configurations will be calculated in DFT until right cluster expansion (evaluated by Eq. 2.36) has been constructed for sufficiently accurate prediction of energies for more configurations using Eq. 2.35.

• The formation energies ($E_f$) for all the configurations considered above were calculate according to Eq. 4.1 for structures from HCP lattice and Eq. 4.2 for structures from BCC lattice. The formation energies were plotted as a function of composition and a convex hull was constructed for results from HCP lattice and BCC lattices, respectively. The structures with formation enthalpies at the convex hull are the ground states. In order to find the final ground states, the formation energies were rescaled according to Eq. 4.3 and Eq. 4.4 to combine the results from HCP and BCC lattices. A final convex hull was constructed that connected the final ground states of W-Os alloys.

4.2.1.1 Formation Energies

Figure 4.6 includes the formation energies of all the calculated configurations from HCP (a) and BCC (b) lattices. Each plotted point indicates the formation energy of a particular atomic configuration at the corresponding composition. The convex hull (blue dotted lines) are constructed by connecting the minimum formation energy points at each W concentration and exclude those points that are above the line that links the adjacent two points. This is because some two-phase states have lower total energy than
the single-phase states at a given concentration (the excluded points). The green points data are calculated from DFT in VASP while the red points are calculated from cluster expansion, with ECIs fitted from DFT calculated structures and energies. As can be seen in both Figure 4.6 (a) and (b), only a small amount of DFT calculates are necessary for the construction of accurate cluster expansion, which were used to efficiently predict the formation energies of a lot more configurations (red point data).

The clusters and corresponding ECIs for the construction of cluster expansion for HCP lattice are shown in Figure 4.7. As seen in Figure 4.7(a), the ECIs of the clusters decreases significantly with increasing diameters (from pairs to quadruplets). And ECIs of quadruplets are already very small, indicating that those clusters are sufficient for the cluster expansion and larger clusters are not necessary. The corresponding clusters: pairs, triplets and quadruplets are included in Figure 4.7 (B)-(D).

As shown in Figure 4.6, there are seven ground states calcualted from HCP lattice with W concentration of 12.5 at.%, 25 at.%, 37.5 at.%, 50 at.%, 67 at.% and 75 at.%. There are only two ground states from BCC lattice with W concentration of 75 at.% and 50 at.%. Since the W concentration range for the ground-state calculations in BCC
lattice was [0.5, 1], the ground states at 50 at.% W from BCC lattice may not be a real ground states but just a boundary for constructing the convex hull. The formation energies rescaled according to Eq. 4.3 and Eq. 4.4 of all the calculated ∼1000 alloy configurations are included in Figure 4.8. Green and blue points represent formation energies of configurations with HCP based lattice structures, while pink and red points are for configurations with BCC based lattice structures. The solid red and blue lines sketch the convex hull of energies for BCC- and HCP-based structures, respectively, and highlight low-energy atomic structures for each set. The overall convex hull is indicated with a solid black line that connects the thermodynamically stable ground states.

In this study, we are mostly interested in the structure stability of W-Os alloys at the high operating temperature of Os-coated tungsten dispenser cathodes (above 1000°C). Although in Figure 4.8, we only obtain two ground states, with W concentrations of 12.5 at.% and 25 at.% from the overall black convex hull. The other ground states (with
Figure 4.8: Formation energies as a function of W concentration for all the calculated W-Os configurations with various atomic arrangements. The blue and red convex hulls are constructed from HCP and BCC-based configurations, respectively. The black one is the absolute convex hull connecting the two ground-state alloys.

formation energies at the blue and red convex hull) are also possible to be stable at temperatures above 1000°C with the contribution of entropy. This is supported by the experimentally observed tetragonal (tP30) W-Os alloy ($\sigma$ phase in Figure 3.4) at above 1000°C. In Figure 4.8, we have identified a tetragonal W-Os alloy at 75 at.% W from BCC lattice, which has much lower formation energy than that from HCP lattice at the same W concentration. Thus we expect that this tetragonal W-Os alloy calculated from BCC lattice can be stable at the high temperatures. The other structures calculated from HCP lattice: WOs$_7$ (12.5 at.%W), WOs$_3$ (25 at.%W), W$_3$Os$_5$ (37.5 at.%W), WOs (50 at.%W), all have much lower, and W$_2$Os (67.5 at.%W) have only a little higher formation energies than the tetragonal W$_3$Os (75 at.%W) from BCC lattice. Thus in this work, we will study the composition-structure-property relationships for these five structures from HCP lattice and the one tetragonal W-Os from BCC lattice.
Figure 4.9 shows the primitive unit cells of the five low-energy HCP-based W-Os alloys identified for W concentrations less than 70 at%, plus the one low-energy BCC-based structure with 75 at.% W concentration, and that of the stable pure BCC W and HCP.
Os. The crystal structure type is represented in the form of chemical-formula在这方面，Pearson-symbol (space group), where oF means a face-centered orthorhombic, hP primitive hexagonal, mC base-centered monoclinic, tP primitive tetragonal, cI body-centered cubic and the numbers following those symbols represents the number of atoms per unit cell. Table 4.2 reports the structural parameters of the 6 DFT-calculated W-Os alloys shown in Figure 4.9.

Previous experimental determinations of crystal structures and lattice parameters are available for a number of alloy compositions close to those of five of the low-energy alloy structures. In those experimental studies, x-ray and micrographic techniques were used to determine the phase and lattice parameters of W-Os alloys that had been rapidly quenched from 2400 °C. As can be seen in Table 4.2, excellent agreement between computed and measured properties is observed for W-Os compositions except those with greater than 50 at% W. While experimentally determined lattice parameters are not available for 50 at% W alloys, the crystal structure has been experimentally identified as orthorhombic AuCd[214], same as found here. Based on the formation energies reported in Figure 4.8, the W-Os system is predicted to have only two absolute ground state alloy structures (face-centered orthorhombic WOs7, and hexagonal WOs3) plus the pure component end points. In contrast, the high-temperature W-Os phase diagram shows no intermediate face-centered orthorhombic alloy phase, but a tetragonal σ phase that is stable at W concentrations greater than ~60 at% W. This corresponds to the composition region where agreement between computed and measured lattice parameters falters. The present calculations do, in fact, identify a low-energy tetragonal structure (W3Os), but its computed formation enthalpy is well above that predicted for a two-phase system consisting of pure BCC W and hexagonal WOs3, see Figure 4.8. Previous calculations screening for W-Os ground state structures using a similar methodology as the present work has identified a tetragonal structure with a larger unit cell, tP30 (W22Os8) that has lower formation energy[215]. Computed structural properties of this
W_{22}Os_{8} (73.3 at% W, see Figure 4.10(a)) tP30 structure give excellent agreement with experimental results of σ phase W-Os, see Table 4.2.

TABLE 4.2: The lattice constants of the W-Os alloys obtained by quantum mechanical calculations, compared with experimental results

<table>
<thead>
<tr>
<th>at%W phase</th>
<th>at%W structure</th>
<th>Lattice constant()</th>
<th>c/a ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>this study</td>
<td>Exp. this study</td>
<td></td>
</tr>
<tr>
<td>10 θ</td>
<td>12.5 oF32</td>
<td>(a=2.74, c=4.34)</td>
<td>1.5825</td>
</tr>
<tr>
<td>30 θ</td>
<td>25 hP8</td>
<td>(a=2.76, c=4.41)</td>
<td>1.5961</td>
</tr>
<tr>
<td>40 σ + θ</td>
<td>37.5 oF32</td>
<td>(a=2.76, c=4.45)</td>
<td>1.6090</td>
</tr>
<tr>
<td>50 σ + θ</td>
<td>50 oF32</td>
<td>(a=2.75, c=4.40)</td>
<td>1.5901</td>
</tr>
<tr>
<td>66.7 σ</td>
<td>66.7 mC12</td>
<td>(a=9.63, c=4.98)</td>
<td>0.5170</td>
</tr>
<tr>
<td>75 σ</td>
<td>75 tP4</td>
<td>(a=9.66, c=5.01)</td>
<td>0.5181</td>
</tr>
<tr>
<td>64~80 tP30</td>
<td>73.3 tP30</td>
<td>(a=9.65, c=4.99)</td>
<td>0.5171</td>
</tr>
</tbody>
</table>

Note: the experimental data of the σ-tP30 phase (at T ≥ 1000 °C) are from Ref. [141]. All the other experimental results are from Ref. [140].

Considering the predicted intermediate face-centered orthorhombic phase, we note the HCP and face-centered orthorhombic primitives identified here differ only by the symmetry of their arrangement of W and Os atoms. That is, they all exhibit HCP layer stacking by atomic positions, but the pattern of which atomic position is occupied by W and Os atoms in the layers breaks the AB stacking symmetry. More generally we note that HCP, FCC, and orthorhombic primitives can all be outlined for the same arrangement of atomic positions (see Figure 4.10 (B)). In a two component alloy like W-Os, the ordering of W and Os on specific atomic sites will determine which symmetries are retained, and what the primitive cell is for the structure. If composition was to be ignored, it would have an HCP primitive (maximum symmetry), but accommodating which atomic positions are W atoms and which are Os atoms yields orthorhombic primitives as symmetry is broken.

In this way, at finite temperature, where W and Os atoms exhibit thermally induced disorder on the crystal lattice sites, time and space averaged measurements of
Figure 4.10: The atomic arrangement of $W_{22}Os_{8}\cdot tP30(P4_2mm)$ (a); The standard unit cell (red), primitive cell (green) and hexagonal cell (deep blue) drawn in the oF32 WOs crystal lattice. The size of W atoms has been enlarged in order to distinguish them from Os atoms. Atoms in green color belong to the primitive cell and deep blue atoms belong to the HCP cell.

atomic structure in experiments (e.g., XRD) will see increased symmetry compared to the ground state structures as lattice sites become indistinguishable from each other due to W and Os site switching. We note that in all HCP and face-centered orthorhombic structures both the W and Os atoms are 12-fold coordinated. Therefore, the energy penalty for site exchange-related disorder in these structures is expected to be low, and at the temperatures relevant for the W-Os phase diagram the symmetry destroying ordering of W and Os on crystal lattice sites is likely not observed: hence, the experimental determination of a single solid solution HCP phase for W-Os with low W concentrations in Os.

In contrast, in BCC-based structures (like $tP30$), W atoms exhibit a range of coordination states, with some W atoms having as few as 5 coordinating neighbors. Os atoms remain 12-fold coordinated. This implies that exchanging W and Os requires overcoming a larger energy penalty than exchanges on HCP-based lattices, and highlights the sensitivity of the overall formation enthalpy of BCC-based structures to details of atomic ordering. This likely explains why the $\sigma$-phase requires a large primitive cell that is not well resolved in the present cluster expansion calculations.
4.2.2 Structures of W-Os-Ru Ternary Alloys

The ground-state structures of W-Os-Ru ternary alloys were calculated in the same way as for the W-Os binary alloys. Since Ru is HCP, same as Os, ground-state calculations were performed also in HCP and BCC lattices. The formation energies, using reference energies of HCP Os, HCP Ru and BCC W, of the ground states calculated from HCP and BCC lattices are included in Figure 4.11. The blue data points are formation energies for ground states from HCP lattice and red data points are that from BCC lattice.

For W-Os-Ru ternary alloys, the convex hull connecting all the ground-state formation energies are in 3-dimensional with concentrations of W, Os, Ru as the three base vectors. Figure 4.11 shows the formation enthalpy of ground states, from HCP (blue curve) and BCC (red curve) lattices, as a function of W concentration. Therefore the curves are not convex hulls as that in Figure 4.8 and thus it is reasonable to see several different alloys, WOsRu$_2$, WOs$_2$Ru and W$_2$Os$_5$Ru that have same W concentration of 25 at.% having different formation energies but are all ground states.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.11}
\caption{Formation energies of the ground states of W-Os-Ru ternary alloys from HCP (blue) and BCC (red) lattices.}
\end{figure}
The primitive unit cell structures of the ground states, WOsRu\textsubscript{6} (hexagonal), WOsRu\textsubscript{2} (base-centered orthorhombic), WOs\textsubscript{2}Ru (base-centered orthorhombic), W\textsubscript{2}Os\textsubscript{5}Ru (base-centered monoclinic), W\textsubscript{3}OsRu\textsubscript{4} (face-centered orthorhombic), W\textsubscript{2}OsRu (base-centered monoclinic), W\textsubscript{4}OsRu (base-centered monoclinic), W\textsubscript{6}OsRu (orthorhombic) are shown in Figure 4.12. The W\textsubscript{6}OsRu with 75 at.% W is the ground state calculated from BCC
lattice, but it has a crystal structure of orthorhombic rather than tetragonal as for W₃Os and the σ phase in Figure 3.4. However, the atomic arrangements are very much like that for tetragonal W₃Os except some of the Os atoms are replaced by Ru atoms. All the other structures are from HCP lattice.

