THEORETICAL ANALYSIS OF LATTICE ENERGY
AND MORPHOLOGY OF TRANSITION METAL
DICHALCOGENIDES

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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

                      Date                      Student Name
Abstract

This work is aim to understand the composition of chemical bonds and explore the mechanism to form different kinds of morphology of TMD nanocluster. We have developed a universal theory and methodology which can well predict the effective charge of a given materials from variant dimensions. The methodology has to be agile which can be extended to all the materials of all the dimensions, including 3D bulks, quasi 2D layer structures and nanoclusters. for the low dimensional materials, the quantum size effect, layer dependent effect and stacking dependent are all typical tasks to verify the robustness of the new theory extended in the low dimensions. The theory also used to understand the materials' properties in both the static property, like geometry shape, edge stability in nanoclusters, and dynamic property, like growth favorite sites in the nanoclusters.
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### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>NRs</td>
<td>Nanoribbons</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-ray Diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TMD</td>
<td>Transition-metal dichalcogenides</td>
</tr>
<tr>
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<td>X-ray Diffraction</td>
</tr>
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<td>Atomic Number</td>
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<td>ZZ</td>
<td>Zigzag</td>
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Chapter 1

Introduction

This chapter briefly introduced the motivation and objectives of this PhD project, stating out the main problem meet in experiment on the most popular material Transition-metal dichalcogenides recent years. A short overview of this thesis is given. Major outcomes of each charter are summarized.
1.1 Problem Statement and motivation

Two-dimensional materials[1] with inter-layer van der Waals (vdW) interactions have attracted intensive fundamental research attention due to their fascinating properties,[2-4] which led to the further development of comprehensive synthetic strategy aimed at preparation of layered materials in large scale size.[5-8] However, further improvements of their properties are essential to make these 2D materials applicable in more widely fields. One optional way to fine-tune the properties is through doping engineering. By far only some of the vdW 2D alloys have been realized by doping methods.[9, 10] Efficiently quantifying the distribution of dopants by understand the interaction between different elements at the atomic scale will remain as a key challenges, and understanding their influence on the material properties is also interest to be investigate. The isomorphism of the transition metal dichalcogenide (TMD) families (MX$_2$: M = Mo, W; X = S, Se, Te) makes them great candidates to form ternary vdW alloys that will not suffer from phase separation. Molybdenum disulfide (MoS$_2$) is a representative member of the TMD family, consisting of two layers of sulfur atoms and a layer of Mo sandwiched in between.

This material has recently been highlighted because by breaking down its inversion symmetry, the special band structure of monolayer MoS$_2$, provides excellent opportunities for applications in optical and electronic devices.[11-13] Synthesis of high-quality and large-area MoS$_2$ single layers has recently been reported.[6, 7, 14] Theoretical calculations also suggest that the band structure of MoS$_2$ could be modified by substituting sulfur atoms by other chalcogen elements like Se, to form TMD alloys.[15] This enables a tunable mechanism for varying the physical and chemical properties of MoS$_2$.