4.2.3 Electronic Properties of W-Os and W-OsRu Alloys

![Figure 4.13: Density of states of hcp Os (a), the predicted ground-state structures (W-Os binary alloys in black line and W-Os-Ru ternary alloys in other colors) (b)∼(g), and bcc W (h). The vertical blue dashed lines are positions of the Fermi level.](image)

Having determined detailed atomic arrangements relevant to W-Os/OsRu alloys in thermionic cathodes, we now turn to assessing the electronic properties of these alloys, the electron density of states that characterizes the distribution of electron states at each energy. For thermionic emission, bound electrons in a solid (cathode material) are excited to unbound vacuum states via thermal energy to overcome the surface barrier (work function) and contribute to the electron emission. Before heating, electrons stay
mainly at bound states at/below the Fermi level. According to Fermi-Dirac statistics, the probability that an arbitrary electron will be thermally excited to the unbound states (with energy of the value of $E_F + \phi$ as for thermionic emission) decays exponentially with energy—that is to say, the ground state electrons most likely to be excited to states with energy sufficiently enough to overcome the surface barrier are simply those in states near the Fermi level. Electrons originating from states farther below the Fermi level require a larger excitation, and therefore are less likely to overcome the barrier. Thus the electrons in states near the Fermi level (before heating) are expected to be most relevant to thermionic emission.

Computed eDOS for low-energy W-Os/OsRu alloy configurations are shown in Figure 4.13, with the Fermi level indicated for each with a dashed blue line. All considered alloys exhibit qualitatively similar eDOS containing a pseudogap (region in energy of low DOS) near the Fermi level—a feature typical of many transition metals or alloys[216]. The position of the Fermi level relative to the pseudogap, though, varies for different W-Os/OsRu configurations. Similar pseudogaps in other alloy systems have been observed, and the positions of Fermi level have been found to be related to a range of bulk properties, including structure stabilities and melting point (low DOS at the Fermi level has been reported to correlate with high structure stability and high melting point)[216, 217].

Here we are particularly concerned with the total eDOS at or just below the Fermi Level, as these “near-Fermi” electrons represent the dominant contributors to the set of electrons thermally emitted from W-Os surfaces during thermionic emission. In Figure 4.13, the eDOS for binary and ternary W-Os alloys with same W concentration were plotted in same graph, which turn out to be very similar (for both the overall eDOS curves and positions of Fermi level). From Figure 4.13 (a)∼(e), for pure HCP Os and WOs$_7$/WOsRu$_6$, the Fermi level sits in the middle of the pseudogap and moves close to the left edge of the pseudogap for W-Os/OsRu alloys with larger W concentrations of
25 at.%, 37.5 at.% and 50 at.% W. For W$_2$Os/W$_4$OsRu with 66.7 at% W, the Fermi level sits right at the edge of the pseudogap with high DOS. However, for both W$_3$Os and W$_6$OsRu, the Fermi level lies inside the pseudogap with very low eDOS just below the Fermi level, similar to HCP Os and BCC W.

Since the states below the Fermi level are occupied by electrons, the high DOS just below the Fermi level for W-Os/OsRu alloys with 25 at.%, 37.5 at.% and 50 at.% W indicate that larger amount of electrons are available to be thermionically emitted at a given temperature than for HCP Os, WOs$_7$/WOsRu$_6$, W$_3$Os/W$_6$OsRu and BCC W, which all have much lower DOS just below the Fermi level. That is, from the perspective of how many electrons are available with energies near the Fermi level, thermionic current from W-Os alloys should first increase with increasing W concentration (HCP Os and WOs$_7$ to WOs$_3$, W$_3$Os$_5$ and WOs), then decrease (WOs$_3$, W$_3$Os$_5$ and WOs to tP30 W$_{22}$Os$_8$ and BCC W). This conclusion from DFT calculated results is exactly as observed experimentally. This same trend also applies to W-Os-Ru ternary alloys due to the same eDOS properties.

### 4.2.4 Summary

Stable atomic configurations of W-Os alloys have been obtained by combining DFT calculations and the cluster expansion for both BCC- and HCP-family lattices. Computed structural parameters are very close to previous experimentally determined values. Differences in atomic structure between HCP, tetragonal and BCC W-Os/OsRu phases alter the position of the Fermi level relative to a pseudogap in the W-Os electron density of states. When the Fermi level is at the left edge of the pseudogap, and therefore there is high eDOS just below the Fermi level—as for high W-content HCP phases—thermionic emission is expected to be enhanced. In contrast, when the Fermi level is located near the top of the pseudogap—as for tetragonal and BCC W-Os phases—low near-Fermi electron density suggests weaker thermionic emission.
The W-Os-Ru ternary alloys have similar structures and about the same eDOS properties as the W-Os binary alloys, which has been proved by experimental phenomena that the thermionic emission from Os-coated and OsRu-coated tungsten dispenser cathodes are about the same. Thus, in this work, it is sufficient to study only the W-Os binary alloys for Os/OsRu-coated tungsten dispenser cathodes and properties/discoveries from the W-Os binary alloys could also be expected for the W-Os-Ru ternary alloys.

Returning to the key questions identified in section 1.2.1, we note that the present results suggest that the difference in electronic property (eDOS at or just below the Fermi level) has an important impact on the variation of thermionic emission with composition. The high eDOS just below the Fermi level for 12-fold coordinated HCP-based alloy phases WO$_3$, W$_3$Os$_5$ and WOs have been experimentally observed to have higher thermionic electron emission than the tetragonal phase with lower eDOS at or just below the Fermi level. This suggests that thermionic cathode lifetime could be extended by stabilizing high-W content HCP phases, which are expected to exhibit stronger thermionic emission. Finally, we note that the eDOS is a readily computed property that can be used in qualitative evaluation of thermionic electron emission for cathode materials.

### 4.3 Structures and Properties of W-Os Surfaces

Surface properties (Ba adsorption and work function) of non-coated tungsten dispenser cathodes have been widely studied and significant work function reduction by Ba adsorption has been demonstrated by both experimental and computational work. The desorption of Ba/BaO from the surface that lead to deterioration of this effect has been an main life-limiting factor for pure tungsten dispenser cathodes. However, for Os-coated tungsten dispenser cathodes, life-termination has been found to be associated with the presence of W-Os tetragonal phase when there are rich W in the Os coatings. While highest thermionic emission has been found with W-Os alloys of 30~40 at. % W.
In Section 4.2, we have determined the structures and investigated the eDOS of bulk W-Os alloys with various compositions and discovered the distinct eDOS properties for the HCP and tetragonal W-Os alloys. Here in this section, we are going to focus on the surface properties of four structures: HCP Os, HCP WOs$_3$, tetragonal W$_3$Os and BCC W in order to explore the differences between the pure elemental metals and alloys, and between the HCP and tetragonal alloys that have highest and significantly reduced thermionic emission, respectively.

4.3.1 Structures of Surface Slabs

![Figure 4.14](image)

**Figure 4.14**: top and side view of the supercell slabs: (a) W (001)/Ba; (b) Os (001)/Ba; (c) hcp WOs$_3$ (001)/Ba top surface; (d) hcp WOs$_3$ (001)/Ba bottom surface; (e) tetragonal W$_3$Os (001)/Ba top surface; (f) tetragonal W$_3$Os (001)/Ba bottom surface; (g) side view of W (001)/Ba supercell slab.
For W(001) surface, Dane Morgan et al.[143] have reported that the surfaces with Ba coverage of 0.25 monolayer (the number of Ba atoms is 1/4 that of the surface atoms) have higher stability and lower work function (comparable with previous experiments) for bare tungsten cathodes. Therefore in this work, (001) surfaces of HCP Os, HCP WOs₃, tetragonal W₃Os and BCC W with Ba coverage of 0.25 monolayer and Ba atoms sits on top of the hollow sites have been studied, see Figure 4.14 (A)∼(F), in order for better comparison. For each supercell slab, there were two surfaces, one on the top of the substrate unit cells (top surface) and one at the top of the vacuum region which is also the bottom of next supercell slab (bottom surface). For HCP Os, HCP WOs₃ and BCC W, the substrate top and bottom surfaces were the same. However, for tetragonal W₃Os, there are two different atomic arrangements along (001) surface, one with only W atoms and one with only Os atoms. The bottom surface was composed of only Os atoms, see Figure 4.14(f). In order to account for the different surfaces, a layer of Os atoms has been removed which left a terminated surface of W atoms, see the top surface in Figure 4.14(e). For the Ba adsorbed surfaces, the Ba atoms sit at the two opposite diagonals of the top and bottom surfaces, see Figure 4.14(c)∼(g), same applies for HCP Os and BCC W (001) surfaces. Because it has been found that putting adsorbed atoms at opposite diagonals of the two surfaces could yield better result than putting both Ba atoms at the same diagonal site of the two surfaces[218]. The Ba normal separation from the terminating substrate surface in the input structure files were about 2.7 Å for all the four structures, determined according to the radius and relative positions of W, Os and Ba atoms. However, after DFT minimum-energy structure calculations, Ba separations were 2.72 Å, 2.69 Å, 2.50 Åand 2.48 Å, for HCP Os, HCP WOs₃, tetragonal W₃Os and BCC W, respectively.
4.3.2 Work Function Results

Previous studies on Os/Ru-coated tungsten dispenser cathodes have discovered that HCP W-Os alloys have much stronger thermionic emission and also much higher substrate work function than for the tetragonal phase alloys with about 75 at.%W. The atomic structures of the HCP WOs$_3$ and tetragonal W$_3$Os as well as that of the elemental HCP Os and BCC W have been obtained in Section 4.2. Here the work functions of HCP Os, HCP WOs$_3$, tetragonal W$_3$Os and BCC W with and without Ba adsorption were determined from quantum mechanical calculation of electro-static potential. (001) surfaces were considered and the electro-static potentials as a function of distance from
the bottom surface of the super-cell are included in Figure 4.15.

In Figure 4.15, the potential energies have been plotted referenced to the Fermi level—the horizontal line at 0 eV. Thus the height of the electro-static potential in the vacuum region relative to the Fermi level depicts the surface work function, according to Eq. 3.3. It shows in Figure 4.15 that Ba adsorption decreases the work function of the (001) surfaces by more than 50% for all the four structures. The exact values of the calculated work functions comparing with known experimental results are included in Table 4.3. For HCP WO$_3$, the atomic arrangements of the top and bottom surfaces (see Figure 4.14) are slightly different, leading to unequal work functions, 1.91 eV and 1.86 eV, respectively. Mean work function value of top and bottom surfaces is reported in Table 4.3.

Table 4.3: Work functions of (001) surfaces without ($\Phi_{sub}$) and with ($\Phi_{sub,Ba}$) Ba adsorption, for HCP Os, HCP WO$_3$, tetragonal W$_3$Os and BCC W from our DFT calculations, compared with previous experimental data (exp.). $\Delta \Phi$ is the work function reduction by Ba adsorption from our calculations.

<table>
<thead>
<tr>
<th>(001)</th>
<th>$\Phi_{sub,exp}$/eV</th>
<th>$\Phi_{sub,Ba}$/eV</th>
<th>$\Delta \Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP Os</td>
<td>5.7[29]</td>
<td>5.39</td>
<td>1.96</td>
</tr>
<tr>
<td>HCP WO$_3$</td>
<td>5.3[128]</td>
<td>5.48</td>
<td>1.88</td>
</tr>
<tr>
<td>tetragonal W$_3$Os</td>
<td>-</td>
<td>4.54</td>
<td>1.86</td>
</tr>
<tr>
<td>BCC W</td>
<td>4.63[219]</td>
<td>4.65</td>
<td>1.97</td>
</tr>
</tbody>
</table>

According to Table 4.3, the work functions of HCP Os, HCP WO$_3$ and BCC W substrate surfaces from quantum mechanical calculations are very close to previous experimental data. The maximum difference of work function between our DFT calculations and previous experiments is 0.3 eV for hcp Os substrate (001) surface. The differences may be attributed to different surface orientations—our calculations only considers (001) surfaces while mixture of surfaces may exist in experiments. For HCP Os and HCP WO$_3$, the reported experimental work functions were not associated with
specific surfaces[29, 128]. However, for BCC W, the difference in work function between our DFT calculation and previous experiment is only 0.02 when W (001) surface was specified[219].

The HCP Os and WOs\textsubscript{3} has substrate work function larger than 5 eV, much higher than that of the BCC W and tetragonal W\textsubscript{3}Os, which have substrate work function of 4.65 eV and 4.54 eV, respectively. After adding Ba atoms onto the surfaces, the work function of HCP Os, HCP WOs\textsubscript{3}, tetragonal W\textsubscript{3}Os and BCC W all decreased significantly, as shown in Table 4.3. As can be noted from Figure 4.15, the Ba atom at the surface lowers the electro-static potential at that position for all HCP Os, HCP WOs\textsubscript{3}, tetragonal W\textsubscript{3}Os and BCC W structures. Meanwhile, the reduction of electro-static potential at the position of Ba atoms for HCP Os and WOs\textsubscript{3} is about 3.40 eV and 3.95 eV, respectively, much larger than that for tetragonal W\textsubscript{3}Os and BCC W, which are only 0.75 eV and 0.63 eV, respectively. This may be the reason for the larger work function reduction by Ba adsorption for HCP Os and WOs\textsubscript{3}, 3.43 eV and 3.60 eV, respectively, than that for tetragonal W\textsubscript{3}Os and BCC W, which both have work function reduction $\Delta \Phi$ of only 2.68 eV.

The work function of Ba-adsorbed (001) surface of HCP WOs\textsubscript{3} is lower than that of BCC W, which is consistent with previous experiments that the effective work function of Os-coated tungsten cathode is lower at HCP WOs\textsubscript{3} than that for the non-coated tungsten cathode. However, the Ba-adsorbed tetragonal W\textsubscript{3}Os (001) surface has smaller work function than Ba-adsorbed HCP WOs\textsubscript{3} (001) surface, different from the previous experimental results that the tetragonal phase has much lower effective work function than the HCP phase. The possible reason could be: 1) The stability of Ba adsorption on tetragonal W\textsubscript{3}Os surface is smaller than that on HCP WOs\textsubscript{3} surfaces, leading to more Ba desorption from the surface. In this case, the work function reduction by Ba adsorption for tetragonal W\textsubscript{3}Os is not effective, resulting in higher cathode work function, or lower thermionic emission. 2) The deterioration of thermionic emission from tetragonal
$W_3\text{Os}$ compared with HCP WOs$_3$ is not an effect of surface work function but due to the difference in bulk $\epsilon$DOS, as discovered in our previous work that tetragonal $W_3\text{Os}$ has much lower $\epsilon$DOS just below the Fermi level, where the electrons are most relevant to thermionic emission, than HCP WOs$_3$. This two possible reasons are going to be evaluated in the rest of this chapter.

4.3.3 Relative Stabilities of Ba Surface Adsorption

![Figure 4.16: Ba adsorption energies on (001) surfaces of HCP Os (0 at.% W), HCP WOs$_3$ (25 at.% W), tetragonal $W_3\text{Os}$ (75 at.% W) and BCC W (100 at.% W).](image)

We have found that Ba adsorption helps decrease the surface work function significantly, as shown in Figure 4.15 and Table 4.3. The DFT-calculated work function of Ba-adsorbed tetragonal $W_3\text{Os}$ (001) surface is smaller than that of HCP WOs$_3$, opposite to the experimentally observed larger cathode work function for tetragonal $W_3\text{Os}$. In order to find out whether this was due to the lower stability of Ba adsorption on the tetragonal $W_3\text{Os}$ surface, the formation energies of surface Ba adsorption on HCP Os, HCP WOs$_3$, tetragonal $W_3\text{Os}$ and BCC W (001) surfaces were calculated using Eq. 4.7. Lower surface formation energy of Ba adsorption surface corresponds to relatively higher stability. The result is included in Figure 4.16.
As shown in Figure 4.16, comparing with BCC W (001) surface, HCP Os, HCP WOs3, tetragonal W₃Os (001) surfaces all have lower Ba surface formation energies indicating relatively higher stability of Ba adsorption on Os-coated than on non-coated tungsten cathodes. Tetragonal W₃Os has the lowest Ba surface formation energy, which implies relatively higher Ba adsorption stability. In other words, Ba desorption is not the reason for the significantly reduced thermionic emission from tetragonal W₃Os than that from HCP WOs3.

4.3.4 Summary

In this section, we have investigated the surface properties (work function and Ba adsorption stability) of HCP Os, HCP WOs3, tetragonal W₃Os and BCC W (001) surfaces. The calculated work function for HCP WOs3 (001) surfaces with Ba adsorption is much smaller, 1.88 than that of HCP Os and BCC W, consistent with previous reported experimental phenomena of higher thermionic emission from HCP WOs3. However, the work function of Ba adsorbed tetragonal W₃Os has the lowest work function and high Ba adsorption stability, in which case a higher thermionic emission than that for HCP WOs3 would be expected. This is obviously opposite to the experimental phenomena that tetragonal phase leads to significantly reduced thermionic emission. As a result, surface properties (work function and Ba adsorption stability) are unable to explain the experimental phenomena of remarkably different thermionic emission from HCP and tetragonal W-Os alloys.

4.4 Thermionic Emission Calculations

4.4.1 Basic Theories

Here we developed an approach to calculate the thermionic current density based on Eq. 3.4, but using a different way to calculate or interpret the terms inside the formula
from previous studies. The supply function $N(T, E_q)$ is described as the number of electrons with energy $E_q$ passing through a unit surface per unit time. We incorporated the full DOS of the cathode materials (as discussed in section 4.2.3), Fermi-Dirac distribution $f(T, E)$, see Eq. 4.10, and electron drift velocity in calculating $N(T, E_q)$. The effects of surface work function was accounted for in the term $D(E_q)$.

$$f(T, E) = \frac{1}{e^{\frac{E-E_F}{k_BT}+1}}$$

(4.10)

As a result, the current density is described as the sum over the product of electron charge $e$, velocity $\frac{\partial E(k)}{\partial k}$, density of states $g(E_q(k))$, Fermi-Dirac distribution function $f(T, E)$ and the probability of overcoming the surface barrier $D(E_q(k))$. That is:

$$J(T, \Phi) = \frac{e}{\pi^3 \hbar} \sum_{E_q(k)} g(E_q(k)) f(E(k), T) \frac{\partial E(k)}{\partial k} D(E_q(k))$$

(4.11)

where $E_q$ has the same meaning as that in Eq. 3.4, describing the part of energy with motion normal to the surface, and $k$ is the wave-vector. The Fermi-Dirac distribution function $f(T, E)$ is a function of total energy $E$ because the occupation of the states is independent of electron emission direction. For thermionic emission, electrons obtained energy from heat sufficient to overcome the surface barrier are able to leave the cathode contributing to electron emission. The external electric field is very small so that the tunneling probability is negligible. Thus we described $D(E_q(k))$ as:

$$D(E_q(k)) = \begin{cases} 
1 & E_q \geq E_F + \Phi \\
0 & E_q < E_F + \Phi 
\end{cases}$$

As a result, Eq. 4.11 becomes:

$$J(T, \Phi) = \frac{e}{\pi^3 \hbar} \sum_{E_q \geq (E_F + \Phi)} g(E_q(k)) f(E(k), T) \frac{\partial E(k)}{\partial k}$$

(4.12)
In our previous work, we have introduced the DOS calculation using density functional theory (DFT) performed in Vienna *ab initio* simulation package (VASP)[193, 196]. In VASP, we obtained $e$DOS as a function of total energy, $g(E)$, that is the number of states at total energy $E$. Thus the number of electrons as a function of total energy $E$ can be easily obtained as $n_0 = \sum g(E)f(E, T)$. However, in order to obtain $e$DOS as a function of $E_q$, we need to figure out, at each state, not only the occupancy and total energy of electrons occupied at that states, but also $E_q$ of the electrons. Thus the density of states $g(E_q(k))$ in Eq. 4.12 are not the ones directly calculated from VASP, but was achieved by transforming Bloch wave functions from VASP to Wannier functions (performed in WANNIER90 program[211]) through VASP2WANNIER90 interface. In this way, the energy $E(k)$ as a function of wave-vector $k$ was obtained.

The electron velocity $\vec{v}_g$ are determined by the first derivative of $E$ to $k$ that were computed using tight-binding methods[87] performed in WNANNIER90:

$$\vec{v}_g = \frac{1}{\hbar \epsilon} \left( \frac{\partial E}{\partial k_x} \hat{x} + \frac{\partial E}{\partial k_y} \hat{y} + \frac{\partial E}{\partial k_z} \hat{z} \right)$$

(4.13)

then we can easily compute the kinetic energy $E_K$ according to:

$$E_K = \frac{1}{2} m_e \vec{v}_g^2 = \frac{m_e}{2\hbar^2} \left( \left( \frac{\partial E}{\partial k_x} \right)^2 + \left( \frac{\partial E}{\partial k_y} \right)^2 + \left( \frac{\partial E}{\partial k_z} \right)^2 \right)$$

(4.14)

Suppose the part of velocity and kinetic energy along the direction of electron emission are $\vec{v}_q$ and $E_{Kq}$, respectively, then

$$\vec{v}_q = \vec{v}_g \cdot \vec{q}$$

(4.15)

$$E_{Kq} = \frac{1}{2} m_e \vec{v}_q^2$$

(4.16)
\[\begin{align*}
E_q &= E_p + E_{Kq} \\
    &= E - E_K + E_{Kq} \\
    &= E - \frac{1}{2}m_e \vec{v}_q^2 + \frac{1}{2}m_e \vec{v}_q^2 \\
\end{align*}\] (4.17)

where \(\vec{q}\) is the unit vector in the direction of electron emission. \(E_p\) is the potential energy and \(m_e\) is the electron mass. We employed the electron mass instead of effective mass because it has been shown that for metals, it is adequate enough to use electron mass[113]. While if the cathode material includes semiconductors, the effective mass may have significant effects and need to be considered, which can also be calculated using the WANNIER90 program by taking the second-derivative of the electron band. Note that this thermionic emission current density calculation approach does not consider the space-charge effects. It only works in the temperature-limited region, where no space-charge effects present and the thermionic current density increases significantly with increase of temperature. However, the cathode operates usually at the highest temperature in the temperature-limited region. Thus this approach is applicable for the study of electron emission for thermionic cathodes.

All the terms in Eq. 4.12 are from first principles calculations on VASP or WANNIER90. The work function that determines \(D(E_q(k))\) has been calculated using DFT as discussed in section 4.3. The sum over all those terms according to Eq. 4.15 ∼ Eq. 4.17 and Eq. 4.12 was computed by our FORTRAN program to calculate the current density.

In Chapter 3, section 3.1.2.3, we have introduced the NEGF method for quantitatively predicting the thermionic current density, based on quantum mechanical calculations with no semi-empirical approximations, as also for our method. If the cathode material and adsorptions (composition and structure) have been determined, the NEGF method is useful for calculating thermionic current density to evaluate the predetermined substrate-adsorption materials. However, NEGF method reveals no structure-property relationships of substrate cathode materials or surface adsorptions, which are
important for understanding the thermionic emission mechanism and the discovery of novel materials.

Instead, our approach has been developed in the aim of exploring the structure-property relationships from materials science perspective, except for quantitatively calculating the thermionic current density. The role of both the surface work function and properties of bulk cathode material on thermionic emission have been elucidated for better understanding of cathode operation mechanism. And it discovered the significance of bulk cathode density of states, which can be readily computed to be used as an initial criteria for screening of composition/structure of bulk cathode material.

4.4.2 Thermionic Emission Current Density Comparing with Richardson Theory

The thermionic emission current density calculation method makes use of the bulk density of states of the cathode substrate materials. Since the work function is a property of the surface that depends on the surface orientation and can be largely tuned by surface adsorption[137, 145], here we calculated the thermionic current density as a function of work function at 1300 K—the operating temperature of Os-coated tungsten dispenser cathodes.