Phototransistors based on single-layer MoS$_2$ material exhibits a better photoresponsivity than that of graphene-based devices. Recent studies found that monolayer MoS$_2$ nanosheets can be considered as an ideal material for
exploring valleytronics and valley-dependent optoelectronics. In addition, low-dimensional MoS$_2$ nanostructures have also been demonstrated as a type of important materials in spintronics, catalysts, solar cells, and Li-ion batteries. In parallel with these advances, the need for high-quality, large-area monolayer materials have incited an incredible amount of work on thin film synthesis and growth. While graphene and the TMDs have historically been isolated via top-down methods such as mechanical exfoliation[16, 17] (the “scotch-tape” method), solution sonication,[1, 18] and electrochemical exfoliation,[19, 20] these methods are plagued by issues of low yield, small lateral dimensions, or poor quality. However, most of the potential applications and device performance of TMD are strongly dependent on the shape, crystallinity, size and edge structures of TMD nanosheets. These parameters will affect the stability of the structure and will influence the scattering of charge carriers at the same time. Thus, developing methods for synthesizing MoS$_2$ nanosheets with controllable shape, size and edge structure is important for optimized device performance and achieving tunable properties. A variety of vapor-phase techniques have since been introduced in order to alleviate these problems; these include, catalyst-free vapor transport,[21, 22] metal film sulfurization,[7, 23] evaporative thinning,[24] organic precursor chemical vapor deposition,[25] and oxide precursor chemical vapor deposition[14, 26, 27] (CVD). It is the latter technique that has become the most widely used method for the direct growth of TMD monolayers. Such CVD-grown monolayers exhibit high optical[28] and electronic quality[29] and achieve the best balance between material quality, areal coverage, and potential for scalability. The technique is based on the reaction of transition metal oxide powders (MoO$_3$, WO$_3$) and a chalcogen in the vapor phase to form the TMD of interest. This method has shown incredible versatility and has been used to synthesize the W- and Mo-based dichalcogenides as well as their doped,[30] alloyed, [31-33] and hetero-structured[34, 35] versions. For these reasons, this method has become an integral part of the progress of the field as a whole. However, while much has
been hypothesized, little is known about the true nature of the nucleation and growth processes and the specific reaction steps that occur during monolayer formation. Two possible reaction pathways have been previously proposed: (1) suboxide (e.g., MoO$_{3-x}$) species condense onto the growth substrate, reacting with the chalcogen(s) and forming the TMD; (2) the oxide and chalcogens react only in the vapor phase, and the TMD deposits directly onto the substrate.[36, 37] However, neither of these mechanisms has been validated nor confirmed. Understanding these mechanisms is integral for the progress of the field and has great implications for suitability of the technique for large-scale growth. Additionally, these concepts underlie the application of the technique for the creation of heterostructured and alloyed 2D semiconductors with precisely controlled structure, position, compositions, and properties.

Materials from the level of fundamental research to real applications, it is essential to enlarge the space of available 2D building blocks beyond the handful of presently considered materials. To this end, not only the band gaps but also the absolute band edge positions, effective masses, and dielectric function will be of key importance for predicting the usefulness of a given 2D material.

Although TMD monolayers and heterostructures have been demonstrated as potential candidates for future electronics, some issues are interest to study before they are applied in large-scale practical devices:

(1) Preparation of large-area single-crystalline TMD monolayers is lacking. The reason of forming different kind of morphology of TMD monolayers stay unclear, which will thus help a lot about to better understand the growth mechanism of TMDs

(2) The difference between the edge state and bulk of two-dimensional material attracted a large interest to investigate the physical issue hide in low dimensional material like MoS$_2$, which been demonstrated as potential candidates for future electronics

To understand these problems, we investigating into the detail in interaction in
between the atoms. The effective charge in semiconductors are very important parameters to describe and predict the electric, optical, magnetic and many other properties. There are dozens of previous researches focusing on the methodology on understanding the principles of this concepts, some successful theories proposed by Pauling[38], Coulson[39], Phillips[40], Sanderson[41], Sziget[42] etc, either physical or chemical, classic or quantum mechanical, provided significant improvements on understanding the nature of chemical bonds and solid-state theories, from both the static and dynamic definition of charge.

However, due to the limitation of fundamental theory, most of the previous theories only work well within the specific ranges of materials, and usually fail in describing and predicting the charge of materials which are out of the ranges. For example, Pauling's iconicity is largely close to his definition of electronegativity, which theory is established based on the spectrostrum of diatomic molecule, when it comes to the ionic crystal in which there are large difference between two elements' electronegativity value, the pauling's theory works poor, it cannot give a different value for the ionicity between NaF and LiF. Coulson's theory has the similar problems, which is based on the localized orbitals, it produces poor results for the materials with delocalized electronic structures. Sanderson's effective charge theory is purely chemical and classic, the effective charge in this theory is just a root function of the Sanderson electronegativity, thus it defines no charge difference for the NaCl molecule gas and the NaCl crystal, the worst part of Sanderson's theory is when it comes to the ternary system, this theory even cannot analytically guarantee the neutral charge states of the materials. Szigeti's charge is defined in a dynamical way, it provides a non-zero effective charge for the elementary substance Si, Ge and Sn, this theory cannot be applied in the study of materials' static property. Phillips' ionicity theory works perfect for the AB type semiconductors, and also can be extended to ternary compounds, however, this theory didn't include the weak interactions from layer structures, and cannot handle the nanostructure as
well.
With the development of the nanoscience and nanotechnology, a theory which can work out the effective charge in nanomaterials is top wanted for the understanding of the remarkable property in the nanoscale materials, like nanotubes, nanoribbons, nanoclusters, etc. The size dependent quantum confinement effect also can be deeply understood under the scheme of effective charge distribution in the non-periodic truncated dimensions, also there are more biological related live phenome which are tightly combined with the charge transfer. An effective and universal theory for the effective charge calculation will provide a widely scoped understanding for all the fundamental scientific research field including physics, chemistry and biology.
In this work, the 3D bulk materials are chosen as benchmark materials for the purpose of benchmark the new methodology to the previous theories. The quasi 2D layer structures are tested for the extension of the methodology to the low dimension materials and the MoS$_2$ nanocluster are comprehensively investigated for 1) the success of the theory on the nanoclusters and 2) the application for the theory in describing the materials' both static (geometry) and dynamic (growth) properties.