According to Richardson equation, Eq. 3.1, \( \ln J = -\Phi/kT + \ln(AT^2) \), \( \ln J \) is linearly related to work function \( \Phi \). Using the temperature of 1300 K and Richardson constant \( A_R \) of 120 \( A \cdot cm^{-2} \cdot K^{-2} \), the \( \ln J \sim \Phi \) relationship from Richardson equation was calculated and shown as the dark linear line in Figure 4.17 (A) and (B), since Richardson constant \( A_R \) is considered the same for different geometries or surface orientations. Using the method of this work, the thermionic current density from (001), (110), (111) surfaces for HCP WOs\(_3\) and tetragonal W\(_8\)Os are included in Figure 4.17 (A) and (B), respectively. According to Figure 4.17, \( \ln J \) calculated from our approach
is also linearly related with work function $\Phi$, same as Richardson theory. This proves, at least qualitatively, the accurate prediction of $\ln J \sim \Phi$ relationship from our method.

However, the values of $J$ vary with different structures and surfaces according to our calculated results, which the Richardson equation failed to address. The differences of thermionic current density between that calculated by our method, $J$, and that from Richardson equation, $J_R$, are depicted in Figure 4.18, where $dJ = J_R - J$. According to Figure 4.18, Richardson equation predicts significantly larger $J$ at work functions larger than 4 eV, than our method. The insets in Figure 4.18 (A) and (B) show more clearly the $J$ differences that is smaller but still distinguishable, at work functions lower than 4 eV.

In other papers, $J$ is reported as a function of temperature to find out the space-charge-limited or temperature-limited region in order to determine the best operating temperature. The operating temperature is usually determined as the highest temperature in the temperamentuer-limited region where the current density is the highest and cathode operates most efficiently. If operating temperature is higher, it goes into space-charge limit region where the increase of temperature leads to much smaller or even no increase in current density. Here we are looking at the relationship between $\ln J$ and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.17.png}
\caption{The $\ln J \sim \Phi$ relationship for HCP WO$_3$ (a) and tetragonal W$_3$Os (b) along different emission directions using our new approach comparing that from the Richardson equation.}
\end{figure}
work function $\Phi$ instead of the relationship between current density and temperature. The first reason is that our approach to calculate thermionic emission current density calculation in this work didn’t consider the space-charge effect. Thus it only works in the temperature-limited region, same as the Richardson equation. This is sufficient for the study of the thermionic emission properties of cathode materials because the cathode operates usually at the highest temperature in the temperature-limited region. Second is that the work function is surface-orientation-dependent and can be tuned by surface adsorptions under different conditions. To determine the exact current density for the thermionic cathode and compare $J$ among different structures, we need to know not only the work function of each surface but also find out which surfaces are presented in real cathodes. Determining the surface orientation of the cathode under the operating conditions can be challenging because it could be a mix of several different surfaces. This is out of the scope of the work described here. However, we have calculated the work function and properties of (001) surfaces for HCP Os, HCP WO$_3$, tetragonal
W₃Os and BCC W. In the following section, we will compute current densities to further test the accuracy of our new thermionic current density calculation approach by comparing with previous experimental results.

### 4.4.3 Thermionic Emission Current Density for Os-Coated Tungsten Dispenser Cathodes

Now that we have both the method and the surface work functions for HCP Os, HCP WO₃₃, tetragonal W₃Os and BCC W, the exact values of thermionic emission current densities at the operating temperature of 1300 K were calculated and the results are included in Table 4.4.

<table>
<thead>
<tr>
<th>structure</th>
<th>J (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>QM</td>
</tr>
<tr>
<td>HCP Os</td>
<td>0.562</td>
</tr>
<tr>
<td>HCP WO₃₃</td>
<td>13.43</td>
</tr>
<tr>
<td>tetragonal W₃Os</td>
<td>7.3</td>
</tr>
<tr>
<td>BCC W</td>
<td>2.58</td>
</tr>
</tbody>
</table>

According to Table 4.4, HCP WO₃₃ has much higher current density than tetragonal W₃Os and BCC W, same as the previous experimental studies. Our calculated $J$ for HCP WO₃₃ and BCC W are very close to experimental results. While the current density for tetragonal W₃Os from our method is smaller than that from experiments. The possible reasons are: 1) only (001) surface is considered here while in experiments, the cathode surface may not be (001) or can be mixture of several orientations. 2) for the cathode with surface layer composition of about 70~80 at% W[33], there may still
be some HCP phase left that contributes to the thermionic emission, leading to larger measured current density. The current density of HCP Os is much smaller than that of HCP WO$_3$, tetragonal W$_3$Os and BCC W, consistent with experiments that the current density is very low at the initial stage of cathode operation (no or few W at the coatings). This may also be the reason why Os is applied only as coatings instead of substituting the W matrix, apart from the reason of higher cost of Os.

To understand the effects of bulk electronic structure vs. surface work function of the cathode materials, we can compare the work functions discussed in the previous section and the current densities for HCP Os, HCP WO$_3$, tetragonal W$_3$Os and BCC W, see Figure 4.19. According Figure 4.19, the Ba adsorbed (001) surfaces of elemental metals BCC W and HCP Os have higher work function and much lower current densities, than that of the alloys. This is expected because current density is reversibly proportional to work function. However, though HCP Os and BCC W have about the same work function, the current density from HCP Os is much smaller, <1 A/cm$^2$. Similarly, the work function of tetragonal W$_3$Os is lower, but the current density is much smaller than that of HCP WO$_3$.

![Figure 4.19: Work function of Ba adsorbed surfaces (dark) and current density (blue) as a function of W concentration.](image)
Due to the surface stability of Ba adsorption for tetragonal W$_3$Os, Ba depletion may not be the reason for thermionic emission reduction of tetragonal W$_3$Os. The work function of Ba-adsorbed (001) surface of tetragonal W$_3$Os is lower than that of HCP WO$_3$, in which case higher thermionic emission from tetragonal W$_3$Os is expected to contradict with experimental results. Thus, we suggest that the thermionic reduction of tetragonal W$_3$Os is attributed to the structure-dependent DOS, which has been overlooked in most of the previous studies, rather than surface Ba adsorption/desorption.

### 4.4.4 Summary

Here we have introduced our new approach to quantitatively calculate thermionic emission current density purely from quantum mechanical calculations, in an aim of understanding the relatively structure-property relationships of both cathode substrate and surface from the materials perspective. This method has been applied on HCP Os, HCP WO$_3$, tetragonal W$_3$Os, and BCC W that involves Os-coated tungsten dispenser cathodes. The results have good agreement with previous experiments. In this method, both the surface work function and DOS of the cathode materials are addressed in studying the thermionic emission current density. Tetragonal W$_3$Os (001) surface with Ba adsorption has a lower work function, and relatively higher stability than HCP WO$_3$ (001) surface. But the calculated thermionic current density with inclusion of eDOS for tetragonal W$_3$Os is much lower than that of HCP WO$_3$. These results suggest that it is not the surface properties—work function or Ba desorption, but the structure-dependent eDOS, that is responsible for the thermionic emission reduction of tetragonal W$_3$Os. This result also supports our previous hypothesis on the qualitative evaluation of thermionic emission according to the DOS properties in section 4.2.

Although only (001) surfaces were considered in this work for HCP Os, HCP WO$_3$, tetragonal W$_3$Os, and BCC W, which may not be the real case for tungsten dispenser
cathodes, the work function and eDOS calculations by DFT are well-developed, and can certainly be used for other surfaces and materials. And the methods introduced in this work can be used to explore the thermionic emission properties of other known or candidate cathode materials.
Chapter 5  Monomer Design for Light-Mediated ROMP

5.1 Azobenzene-Containing Molecules Under Consideration

Here we use quantum chemical calculations to design novel AB-containing monomers in which RSE (and therefore ROMP) can be controlled by the reversible cis-trans photoisomerization of AB. The monomers designed here are expected to enable light-controllable ROMP, specifically, to allow the application of different wavelengths of light to activate or deactivate ROMP by modulating RSE. Light-controllable ROMP will not only enable a remote, non-invasive and instantaneous temporal control of ROMP beyond reliance on the exhaustion of added catalyst or the addition of a termination reagent[75, 169, 170, 220] (see Figure 3.5), but also, through the use of optical masks and filters, allow coincident spatial control of ROMP, allowing unprecedented ability to fabricate complex, patterned, photo-responsive polymers.

The composition of AB-containing monomers AB(m,n) to be considered in this work have been shown in Scheme 1.1. As shown in Figure 1.3, the ROMP process involves a closed ring-shaped monomer as reactant but also a open form (C=C double bond in the attached linker is broken) of it as product. The dangling C bonds for the open form are passivated with methylene groups at each end (that is, -C* groups are passivated to form -C=CH₂) that are used to bind to nearby open molecules in ROMP. The open and closed form of the monomer will be depicted as open-AB(m,n) (see Figure 5.1) and closed-AB(m,n), respectively in this work.

As a result, in this work, we will first calculate the geometries and properties of single AB, ABn molecules for comparison with previous experimental and computational results in order to verify the accuracy of our calculations. Then the isolated linkers L(m,n), open- and closed-AB(m,n) monomers (both in trans and cis) with various size
with AB in cis conformation. trans open-AB(m,n) is not shown but has the same structure except AB in trans.

Figure 5.1: The structure of open-AB(m,n)

of (m,n): (1,1), (1,2), (2,2), (2,3), (3,3), (3,4), (4,4) and (5,5) will be studied in order to identify the optimal monomer for mediated ROMP synthesis following the three design criteria as specified in section 1.3. trans and cis refers to the conformation of AB in the monomers.

5.2 Computational Details

All the quantum chemical calculations based on DFT and TDDFT for azobenzene-containing molecules were performed in the Gaussian09[221] package, available in the high-performance supercomputer in University of Kentucky, using the orbital basis sets expansion as introduced in section 2.7. The calculation details on geometries, energies and properties, e.g., ring strain energy, UV/Vis spectra, nuclear magnetic resonance (NMR) spectra and molecular orbital, will be introduced.

5.2.1 Geometry Optimization of Azobenzene-Containing Molecules

The B3LYP exchange-correlation functional[80] and 6-31G* basis set for wave function expansion[222] were employed in this work based on the excellent agreement between computed and measured results in numerous previous studies[18, 99, 192, 223, 224]. Full geometry optimization (ground-state structure calculation) was performed
for each of the molecules, with similar processes as for periodic W-Os systems except for the use of orbital wave function expansion. Since it is not easy to find the minimum-energy geometry, several initial input geometries generated from either by drawing and optimizing using MMFF94 force field in the software Avogadro[225], or from the conformation search using the chemical package Marvin (version 14.12.15, http://www.chemaxon.com), were optimized in Gaussian. Those calculations ended up with different local-minimum energy geometries and the one with lowest energy was further checked (stability verification by harmonic vibrational frequency calculations) and then studied as a stable structure when there were no imaginary frequencies. The frequency calculations also produce energy informations with thermal corrections (enthalpy, Gibbs energy, and even entropy) at finite temperature, e.g., 298 K as in this work.

Geometry optimization calculations were first performed in gas phase (default). In order to obtain stable geometries in a solution like in experiments, a following optimization calculation was performed by using the optimized geometry in gas phase as input, and specifying the solvent e.g., dichloromethane (CH$_2$Cl$_2$, DCM, used in this work except as noted below)—a widely used organic solvent that could dissolve azobenzene-containing molecules, in the route section of Gaussian input file. The solvation effects were accounted for by using the integral equation formalism variant of polarizable continuum model (IEFPCM), where the solute is placed in a cavity created via a set of overlapping spheres within a continuous medium (the solvent) with dielectric constant $\epsilon_r$[226, 227].

All the following calculations for studying properties like ring strain energy, excitation energies, UV/vis spectra, NMR, etc. used the minimum-energy geometries from optimization calculations.
5.2.2 Enthalpy of Formation and Ring Strain Energy

In order to address criterion (i), the formation enthalpies were calculated for open and closed AB(m,n) rings to compare the thermodynamic stability of the ring monomers.

![Scheme 5.1: Constitution of cis AB(m, n) ring monomers (same applies for trans ring monomers) from ABn and half linkers, L(m) and L(n). This is used for calculation of formation enthalpy for AB(m, n) rings.](image)

Reference energies for formation enthalpy calculations are those corresponding to ABn, isolated linkers, and other relevant small molecular, e.g. HCl, H₂C=CH₂. To model formation enthalpies likely relevant to possible AB(m,n) synthesis pathways, we chose reference molecules for the linker portion as CH₂CH(CH₂)ₙCOCl “half” linkers [denoted L(m)/L(n)] for AB(m,n) monomers, which attach at opposite ends of ABn and close at C=C to yield AB(m,n) ring molecules, see Scheme 5.1. This reaction produces HCl and C₂H₄ as byproducts. As noted above, open linkers are passivated with methylene groups to mimic polymerized chains, and therefore enthalpy changes due to ring closing must account for two CH₂ groups, which we reference as H₂C=CH₂ molecules. The formation enthalpy can be calculated for open [oAB(m,n)] molecules as:

\[
\Delta H_f[oAB(m,n)] = H[oAB(m,n)] + 2H[HCl] - H[ABn] - H[L(m)] - H[L(n)]
\]

(5.1)

and for closed [cAB(m,n)] ring molecules as:
\[ \Delta H_f[cAB(m, n)] = H[cAB(m, n)] + 2H[HC\mathrm{I}] + H[H_2C = CH_2] - H[ABn] - H[L(m)] - H[L(n)] \] (5.2)

Scheme 5.2: Homodesmotic equation for the RSE calculation.