1.2 Objectives and Scope

The main objectives of this PhD study are to develop a universal theory and methodology which can well predict the effective charge of a given materials from variant dimensions, and the theory also can help to understand the morphology and the growth of different TMD monolayers materials by investigate the composition of chemical bonds and the edge state of the nanocluster.
To achieve the goal mentioned above, first of all we have to re-visit the previous works, especially their strength and weakness, and find out the possible key factors, and propose a new theory which can well benchmark the
previous theories and the available experimental results. The methodology has to be agile which can be extended to all the materials of all the dimensions, including 3D bulks, quasi 2D layer structures and nanoclusters. For the low dimensional materials, the quantum size effect, layer dependent effect and stacking dependent are all typical tasks to verify the robustness of the new theory extended in the low dimensions. The effective charge predicted by the theory also should be applicable to understand both the static property, like geometry shape, edge stability in nanoclusters, and dynamic property, like growth favorite sites in the nanoclusters. This theory covers all the merits, corrects most of the weakness of the previous theories, and most importantly, can be well agile for the application of materials property description and prediction.

1.3 Dissertation Overview

The thesis addresses the new theory and methodology on calculating the effective charge of materials of all dimensions, and the application on the description and prediction for materials properties, especially on 2D material. It contains 7 chapters.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 brief introduce the background of TMD, growth method using in experiment and the common morphology observed under STEM. review the previous theories on effective charge and iconicity calculations proposed by Pauling, Phillips, Coulson, Sanderson, Szigeti etc, stress the focus and limitation of each theory, provided a general scheme on the background and characteristic of this research topic.

Chapter 3 discusses theoretical methods to be employed in this thesis, including
the basic theories of density function theory, the local density approximation, nudge elastic band methods.

Chapter 4 introduced the key thinking, physics picture and the math formula of the new theory, with benchmark with the previous theories and experimental data in the study of alkali metal halides, alkali earth metal oxides, and some transition metal compounds. Providing a new physics picture for the crystallization from the Born-Harbor cycle and Madelung energy, the new theory widens the coverages and narrows the limitations compared with the previous theories.

Chapter 5 extended the new theory to the quasi 2D layered materials, which is beyond the capability of the previous theories, which makes the new theory more superior. Also applied the methodology on calculating the effective charge between monolayer MoS$_2$ and WS$_2$, providing reasonable explanation to the higher Raman frequency in mono WS$_2$. Also calculated the layer dependent and stacking dependent effective charge, verified by the experimental results.

Chapter 6 keep on extending the new theory to the MoS$_2$ nanoclusters, concluded both the quantum size dependent and the edge geometry dependent effective charge distribution regularity. Translate the center-edge charge gradient into the concept "line tension", which can well describe the chemical potential changing in the non-stoichiometry nanoclusters. The effective charge also can be used to describe and predict the shape dependent edge stability and the growth direction of the nanoclusters.

Chapter 7 summarizes the accomplishments and highlights of this thesis and research plan for the future work extended on the available results, raise some possible work can been done latter based on the theory used in this work, include studying the phase transfer, bond energy composition in lithium battery
etc. The future plan includes the calculation of the effective charge in the complex materials, like ternary materials, organics, metal organic frameworks (MOF), and the seconders with dopants and defects, by update the Born-Harbor energy term and the Madelung energy.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:
1. Establishing a general theory to understand the composition of chemical bonds, and study the effective charge on atom

2. Investigate and explain the quantum size effect in low dimensional materials, layer dependent effect and stacking dependent in TMDs

3. Explore the mechanism to form different kinds of morphology of TMD nanocluster, apply the theory to understand both the static property and dynamic property of low dimensional material
Chapter 2