Ring strain energies, the driving force behind ROMP, for closed AB\((m, n)\) monomers were computed using a relative approach introduced by previous studies which showed good agreement with experimentally measured RSEs\([228–230]\). This approach is based on a homodesmotic equation from a reaction scheme\([229]\) with the closed ring as reactant and a strain-free open ring as the product, balanced with small alkane or alkene equivalents to keep the number of each type of carbon-carbon bonds (e.g., C-H, C-C, C=C) equal in reactants and products. For the ROMP reaction, the RSE is released by opening the closed monomers—that is, breaking the C=C bond. Thus in this study, the ring strain energy related to ROMP, is calculated according to Scheme 5.2 where a \(H_2C=CH_2\) reference molecule was used to ensure equivalent numbers of C=C double bonds in both reactants and products.

5.2.3 Excitation Energies and UV/Vis Spectra

Time-dependent DFT (TDDFT), as implemented in Gaussian 09 was used to explore the optical excitation energies and UV/Vis spectra. A number of previous calculations of the excitation energies of AB and AB derivatives have been reported based on different theories. Calculations employing TDDFT\([99]\), complete active space self-consistent field (CASSCF)\([151, 231]\) and perturbative iterative selection (CIPSI)\([232]\)
have all been reported, and while all methods have been demonstrated to deviate from experimental measurements, it has been shown that TDDFT generally predicts excitation energies that are below, but within 10% of experimental results[99]. Therefore TDDFT was used in this study to calculate vertical excitation electronic energies of AB\((m,n)\) monomers, by specifying ‘TD=(NStates=5, Singlets)’ in the route section of Gaussian input file, in order to determine the wavelengths necessary to trigger photoisomerization. Then energies for the first five excitations can be obtained and the UV/Vis spectrum can be evaluated from softwares like GaussView5[233].

5.2.4 Potential Energy Curves

Potential energy curves (PEC) allow investigation of the pathways and barriers for the photoisomerization of AB and AB-derivatives. According to the introduction in section 3.2.3, there are different pathways for the photoisomerization of azobenzene-containing materials. Here in this study, we performed PEC calculations for a subset of AB\((m,n)\) monomers, using the same method reported by Crecca and Roitberg[99]. For the investigation of rotation pathway, the variation of energy with the C-N=N-C (CNNC) dihedral angle (see Figure 1.2) changing from -40.0° to 220.0° at 10.0° intervals was calculated for the considered AB-containing molecules. For inversion pathway, the N=N-C (NNC) angle (see Figure 1.2) was changed from 80.0° to 180.0° also at a interval of 10.0° and local minimum-energy geometry at each angle was calculated. Atoms other than those in the CNNC or NNC angles were fully relaxed to their low-energy configurations. PECs for electrically excited monomers in the \(S_1\) and \(S_2\) states were generated by calculating the singlet vertical excitation energies for every point in the ground-state PEC using TDDFT[100] in the level of B3LYP/6-31G*. 
5.2.5 \( ^1\text{H} \text{ Nuclear Magnetic Resonance (NMR)} \)

NMR spectroscopy is a powerful technique for determining the structures of organic compounds[234]. Determination of NMR spectroscopy by both experiments and computations are well-developed, thus it can be an excellent tool for comparing details of computed and synthesized molecules.

In \( ^1\text{H} \) NMR spectroscopy, the chemical shift—the resonant frequency of proton relative to a standard reference in response to a magnetic field—of \( ^1\text{H} \) is detected for determining which functional groups and their positions are present. A commonly used standard for reference (also as solvent) of chemical shift measurement in experiments is deuterated chloroform (CDCl\(_3\)). In Gaussian09, deuterated chloroform is not available as a solvent but chloroform (CHCl\(_3\)), which has about the same dielectric constants of \(~4.711\) as CDCl\(_3\). Thus CHCl\(_3\) was used in our NMR calculations, where similar solvation effects and NMR chemical shifts would be expected as for CDCl\(_3\).

In this work, DFT was used to compute NMR chemical shift from calculations of magnetic shielding. Calculations used the Gauge-Independent Atomic Orbital (GIAO) method[235] in a two-step spin-spin coupling calculation[221] applied to relaxed molecular geometries—molecules optimized with solvation effect of CHCl\(_3\). Geometry optimization calculations for the standard reference molecule CHCl\(_3\) has also been performed and NMR chemical shift calculated. Then NMR chemical shifts, \( \delta \), were estimated as the magnetic shielding difference between the sample and the reference[236] for each proton in the sample molecules:

\[
\delta = \sigma_{\text{CHCl}_3} - \sigma_{\text{sample}} \tag{5.3}
\]

The NMR chemical shifts calculated in this work provides a reference for future experiments to evaluate the synthesized molecules.
5.3 Optimized Geometries

5.3.1 Calculated AB and ABn molecules

Before considering complete AB\((m,n)\) monomers, the structure and properties of isolated AB, and ABn molecules were studied. The calculated geometries of \textit{trans} and \textit{cis} AB, ABn are shown in Figure 5.2. Table 5.1 reports computed structural parameters and relative enthalpies (enthalpies of \textit{trans} conformations as references) for relaxed (minimum energy) \textit{cis} and \textit{trans} AB and ABn structures. Those results include that calculated in gas phase and in solvent DCM, and agree well with both previous experimental results for \textit{trans} AB crystals\cite{237} and \textit{cis} AB in benzene\cite{238}, as well as previous theoretical calculations\cite{99, 240–243}.

Note that the enthalpy differences in Table 5.1 are given for the higher enthalpy isomer of each molecule, which is, in this case, the \textit{cis} conformation. The calculated enthalpy of \textit{cis} AB is 0.64 eV higher (in gas phase) and 0.58 eV higher (in DCM) than
Table 5.1: Optimized geometries of trans and cis isomers of AB and ABn calculated in gas phase and with solvation effect of DCM, comparing with previous experimental results.

<table>
<thead>
<tr>
<th></th>
<th>angle/degree</th>
<th>distance/Å</th>
<th>∆ H*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>∠CNNC</td>
<td>∠NNC</td>
<td>d(N = N)</td>
</tr>
<tr>
<td><strong>trans</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB(gas)</td>
<td>180.0</td>
<td>114.8</td>
<td>1.26</td>
</tr>
<tr>
<td>AB(DCM)</td>
<td>180.0</td>
<td>115.0</td>
<td>1.26</td>
</tr>
<tr>
<td>AB exp.</td>
<td>180.0</td>
<td>114.1</td>
<td>1.25</td>
</tr>
<tr>
<td>ABn(gas)</td>
<td>179.9</td>
<td>115.0</td>
<td>1.27</td>
</tr>
<tr>
<td>ABn(DCM)</td>
<td>179.9</td>
<td>115.4</td>
<td>1.27</td>
</tr>
<tr>
<td><strong>cis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB(gas)</td>
<td>9.8</td>
<td>124.1</td>
<td>1.25</td>
</tr>
<tr>
<td>AB(DCM)</td>
<td>9.9</td>
<td>124.1</td>
<td>1.25</td>
</tr>
<tr>
<td>AB exp.</td>
<td>0.0</td>
<td>121.9</td>
<td>1.25</td>
</tr>
<tr>
<td>ABn(gas)</td>
<td>11.8</td>
<td>124.6</td>
<td>1.26</td>
</tr>
<tr>
<td>ABn(DCM)</td>
<td>12.5</td>
<td>124.9</td>
<td>1.26</td>
</tr>
</tbody>
</table>

*enthalpies here are relative to the thermodynamically more stable trans isomers.a. Ref.[237]; b. Ref.[238]; c. Ref.[239].

that of trans AB. This is very close to previously reported experimental values of 0.58 eV obtained for AB in solid phase[239]. For ABn, the enthalpy differences between cis and trans are 0.72 eV and 0.67 eV in gas phase and DCM solvent, respectively, both a little larger than for AB itself. The relative enthalpy for cis AB and ABn in gas phase are a little larger (about 0.05 eV) than the DCM-solvated values. These results indicates effects of DCM solvent and -NH₂ substitution functional group on the geometries and energies of AB.

5.3.2 Geometries of Isolated Linkers

The DFT optimized geometries of isolated linkers with different numbers of methylene groups—m and n values—with solvation effects of DCM are shown in Figure 5.3. Most of the linkers are planar, while L(1,2) and L(2,3) are not. This is likely a conformation effect to allow the carboxyl groups at the end of the linkers to align their anionic oxygen atoms on opposite sides of the linker chain. This occurs naturally for planar chains with even sums of m+n, but requires an internal rotation leading to non-planar chains for odd
Figure 5.3: Optimized geometries of the linkers with DCM solvation.

Figure 5.4: The lengths of the linkers (linked by the black line) as a function of \((m,n)\) values, and the end-to-end length of ABn (see the red data points). Those linkers are all obtained considering the solvation effects of DCM.

For longer chains like L(3,4), the importance of this effect diminishes, as the distance between the two carboxyl groups increases. In addition, solvation, specifically the dielectric effects of any solvent, will modify the lengths for which this effect is appreciable.

Regardless of linker planarity, the olefin linkers all have C=C in trans conformation, indicating that the trans olefin linkers are more thermodynamically stable than the cis olefin linkers. Meanwhile, the effective lengths of the linkers increase with increasing \(m, n\) values, as shown in Figure 5.4. The length of cis ABn is very close to that of
L(2,2) and the length of trans ABn is between that of L(3,3) and L(3,4). This suggests that it would be easier for cis ABn to form closed rings with linkers equal or larger than L(2,2). However, high strain would be expected for trans ABn closed by linkers shorter than L(3,4).

### 5.3.3 Geometries of AB(m,n) monomers

![The optimized geometries of the closed and open AB(m,n) ring molecules in cis and trans conformations with m= n.](image)

**Figure 5.5:** The optimized geometries of the closed and open AB(m,n) ring molecules in cis and trans conformations with m= n.
The optimized geometries of closed and open AB\((m,n)\) molecules in both *cis* and *trans* conformations are shown in Figure 5.5 for each L\((m,n)\) with \(m=n\) (as above structures were optimized with DCM as the solvent) and in Figure 5.6 for ring molecules with L\((m,n)\) of \(m\neq n\). Geometric parameters for all considered ring molecules are reported in Table 5.2. The AB units in open AB\((m,n)\) molecules, both *trans* and *cis* conformations, have quantitatively similar geometric parameters as isolated AB and AB\(_n\) molecules (see Table 5.2), with NNCC/NNC angles varying by at most 0.4° \((\Delta_{\text{max}} \leq 0.4°)\). In contrast, for closed-*trans* AB\((m,n)\) ring molecules the dihedral angles (CNNC) are all much smaller than the equivalent angles for open-*trans* AB\((m,n)\), and decrease with smaller linker lengths from 169.3° to 138.2°, where \(\Delta_{\text{max}}\) is as large as 31.1°. It can also be observed from Figure 5.5 that *trans* AB units in closed rings are not planar and are increasingly non-planar with decreasing linker lengths.

For closed-*cis* AB\((m,n)\) rings, CNNC and NNC angles vary with different length
TABLE 5.2: Bond angles (in degree) of the optimized closed and open trans and cis AB(m,n) ring molecules with different linker sizes. NNC1 and NNC2 are two of the NNC angles of AB. $\Delta_{max}$ is the range over which each bond angle varies among the AB(m,n) molecules.