Literature Review

This chapter briefly review on the structure of monolayer TMDs, the properties most interested in recently, possible applications and previse work have done to understand the morphology of TMD materials and other 2D materials. Review the previous theories on effective charge and ionicity calculations proposed by Pauling, Phillips, Coulson, Sanderson, Szigeti etc., stress the focus and limitation of each theory.
2.1 Monolayer TMDs

2.1.1 Crystal structure

TMDs consist of transition metal atoms (such as tungsten and molybdenum) and chalcogen atoms (sulfur, selenium and tellurium). Similar to graphite, TMD crystals have a layered structure (figure 2.1(a)) in which TMD monolayers stack along the direction out of the plane, with weak van der Waals interaction[43]. Three bulk phases (2H, 3R and 1T, as shown in figure 2.1(b)) exist based on the composition monolayers and their stacking orders.

![Figure 2.1 Schematic of TMD crystals.](image)

Unlike graphene, in which the monolayer consists of only one atomic layer, a TMD monolayer consists of metal atoms sandwiched between two layers of chalcogen atoms. In a basic crystal TMD cell, one metal atom is surrounded by six chalcogen atoms with chemical bonds in a prismatic column structure (H phase) (figure 2-2(a)) belonging to the P-6M2 (D3h) point group or an octahedral structure (T phase) (figure 2-2(b)) belonging to the P-2M1 (D3d) point group.[44-46] These phases can be observed and characterized with scanning transmission electron microscopy (STEM) and electron diffractions. It has been demonstrated that the H phase can be transformed to the T phase by Li+ ion intercalation and that it can be converted back to the H phase by annealing at 300 °C.[47-50] Usually, the H phase is more stable and preferred.
from the view of formation energy.\[44\] As a result, the monolayers grown by CVD are usually H phase instead of T phase, and the following discussion of this thesis will be focused on H phases.

![Figure 2.2](image.png)

**Figure 2.2** Schematic of monolayer TMDs.\[49\] (a) Trigonal prismatic H-phase, (b) Octahedral T-phase. The top diagrams in (a) and (b) are 3D schematics of the structures, the lower panel shows the c-axis view of single-layer TMD structures. Atoms colored purple are the metal; yellow ones are chalcogen.

### 2.1.2 Vibration properties

Four first-order of Raman-active modes with one IR-active mode (E1u) appear in the unit cell of the TMD bulks (figure 2.3(a)).\[51, 52\] Among the four Raman-active modes, the $E_{2g}$ and $A_{1g}$ modes are usually accessible in the range from 100 cm\(^{-1}\) to 400 cm\(^{-1}\); the $E_{2g}^2$ mode occurs at extreme low frequencies, and the $E_{1g}$ mode is forbidden due to back-scattering geometry of a basal plane. \[53\] When the thickness decreases from bulk to monolayer, on one hand, the $A_{1g}$ mode softens because the interlayer vdW interactions increase the effective restoring forces applying on the atoms. On the other hand, the $E_{2g}^1$ mode stiffens, perhaps due to the application of stacking pattern caused structural
In the case of WS\textsubscript{2}, it should be noted that the $E_{2g}^1$ peak around 355 cm\textsuperscript{-1} overlaps with the strongest second-order mode, 2LA(M) at 352 cm\textsuperscript{-1}, which depends on the layer numbers as well, when a laser of 514.5 nm is used as an illumination source. \cite{55} As the vibration frequencies of the $E_{2g}^1$ and $A_{1g}$ modes and their differences shift as a function of the thickness, it should notice that the $A_{1g}$ modes, which only includes the S atoms’ vibration component, is higher in WS\textsubscript{2} than in MoS\textsubscript{2}. (Figure 2.3(b))

**Figure 2.3** Raman characterization of TMD crystals.\cite{51, 54} (a) Four first-order Raman-active modes and one IR-active mode ($E_{1u}$). (b) Raman spectra of a MoS\textsubscript{2}
monolayer, a WS$_2$ monolayer, and a WS$_2$/MoS$_2$ bilayer recorded at ambient pressure (P $\approx$ 0).[56] The $A_{1g}$ (out-of-plane) and $E_{2g}$ (in-plane) peaks of each layer are labeled, and their oscillation modes are shown in the inset.[57]

### 2.1.3 Growth of TMD

Until lately, the approach to synthesis of single layer MoS$_2$ films usually using chemical vapor deposition (CVD). In this method, MoO$_3$ and S powders is used as the reactants and chemical vapor deposition is performed directly on SiO$_2$/Si substrates. Different shape of MoS$_2$ cluster like triangle and hexagon has been observed by experiment. Previous work[58, 59] indicates some possible configurations between molybdenum atom and sulfur atom. Numbers of work has done on the edge site configuration,[60, 61] the grain boundary[61, 62] and defects[63, 64] also been studied.