<table>
<thead>
<tr>
<th>AB(m,n)</th>
<th>closed-cis</th>
<th>open-cis</th>
<th>closed-trans</th>
<th>open-trans</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CNNC</td>
<td>NNC1</td>
<td>NNC2</td>
<td>CNNC</td>
</tr>
<tr>
<td>AB(1,1)</td>
<td>8.3</td>
<td>120.3</td>
<td>120.3</td>
<td>11.6</td>
</tr>
<tr>
<td>AB(1,2)</td>
<td>9.4</td>
<td>121.3</td>
<td>121.5</td>
<td>11.7</td>
</tr>
<tr>
<td>AB(2,2)</td>
<td>11.3</td>
<td>123.2</td>
<td>123.2</td>
<td>11.6</td>
</tr>
<tr>
<td>AB(2,3)</td>
<td>10.8</td>
<td>121.8</td>
<td>123.2</td>
<td>11.5</td>
</tr>
<tr>
<td>AB(3,3)</td>
<td>8.6</td>
<td>120.0</td>
<td>120.0</td>
<td>11.6</td>
</tr>
<tr>
<td>AB(3,4)</td>
<td>11.8</td>
<td>124.1</td>
<td>124.2</td>
<td>11.6</td>
</tr>
<tr>
<td>AB(4,4)</td>
<td>10.7</td>
<td>123.7</td>
<td>124.8</td>
<td>11.6</td>
</tr>
<tr>
<td>AB(5,5)</td>
<td>10.5</td>
<td>123.5</td>
<td>124.1</td>
<td>11.6</td>
</tr>
</tbody>
</table>

$\Delta_{max}$ | 3.5  | 4.1  | 4.8  | 0.2  | 0.4  | 31.1 | 2.2  | 1.8  | 0.2  | 0.1 |

linkers, analogous to the increased non-planarity of trans AB in closed rings. Smaller CNNC angles are observed for closed-cis AB(1,1) and AB(1,2) since L(1,1) and L(1,2) are themselves shorter than cis ABn, which is therefore forced to bend closed more so than isolated cis AB or ABn. The length of L(2,2) is very similar to that of cis ABn, as shown in Figure 5.4, and the CNNC angle for closed-cis AB(2,2) is very similar to that of isolated AB, 9.9° (Table 5.1). Longer linker lengths result in relatively larger CNNC angles in closed-cis AB(m,n) ring molecules, except for AB(3,3) where the linker configuration seems to drive the ABn amino end-groups towards each other, resulting in a smaller than expected CNNC angle. Different NNC1 and NNC2 angles are present among the closed rings, likely resulting from details of the linker chain C-C backbone arrangement. In certain cases these internal effects result in asymmetric NNC1 and NNC2 values, while highly symmetric geometries connecting the N=N (at AB) and C=C (at the linker) bonds yield equal NNC1 and NNC2 angles and are observed for closed-trans AB(1,1), cis AB(1,1), cis AB(2,2) and cis AB(3,3), as seen in Figure 5.5.

As seen in Figure 5.5 and Figure 5.6, some of the alkene linkers in geometry optimized AB(m,n) molecules exhibit trans alkene conformations while others exhibit cis
Figure 5.7: Geometries of the closed cis (A) and trans (B) AB(2,2) monomers with alkenes in cis conformations calculated with solvation effect of DCM.

Table 5.3: Enthalpies of AB(2,2) with AB and olefin linkers in cis/trans conformations. The enthalpies for the molecules are in Hartree. ∆H are in kcal/mol. ∆H_{alkene} indicates the enthalpy change due to the conformation change of olefin-linker from cis to trans. ∆H_{AB} indicates the enthalpy change due to the conformation change of AB from cis to trans.

<table>
<thead>
<tr>
<th></th>
<th>alkene</th>
<th>∆H_{alkene} (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>cis</td>
<td>-1143.1968</td>
</tr>
<tr>
<td></td>
<td>trans</td>
<td>-1143.1977</td>
</tr>
<tr>
<td>∆H_{AB} (kcal/mol)</td>
<td>15.686</td>
<td>10.171</td>
</tr>
</tbody>
</table>

alkene conformations. The structures in Figure 5.5 and Figure 5.6 are optimized geometries in minimum energy configurations. At finite temperature, AB(m,n) molecules will sample a range of possible conformations, with the lowest energy conformations (highlighted in Figure 5.5 and Figure 5.6) dominating. We have studied the structures and energies of AB(m,n) molecules in local minimum energy configurations with the alkene in alternative conformations to those shown in Figure 5.5 and Figure 5.6. For example, the minimum-energy geometries of closed AB(2,2) have trans alkene as shown in Figure 5.5. Closed AB(2,2) with cis alkene linkers have also been calculated and are reported Figure 5.7 and the enthalpies of molecules in these alternative configurations.
are included in Table 5.3. Those results showed that closed AB(2,2) (both with AB in *trans* and *cis* conformations) with *cis* alkene have higher enthalpies than that with *trans* alkene configurations as that shown in Figure 5.5. Table 5.3 highlights that the influence of alkene conformation on enthalpy is small compared to the effect of AB *trans* or *cis* conformation. That is, while alkene conformations other than those reported in Figure 5.5 can likely be observed at finite temperature, alkene conformation changes will not alter the AB-conformation-driven trends in formation energy and RSE. Therefore, in the following we adopt a naming convention for AB(\(m,n\)) ring molecules that only specifies the AB conformation—that is, *cis* AB(\(m,n\)) denotes that the molecule has AB in the *cis* conformation, regardless of the alkene conformation.

### 5.4 Geometry Stability by Formation Enthalpy

To assess stability of AB-containing rings—that is, effectively criterion (i)—the enthalpy of formation of AB(\(m,n\)) ring monomers was calculated for both open and closed ring configurations. As noted above, we use the enthalpies of ABn and half linker precursors as reference energies. While other reaction precursors may be used to synthesize AB(\(m,n\)) rings, we employ this particular energy reference primarily to assess relative stability among different rings.

![Figure 5.8: Enthalpy of formation for closed and open *cis* AB(\(m,n\)) (a) and *trans* AB(\(m,n\)) (b).](image)

111
Although quantitative prediction of free energy changes for the opening/closing reaction are not possible due to kinetic and entropic effects that are beyond the scope of the present work, comparison of formation enthalpies of optimized closed and open AB\((m,n)\) molecules provides important insight into the relative stability and potential ease of synthesis of those ring molecules, as demonstrated by previous studies on other molecular systems[244–247]. Formation enthalpies calculated according to Eq. 5.1 for open AB\((m,n)\) molecules and Eq. 5.2 for closed AB\((m,n)\) rings are reported in Figure 5.8. Solvent (DCM) effects have been included in those calculations.

For cis AB\((m,n)\) ring molecules, formation enthalpies are all negative (exothermic) for both open and closed AB\((m,n)\) [Figure 5.8(a)], indicating high thermodynamical stability. However, for trans AB\((m,n)\) [Figure 5.8(b)], the formation enthalpies of the closed-trans AB\((m,n)\) are all positive (endothermic), but decrease as linker lengths become larger. This makes sense because short linkers can be seen bending the trans AB (see Figure 5.5), indicating high strain energy that increases the overall energy of the molecule–an effect that would decrease with longer linkers, as observed here. This indicates that closed-cis AB\((m,n)\) ring molecules are more stable than equivalent closed-trans AB\((m,n)\) ring molecules.

![Figure 5.9: The enthalpy differences between trans and cis AB\((m,n)\), \(\Delta H=H[cis\ AB(m,n)]-H[trans\ AB(m,n)]\).](image)

In contrast to some closed ring molecules, for both isolated AB and ABn, the thermodynamically stable conformation is the trans isomer. This is also the case for open AB\((m,n)\) molecules, see Figure 5.9 which shows the relative enthalpies of trans and cis
AB(m,n) ring molecules in open and closed forms. Positive values indicate that trans AB(m,n) conformations are thermodynamically more stable, while negative values indicate cis AB(m,n) conformations are more stable. For closed ring molecules, the relative stability of the trans and cis AB(m,n) isomers can be reversed, with cis AB(m,n) isomers becoming thermodynamically stable when linkers are shorter than L(3,4). This, of course, is just a restatement of the fact that sufficiently short linkers introduce non-trivial ring strain energy into closed-trans rings.

In combination these results point to two conclusions. First, closed AB(m,n) ring molecules are minimum-energy structures, and are stable against spontaneous decomposition. Second, open AB(m,n) molecules are more stable in trans conformations, similar to isolated AB and ABn molecules, while certain closed rings are more stable in the cis conformation. This second point implies that smaller closed-trans rings will exhibit a thermodynamic driving force for transformation to closed-cis conformations, and therefore that small [linkers shorter than L(3,4)] closed rings may not be shelf stable as trans isomers but as cis isomers.

5.5 Ring Strain Energies

The RSE for closed-trans and cis AB(m,n) rings was calculated according to Scheme 5.2 and the results are included in Figure 5.10. The RSE of closed-trans AB(m,n) rings is large (∼50 kcal/mol) for the small ring AB(1,1), and decreases monotonically with increasing linker length. The RSE of closed-cis AB(m,n) rings oscillates with increasing linker length in a narrow energy window between about 6 to 11 kcal/mol. Overall, cis AB(m,n) rings have smaller RSE than trans AB(m,n) rings for all except the largest considered one, AB(5,5) ring molecule.

The RSE trends in Figure 5.10 arise directly from the structural and thermodynamic data presented above. Effectively, for small linkers, closing trans ring molecules requires substantial bending of the AB (and linker) portions of the ring. For shorter

113
linkers, e.g. shorter than L(2,3), the linkers will also be stretched to bridge the ends of the longer ABn unit (see Figure 5.5). Longer linkers can arrange their C-C bond conformations to better accommodate both trans and cis ABn, reducing bending (that is, stretched or compressed bond lengths or angles) along the ring. Closed-cis rings exhibit low ring strain energies for at least two reasons. First, in contrast to trans ABn, the cis ABn has already closed about 120 degrees (sum of the supplementary angles of NNC1 and NNC2) of the ring. In addition, cis ABn is shorter than all but the two shortest linkers, implying that linkers larger than L(1,2) need not be stretched to close the ring. Finally we note that linkers substantially longer than either cis or trans ABn tend not to “force open” the ABn, rather they internally reconfigure their C-C backbones at no or very little energy cost.

We are now in a position to identify whether any of the considered ring molecules satisfy both criteria (a) and (b), above, and, if so, which monomer is optimal for enabling light-mediated ROMP. Fundamentally, we seek a ring monomer that is thermodynamically stable in the less-strained cis conformation, and exhibits a substantial difference in RSE between trans and cis conformations. Based on these criteria, we note
that all cis AB\((m,n)\) ring monomers are thermodynamically stable, but that the closed AB\((2,2)\) ring has a small RSE of 6.6 kcal/mol in cis conformation and a large difference in RSE between cis and trans isomers. It has been reported that the minimum required RSE for surface-initiated ROMP carried out in solution is 13.3 kcal/mol[248]. The RSE of cis AB\((2,2)\) is lower than this threshold value, while trans AB\((2,2)\) has a much higher RSE. This implies that for an AB\((2,2)\) ring monomer ROMP will be inactive when the monomer is in the cis conformation, but will be active when in the trans conformation. Therefore, if the AB unit in AB\((2,2)\) rings can be photoisomerized similarly to isolated AB and ABn, then AB\((2,2)\) rings will allow ROMP to be activated or deactivated simply through controlled exposure to light.

We also note that AB\((1,1)\), AB\((1,2)\) and AB\((2,3)\) have large differences in RSE between their cis and trans conformations. In these cases, though, the computed cis RSE is \(\sim 10\) kcal/mol, which is close to the critical RSE for driving ROMP. Therefore it may not be possible to deactivate ROMP simply by photoisomerization to the cis conformation of these ring monomers. In addition, the symmetric AB\((3,3)\) and AB\((4,4)\) rings also have very low RSE in cis conformations, but exhibit much smaller differences in RSE between cis and trans conformations compared to AB\((2,2)\). Therefore, AB\((2,2)\) would be expected to exhibit better photo-control of ROMP kinetics than either AB\((3,3)\) or AB\((4,4)\). In combination, the present results clearly identify AB\((2,2)\) as the optimal AB-containing ring monomer for enabling light-actuated ROMP.

5.6 Photoisomerization Mechanisms

5.6.1 Excitation Energies and UV-Visible Spectra

While AB\((2,2)\) ring monomers exhibit thermodynamic and structural properties that satisfy criterion (i) and (ii) for ring monomers that will enable light-actuated ROMP, it must also be determined whether such rings retain the favorable photoisomerization
capabilities of isolated AB molecules. This is simply criterion (c) from above: is photoisomerization of AB(2,2) possible and controllable? To assess this we first consider the absorption spectra of AB(2,2) rings. The UV-Vis absorption spectra of AB(2,2) molecules can be derived from TDDFT-based calculations of the electronic excitation energies.

![Absorption spectra](image_url)

**Figure 5.11:** TDDFT calculated UV-Visible absorption spectra for trans and cis AB, ABn, open and closed AB(2,2) monomers. For trans isomers, only closed-trans AB(2,2) has two absorption peaks, as seen in the inset.

Electron excitation energies along with oscillator strengths, $f$, for isolated AB, ABn, open and closed AB(2,2) monomers have been obtained from TDDFT calculations and are reported in Table 5.4. Calculated UV-Vis spectra are shown in Figure 5.11. Previous experimental studies have reported that the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitation energies for trans AB are 2.79 and 3.95[249] eV, respectively. For cis AB, the first and second excitation energies are 2.82 and 4.77[249] eV, respectively. All the excitation energies calculated by TDDFT will be systematically smaller than experimental measurements.
as observed here for AB, an effect previously ascribed to a charge-transfer effect between excited states[250]. Despite this, the qualitative trends in TDDFT excitation energies are considered to be accurate[250].

TABLE 5.4: Excitation energies and oscillator strengths $f$ for AB, ABn, open and closed trans and cis AB(2,2) monomers.

<table>
<thead>
<tr>
<th>structures</th>
<th>$S_0 \rightarrow S_1$ ($n \rightarrow \pi^*$)</th>
<th>$S_0 \rightarrow S_2$ ($\pi \rightarrow \pi^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E/eV</td>
<td>$f_1$</td>
</tr>
<tr>
<td>trans</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>2.58</td>
<td>0.0000</td>
</tr>
<tr>
<td>ABn</td>
<td>2.75</td>
<td>0.0002</td>
</tr>
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<td>open AB(2,2)</td>
<td>2.61</td>
<td>0.0003</td>
</tr>
<tr>
<td>close AB(2,2)</td>
<td>2.38</td>
<td>0.0733</td>
</tr>
<tr>
<td>cis</td>
<td></td>
<td></td>
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<tr>
<td>AB</td>
<td>2.61</td>
<td>0.0529</td>
</tr>
<tr>
<td>ABn</td>
<td>2.43</td>
<td>0.0979</td>
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<td>2.45</td>
<td>0.1042</td>
</tr>
<tr>
<td>close AB(2,2)</td>
<td>2.53</td>
<td>0.0877</td>
</tr>
</tbody>
</table>

Comparison of excitation energies among isolated AB, ABn, open and closed AB(2,2) monomers shows that while detailed excitation energies vary by up to $\sim 0.2$ eV ($\sim 0.7$ eV) for the $S_0 \rightarrow S_1$ ($S_0 \rightarrow S_2$) excitations, the ring monomer excitation energies are generally bounded by excitation energies for AB versus ABn. This implies that the effects on optical and photoisomerization properties of the AB unit by its presence within both open and closed AB(2,2) monomers are no larger than the effects of altering the end group of isolated AB. As ABn retains the favorable optical absorption and photoisomerization properties of AB, this is promising for the behavior of AB(2,2) rings. Interestingly, variations in oscillator strength are larger, suggesting that details of charge redistribution upon excitation may differ among isolated AB and AB(2,2) rings.

Moving beyond excitation energies, Figure 5.11 reports UV-Vis absorption spectra computed from the excitation energies and oscillator strengths reported in Table 5.4. Figure 5.11 shows that there is a single dominant absorption peak for AB, ABn, open
and closed AB(2,2) monomers with AB in the \textit{trans} conformation. This peak corresponds to the $S_0 \rightarrow S_2$ ($\pi \rightarrow \pi^*$) excitation. This is because the $n \rightarrow \pi^*$ transition is forbidden by symmetry, and is consistent with the (effectively) zero oscillator strengths reported in Table 5.4. However, the AB unit in closed-\textit{trans} AB(2,2) is no longer planar leading to a breaking of symmetry and a significantly larger (but still relatively small) oscillator strength of 0.0733 for the $n \rightarrow \pi^*$ excitation. Thus upon careful inspection (see inset), there is a second lower-intensity peak (the intensity is larger than that of $n \rightarrow \pi^*$ peak of \textit{cis} AB, see Figure 5.11(b)) at larger wavelength of about 521 nm, as seen in the inset of Figure 5.11 (a), indicating that $n \rightarrow \pi^*$ excitation is available for closed-\textit{trans} AB(2,2). In contrast, all the \textit{cis} conformations exhibit two distinct absorption peaks corresponding to $S_0 \rightarrow S_1$ (at larger wavelength) and $S_0 \rightarrow S_2$ (at smaller wavelength), respectively.

It is also noteworthy that, like for ABn, absorption peaks for AB(2,2) rings are red-shifted relative to peaks for AB. This effect is greater for \textit{trans} conformations, and is large enough to move the $S_0 \rightarrow S_2$ absorption peaks for \textit{trans} AB(2,2) into visible wavelengths. This may enable visible-light-based applications of both ring monomers and ring-based ROMP polymers. Finally, we note that successful light-mediated ROMP requires that \textit{cis}-to-\textit{trans} and \textit{trans}-to-\textit{cis} photoexcitation energies are distinct (that is, occurring at different wavelengths). As can be seen, both open and closed AB(2,2) monomers satisfy this requirement, and exhibit even larger differences in \textit{trans} versus \textit{cis} absorbed wavelengths than isolated AB molecules.

5.6.2 Potential Energy Curves

While excitation energies and UV-Vis spectra of AB(2,2) rings are qualitatively similar to those of isolated AB molecules, the ring structures do quantitatively modify excitation energy values (and absorption peak positions) and oscillator strengths. This leaves open the possibility that though light absorption by AB(2,2) is similar to that by isolated
AB, absorption (and therefore electron excitation) may not trigger photoisomerization. In addition, even if AB(2,2) monomers undergo photoisomerization, do they follow isomerization mechanisms similar to those for isolated AB?

To address these questions, potential energy curves (PEC) along the rotation and inversion photoisomerization pathways have been calculated in the $S_0$, $S_1$ and $S_2$ states. These pathways are calculated using the approach introduced by Crecca and Roitberg[99], which they applied to study the photoisomerization mechanism of isolated AB and ABn. We have calculated the PECs for the open and closed monomers as well as for isolated AB and ABn in order to compare with previous results and to verify our calculations.

**Figure 5.12**: Potential energy curves for (A) AB, (B) ABn, (C) open and (D) closed AB(2,2) along the rotation pathway. There are two minima for each PEC at ground state $S_0$. The left minimum corresponds to cis isomers and right minimum is the trans isomers.

**Figure 5.13**: Potential energy curves for (A) AB, (B) ABn, (C) open and (D) closed AB(2,2) along the inversion pathway. The left minimum at $S_0$ corresponds to cis isomers and right minimum is the trans isomers.
For the photoisomerization of unsubstituted AB, a conical intersection has been found between $S_0$ and $S_1$ along the rotation pathway at a CNNC dihedral angle of about 90° according to both CASSCF[192] and constrained TDDFT[240] calculations. The TDDFT-calculated PECs for isolated AB and ABn along the rotation [see Figure 5.12 (A) and (B)] and inversion [see Figure 5.13 (A) and (B)] pathways are very similar to previous studies. The PECs along the rotation pathway for open and closed AB(2,2) monomers [see Figure 5.12 (C) and (D)], are both similar to that of isolated AB and ABn (except an inverse relative stability of cis and trans conformations for closed AB(2,2) monomer), indicating that photoisomerization along the rotation pathway is also available for cis-to-trans isomerization of open and closed AB(2,2) monomers. For open AB(2,2) monomer, the PECs along the inversion pathway is very similar to that of isolated ABn [see Figure 5.13 (B) and (C)], that the $S_0 \rightarrow S_2$ excitation ends up to near the $S_2$ minimum, where the $S_1$-$S_2$ energy gap is very small, so that fast relaxation from $S_2 \rightarrow S_1$ can be expected. Therefore, though $n \rightarrow \pi^*$ transition is symmetry forbidden for trans ABn and open AB(2,2) monomer, $S_2 \rightarrow S_1$ relaxation after $S_0 \rightarrow S_2$ excitation allows for trans-to-cis photoisomerization following the rotation pathway at $S_1$ state. For isolated AB, there are no intersection between $S_1$ and $S_2$ for inversion pathway, as shown in Figure 5.13 (A), where concerted-inversion pathway is proposed for trans-to-cis isomerization[99, 179, 251, 252].

On the contrary, for closed-trans AB(2,2), there is no intersection between $S_1$ and $S_2$ along the inversion pathway, similar to that for isolated AB (see Figure 5.13). However, the $S_0 \rightarrow S_1$ excitation is not forbidden by symmetry due to the non-planar structure of the AB unit. Therefore, the rotation pathway at $S_1$ for trans-to-cis isomerization is available for closed-trans AB(2,2) monomers: after $n \rightarrow \pi^*$ excitation, the geometry of transAB(2,2) relaxes at $S_1$ surface from about 150° to 90° where $S_1$-to-$S_0$ transition occurs, following with further geometry relaxation at $S_0$ surfaces to ground states of either cis (in this case, trans-to-cis photoisomerization achieved) or trans (in this case,
this trans AB(2,2) at S0 can be excited to S1 again under same light). The cis-to-trans photoisomerization can occur in the same way after n → π* excitation for cis AB(2,2). However, n → π* excitation energies (or light wavelengths) for cis and trans AB(2,2) are different, see Figure 5.11, indicating the possibility for independent cis-to-trans and trans-to-cis photoisomerization by using blue and green light, respectively. It can also be seen in Figure 5.12(d) that the S1 PEC has a large gradient with respect to configuration, indicating fast structural relaxation can be achieved at S1 surface, which leads to faster trans-to-cis photoisomerization for AB(2,2) than for AB.

In summary, cis-to-trans photoisomerization can be achieved following the energy curve at S1 after n → π* excitation along the rotation pathway for all studied isolated AB, ABn molecules, as well as open and closed AB(2,2) molecules. The trans-to-cis photoisomerization can be achieved after S0 → S2 excitation for both ABn and open AB(2,2) molecule. The light wavelengths for cis-to-trans and trans-to-cis photoisomerization of open AB(2,2) molecule are different, 506 nm and 407 nm, respectively. For closed AB(2,2) ring molecules, cis-to-trans photoisomerization can be achieved under 489 nm (blue) light that induces the n → π* excitation for cis AB(2,2). Due to the presence of n → π* transition for trans AB(2,2), it is possible to reverse the isomerization and return to the cis conformation under 521 nm (green) light. Therefore, the light wavelengths for cis-to-trans and trans-to-cis photoisomerization of both open and closed AB(2,2) molecules are similar but distinct, allowing for separate control of the cis-to-trans and trans-to-cis processes—and therefore RSE modulation in closed AB(2,2) leading to activation/deactivation of ROMP—with monochromatic blue versus green light.

5.6.3 Molecular Orbitals

As noted in AB(m,n) monomers, there is the -C=C- part that is possible to undergo photoisomerization other than the azobenzene group. In order to make sure the S0 → S1
and $S_0 \rightarrow S_2$ excitation that enables the photoisomerization involves only the azogroup, we calculated the molecular orbitals using the HF/6-31$^*$ method. Figure 5.14 shows the resulted HOMO-1 ($\pi$), HOMO ($n$) and LUMO ($\pi^*$), where HOMO means highest occupied molecular orbital and LUMO means lowest unoccupied molecular orbital, for closed $trans$ and $cis$ AB(2,2) monomers.

Figure 5.14 shows that the first and second excitation involves only the azobenzene which indicates that using the calculated wavelengths of first and second excitation, only the azogroup in AB(2,2) monomers will be photoisomerized while the linkers arrange to maximumly reduce the energy of the monomer, with alkenes in either $cis$ or $trans$ conformation, not depending on the light.
Table 5.5: DFT calculated $^1$H NMR chemical shifts for open and closed AB(2,2) monomers. The positions of the protons are labeled in Figure 5.15. Note that closed rings doesn’t have $g$ protons because $e$ protons are adjacent to the symmetric $e$ protons when the ring closed at the C=C double bond. The open AB(2,2) has been successfully synthesized by collaborators Ishan Fursule in Dr. Brad Berron’s group. And the experimental NMR results are included for comparison.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$</th>
<th>$a$</th>
<th>$b$</th>
<th>$(c, d)$</th>
<th>$e$</th>
<th>$g$</th>
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<td>trans</td>
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<td>7.23</td>
<td>1.58</td>
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<td>5.55</td>
<td>-</td>
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</tbody>
</table>

Figure 5.15: The $^1$H protons in AB(2,2) molecules. Note that the molecule is symmetric around N=N thus only half of the molecule is shown, same for closed AB(2,2) with no $g$ protons.