The epitaxial growth of MoS$_2$ on substrate surfaces by a CVD method was regarded as the most promising method for controlling the synthesis of MoS$_2$ nanosheets, in particular for fabricating monolayer MoS$_2$. The epitaxial growth of monolayer MoS$_2$ nanoclusters was first reported by Helveg et al.[65] on an Au(111) surface. The MoS$_2$ nanoclusters exhibit uniform triangular shape, and the edge structure was found to be strongly related their catalytic activity. Shi et al.[66] demonstrated van der Waals epitaxy of MoS$_2$ layers on graphene substrate. The MoS$_2$ nanostructures synthesized on a graphene surface will make the reactants of single crystalline hexagonal flakes whose size can be ranging from hundred nanometers to micrometers level. In recent years, the CVD-grown MoS$_2$ monolayer on insulator SiO$_2$ substrate has been widely reported.[6, 59, 61] In these studies, the triangular MoS$_2$ islands have been identified in the growth process, and the continuous MoS$_2$ films are formed by merging of the triangular islands. The above studies provide a solid basis for producing large-area monolayer MoS$_2$, but some fundamental problems apparent in the growth process have not been clarified, including the
microscopic mechanism for the formation of uniform triangular or hexagonal MoS$_2$ islands, the edge structure characteristics of growing MoS$_2$ islands, and the relationship between MoS$_2$ morphology and the chemical environment.

![Figure 2.4](image-url) The configuration used in experiments for MoS$_2$ film preparation. In this configuration, the MoO$_3$ precursors are dispersed on SiO$_2$/Si substrates and placed in the center of the quartz container, designated for MoS$_2$ growth, are labeled Mo sample in the figure. The sublimated sulfur is placed close to the opening of the furnace, where it evaporates as the temperature at the center of the furnace approaches 850°C. Nitrogen is continuously streamed through the furnace.

To synthesize MoS$_2$ mono layers in a vapor phase deposition process, MoO$_3$ and sulfur vapor were applied as precursor and reactant materials, respectively. The insulating SiO$_2$/Si structures were used as substrates.[7] Figure 2.4 indicate the configuration used in experiments for MoS$_2$ film preparation and the experiments were carried on with a reaction temperature of 850°C. MoO$_3$ films can be prepared by the filtration or dispersion of their highly crystalline nanoribbons, which were synthesized hydrothermally through a routine process of this type of single-crystalline material. Sodium molybdate (Na$_2$MoO$_4$) or hexaammonium heptamolybdate tetrahydrate (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O were used to synthesize MoO$_3$ nanoribbons.[14] The ribbons were then filtered or dispersed and films of large-area can be formed, cut into small pieces, and arranged on the silicon substrates. This MoO$_3$-covered silicon substrate, along with several bare substrates designated for the growth of MoS$_2$ were placed.
close to each other at the center of the furnace vented with nitrogen. At the opening of the furnace, a container with sulfur was placed at an area in which the highest temperature can approximately reach 600°C, the sulfur slowly evaporated, the vapor phase reaction between MoO$_3$-$x$ species and sulfur and the deposition of MoS$_2$ on a designated substrate.

2.1.4 Morphology of TMD

In previous work, different shapes of MoS$_2$ domains were synthesized by adjusting the ratio between MoO$_3$ and S precursor amounts. The experiments demonstrate that, in the case of an insufficient sulfur supply, oxisulfide rectangular domains nucleate and grow, instead of MoS$_2$ triangles and films (Fig 2.5 a). As the sulfur concentration is increased to 0.5-0.7 grams (2.6-3.65), hexagonal MoS2 domains nucleate, and at >1 grams (5.2) of sulfur, triangular domains dominate (Fig 2.5 b & c).

![Figure 2.5](image)

**Figure 2.5** Effect of sulfur concentration on the growth process. (a) At low sulfur concentrations, < 0.5 grams, rectangular domains are nucleated. (b) Nucleation of MoS$_2$ begins at sulfur concentrations in the range of 0.5-0.7 grams; however, the domains construct a hexagonal geometry. (d) At higher sulfur concentrations, >0.7 grams, triangular domain nucleation dominates the process.