5.7 $^1$H NMR Chemical Shift

Having identified a specific target monomer AB(2,2) with optimal properties for light-mediated ROMP, we turn to the determination of quantitative monomer properties that will be experimentally measurable, and therefore of critical importance to synthesis and purification efforts. NMR spectroscopy has been widely used to reveal configurational information about organic compounds and to explore molecular properties, including the structure, composition and chemical state of reactants and catalysts. As such, NMR will be a powerful tool for determining whether the specific ring monomer designed here actually results from synthesis efforts. The $^1$H NMR chemical shifts for cis and trans AB(2,2) monomers have been calculated and are presented in Table 5.5.
Open AB(2,2) monomer has been successfully synthesized by Ishan Fursule from Dr. Brad Berron’s group, collaborators who are responsible for the experimental part of this work. And the experimentally measured values are also included in Table 5.5. Corresponding protons in the system are indicated in Figure 5.15. As can be seen, the $^1\text{H}$ NMR chemical shifts for open AB(2,2) calculated in this work by DFT is very close to experimental results, which supported the accuracy of our DFT calculations, and verifies that the open AB(2,2) has been successfully synthesized. Meanwhile, NMR is able to distinguish between trans and cis AB(2,2), with observable differences present for the chemical shifts of the phenyllic a and b protons, for both open and closed configurations. Closed ring monomers also exhibit trans versus cis differences in chemical shifts associated with c, d, and e protons. These changes arise from a combination of the differences in electronic structure between trans and cis and the structural changes in closed rings when high RSE is present (e.g. bond stretching and bond angle bending). In short, NMR spectroscopy is capable of fingerprinting AB(2,2) and distinguishing both the state of the AB unit (trans or cis), and whether the rings are open or closed.

5.8 Summary

We have successfully designed a new type of azobenzene-containing monomer allowing for light-controllable fabrication of photo-responsive polymers through light-mediated ROMP by modulating RSE from photoisomerization of azobenzene. Based on investigation of stability, RSE and photoisomerization mechanism, the optimal monomer that maximizes light-mediated control of ROMP was determined to be the AB(2,2) ring molecule. Closed AB(2,2) ring monomers have low RSE (6.6 kcal/mol) and high stability in the cis conformation and high RSE (35.2 kcal/mol) in the trans conformation. The wavelengths for trans-to-cis and cis-to-trans photoisomerization of both open and closed AB(2,2) monomers are distinguishable so that reversible photoisomerization is possible and controllable using different wavelengths of light. The photoisomerization
mechanism for open AB(2,2) monomers is similar to that for isolated ABn, with cis-to-
trans isomerization triggered at the wavelengths of 506 nm after S₀ → S₁ excitation, and trans-to-cis isomerization triggered at 407 nm after S₀ → S₂ excitation. For closed AB(2,2) monomer, due to the availability of S₀ → S₁ excitation for trans AB(2,2) monomer, both cis-to-trans and trans-to-cis photoisomerization can occur along the rotation pathway after S₀ → S₁ excitation, but triggered at light wavelengths of 489 nm and 521 nm, respectively. The NMR chemical shifts and UV-Vis spectra calculated for open and closed AB(2,2) monomers are provided as a reference for future experimental studies.

This study of modulating the RSE by photoisomerization of AB unit in ring-shaped monomers opens up new applications for both ROMP synthesis and ring-shaped AB-containing compounds because RSE plays an important role in a number of reactions in organic chemistry. The large difference in RSE for closed AB(2,2) monomer in trans and cis conformations allows for control of ROMP using light of different wavelengths. When the monomer is in cis conformation, the RSE is very small so that ROMP is inactive with no polymers formed. The cis-to-trans photoisomerization results in highly-strained trans monomers readily to open up and form polymers (ROMP activated). After shining green light, trans-to-cis isomerization would occur and the closed monomers will remain closed so that ROMP become inactive again. This reversible isomerization allows for instantaneous control of activation/deactivation of ROMP, and thus the thickness of the films. By applying different light at different regions or by blocking light at certain regions, patterning is enabled. Therefore, by using this new type of monomer, temporal and spatial control of ROMP are available.
Chapter 6  Conclusions and Future Work

In this work, we have used first-principle methods based on fundamental quantum mechanics for: a) investigating thermionic emission mechanism for Os-coated tungsten dispenser cathode by exploring the composition-structure-property relationships of W-Os alloys; b) design of an innovative azobenzene-containing monomer for light-mediated ROMP towards unprecedented synthesis of patterned, photoresponsive polymers. Those two studies have proved that first-principles methods are powerful for studying and predicting the structure-property relationships related to their applications for both known and unknown materials.

6.1  Thermionic Dispenser Cathodes

6.1.1  Conclusions

Thermionic dispenser cathodes generates dense electron beams which are essential for high power electron devices. The demand for higher-power electron devices requires better thermionic cathodes with higher current-density beams. However, without comprehension of thermionic emission mechanism and understanding of the problems of current cathodes, it is difficult to design new cathodes. In this work, we investigated the composition-structure-property relationship of W-Os alloys searching for understanding of thermionic emission variation with composition for Os/OsRu-coated tungsten dispenser cathodes. Results and conclusions are:

- Bulk W-Os/OsRu alloys: Structures of W-Os alloys with various compositions have been calculated. The DFT identified stable W-Os alloys include HCP-based alloys with W concentration of 12.5 at.%, 25 at.%, 37.5 at.%, 50 at.%, 67.5 at.% and tetragonal alloys with about 75 at.% W. The lattice parameters of W-Os alloys
are comparable to previously known experimental studies. Structures and eDOS properties of the W-Os-Ru ternary alloys are very similar to that of W-Os binary alloys with same W concentrations. HCP-based alloys (except that with 12.5 at.% W) all have very high eDOS peaks just below the Fermi level. However, HCP Os, HCP WO$_{87}$ that has very low W content, and BCC W, tetragonal W-Os/OsRu alloys that are rich in W all have much lower eDOS just below the Fermi level. Since the electrons near the Fermi level are most relevant to thermionic emission, the thermionic emission from alloys with high eDOS peak just below the Fermi level is expected to be much larger. This result explains, at least qualitatively, the variation of thermionic emission with W-Os/OsRu composition.

- Surface W-Os alloys: The surface work function and Ba adsorption stability for HCP Os, HCP WO$_{83}$Os, tetragonal W$_3$Os, BCC W that represents the highest and lowest thermionic emission structures related to tungsten dispenser cathodes have been investigated. Ba adsorption lowers the work function of more than 2.0 eV for all those four structures. However, the calculated work function of Ba-adsorbed tetragonal W$_3$Os is lower than that of Ba-adsorbed HCP WO$_{83}$ surfaces. Meanwhile, the Ba adsorption stability is relatively larger on tetragonal W$_3$Os surfaces than on HCP WO$_{83}$. These surface property results suggest that higher thermionic emission can be expected for tetragonal W$_3$Os, which is opposite to previously reported experimental results. As a result, the surface properties, which are the focus of most previous research, are not the reason for reduced thermionic emission from tetragonal W$_3$Os.

- Thermionic emission current density calculations by incorporating both bulk eDOS and surface work function: We have developed a new approach based on quantum mechanics, with no semi-empirical approximations, to quantitatively calculate the thermionic current density. The calculated current density for HCP WO$_{83}$,
tetragonal $W_3$Os and BCC W are comparable to previous experimental results. Meanwhile, the analysis of effects of bulk (eDOS) and surface properties suggest that the significantly reduced thermionic emission from tetragonal $W_3$Os is attributed to properties of bulk eDOS, rather than surface work function.

Although we have only investigated the thermionic emission mechanism of Os-coated tungsten dispenser cathodes, the methods used in this work can also be applied to other materials systems. Meanwhile, we propose that the eDOS property of substrate cathode materials can be used to qualitatively predict the thermionic emission. Since eDOS is a property that can be readily obtained by DFT calculations, it can be used as a criterion for screening substrate cathode materials. While further verification of the cathode material screened from eDOS can be achieved by quantitatively calculating the thermionic emission current density. This could largely promote the process of better thermionic cathodes design.

6.1.2 Future Work

The current thermionic cathodes with highest thermionic emission current density are the scandate cathodes, which has emitted current densities greater than 100 A/cm$^2$. However, the problems of unstable and nonuniform thermionic emission have limited the large scale industry production of scandate cathodes. In the future, we expect to uncover the reason for those problems to finally solving these problems if possible, or designing better cathode materials using the screening criteria and computational methods as discussed in this work.
6.2 Cyclo-Azobenzene-Containing Molecules

6.2.1 Conclusions

We have designed an optimal cyclic monomer, closed AB(2,2), which consists of 4,4′-diaminoazobenzene (ABn) and alkene-α,ω-dioic acid linkers that possesses the following properties:

- High stability in a closed ring with cis AB. The thermodynamically more stable AB(2,2) monomer is the cis conformation that has a very low formation enthalpy of about -13 kcal/mol. The calculation of formation enthalpy uses reference energies of ABn, isolated linkers, and other small molecules likely relevant to possible AB(2,2) synthesis pathways.

- The RSE of trans AB(2,2) monomer is much larger than that of cis AB(2,2) monomer. Since the driving force for ROMP is RSE, it can be activated by trans AB(2,2) monomer while being inactivate with cis AB(2,2) monomer. This makes light-mediated ROMP possible through reversible trans-to-cis isomerization of AB(2,2) monomers.

- Reversible photoisomerization of trans and cis AB(2,2) monomers can be achieved with different wavelengths of light. The pathways for trans-to-cis and cis-to-trans photoisomerization has been investigated through the calculated potential energy curves and the light wavelengths have been determined through excitation energy calculations using TDDFT. Both trans-to-cis and cis-to-trans photoisomerization for closed AB(2,2) monomer can be achieved by geometry relaxation (the rotation of the CNNC dihedral angle) after \( n \rightarrow \pi^* \) excitation to \( S_1 \) surface, but with different wavelengths of light, 521 nm (green light) and 489 nm (blue light), respectively.
With this designed AB(2,2) monomer that is capable of modulating RSE by reversible cis and trans photoisomerization, ROMP can be activated under monochromatic blue light (trans AB(2,2) monomer) to trigger the formation of polymers. While under monochromatic green light (cis AB(2,2) monomer), ROMP is inactive with no formation of polymers. By applying different light in different regions or different time period, the thicknesses and patterns of the polymer films can be modulated regardless of complexity of surface geometries. Meanwhile, this synthesized polymers also have photoresponsive properties due to the AB group. As a result, this innovative monomer allows for unprecedented reversible, temporal and spatial control of ROMP for the synthesis of patterned, photoresponsive polymers.

### 6.2.2 Future Work

Beyond ROMP, RSE has also been found to promote click-reactions, for example, Diels-Alder\cite{253} reactions where cycloaddition of strained cycloalkynes/cycloalkenes and azides occur rapidly without using the conventionally toxic Cu(I) catalyst\cite{254–258}. Higher-strained cycloalkynes/cycloalkenes are desired for those click-reactions to enhance the reaction kinetics. However, the synthesis of high-strained molecules is difficult and the yield is low. With the ability to modulate RSE with light, the azobenzene-containing molecule designed in this work is promising in the application of click-chemistry: the ring molecule can be more easily synthesized in the low-strained and more stable cis conformation. Upon exposure to light of suitable wavelengths, the high-strained trans conformation can be obtained to activate the click reaction. This avoids difficulty in synthesizing high-strained ring-molecules and would allow for temporal and spatial light-mediation of click reactions used in drug delivery, in-vitro and in-vivo imaging or labeling.

The cyclic azobenzene-containing monomers studied in this work are capable of modulating RSE through reversible trans and cis photoisomerization and has also alkene
group in it. Thus we can directly use those molecules as cycloalkene reactants and study the click-reaction with tetrazines or other azides. Or we can modify these cyclic monomers a little bit by replacing the C=C double bond with triple bonds to form a cycloalkyne for the click reaction with azides. The stability of those cycloalkynes and reaction mechanisms of these click reactions can be studied and compared with that of currently well-known cyclooctene/cyclooctyne reactants. If it works as expected, this would be remarkable in the area of click chemistry and allows for combination of photo-chemistry with click-chemistry.
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