Alternatively, considerable efforts have been devoted to insight into the edge role in electronic, optical, magnetic, and catalytic properties of monolayer MoS$_2$ nanostructures. For instance, Li et al[67] performed the first principle DFT calculation to investigate the electronic and magnetic properties of MoS$_2$ nanoribbons (NRs). They found that zigzag NRs exhibit both ferromagnetic and
metallic character and that armchair NRs are nonmagnetic and semiconducting. Moreover, the electronic properties and edge magnetism of these MoS$_2$ NRs are sensitive to external stress and electric field.

[68, 69] Jaramillo et al.[70] reported electro-catalytic properties of MoS$_2$ nanoclusters in the hydrogen evolution reaction (HER), and their measurement results indicated that the electro-catalytic efficiency for the HER correlate in linear relationship with the edge sites numbers of the MoS$_2$ catalyst. The catalytic activity of MoS$_2$ can be improved by increasing active edge sites, achieved by patterning holes on MoS$_2$ atomic layers.[71]

In the previous research work, Jeppe V. Lauritsen etc[72] use atomic resolution scanning tunnelling microscope (STM) images to trace the structure evolution in the triangular MoS$_2$ nanoclusters and the dependence on the size, and provided insightful results about the size dependent ground structure geometry changing. A comprehensive study shows that some ‘magic’ clusters are energetically favored regarded to the size dependence. Examined the structure of the large size single-layer MoS$_2$ nanoclusters (>500 Å$^2$) in STM image,[65, 73, 74] most of which are appear in triangular shape. There are two types of low index edge terminations of a MoS$_2$: the Mo and the S edges., here illustrated in hexagonal shaped MoS$_2$ cluster for easy understanding (Fig. 2.6b). A triangular shape usually has only one edge type.
Figure 2.6  Atomic models for a hexagonal MoS$_2$ nanocluster terminated with the Mo and S edges in blue and yellow color respectively. The geometry shape and energy stability of all the edge optional configurations are simulated with different sulphur concentration by DFT method. The shown configurations are adapted from previous refs, [60, 75] (a) Side view for the structure of Mo edge, presenting a fully stripped 0% edge and two equally stable edge configurations with 50% or 100% sulfur concentration coverage individually. (b) Atomic model for the hexagonal MoS$_2$ nanocluster. (c) Side view for the structure of S edge, presenting three configurations with 50%, 75% or 100% sulfur concentration coverage, respectively.
Figure 2.7  The number of sulfur/ Molybdenum ratio of S atoms to Mo atoms simulated related with the triangle side length of triangular Mo$_x$S$_y$ nanoclusters, each of the five lines represents the clusters terminated with the most stable edge configurations corresponding to either the Mo edge with 50% or 100% sulfur coverage on the S edge or 50%, 75% or 100% Mo coverage.

2.2  Chemical bond

The chemical bonds can be traditionally classified into ionic, covalent, donor-acceptor, metallic and van der Waals (vdW) etc, depending on different intrinsic and extrinsic character. However, in reality, a specific chemical bond is always a combination of several types, or even possible that of these types could be included, as named by Arkel-Ketelaar triangle[76, 77] shown in Figure 2.8 , takes Li to F for examples. The standard covalent bonding only can be formed in elemental substances or in homo-nuclear bonds with symmetric
molecules, this tough condition make the pure covalent bonds only occupy a tiny fraction of the substances known so far.

![Figure 2.8: van Arkel-Ketelaar triangle for chemical bond types, the chemical bond type transitions among the three types.](image)

However, quite lots parts of the elemental substances are formed by metallic bonds, which is delocalized all over the crystals. Strictly speaking, perfect ionic bonds do not exist at all (although alkali metal halides come close) because due to the atomic orbital overlapping, the emergence of partial covalent character always included. Nevertheless, to understand real chemical bonds, it is necessary to begin with the ideal types and their connections.

### 2.2.1 Ionic bond

The ionic bond results from the Coulomb attraction of oppositely charged ions. It also can be understood as transferring of electrons between a metal and a non-metal atom and resulting a so called “ionic compound.”, as shown in
Figure 2.9, the NaCl formation for example, its strength is characterized by the electrostatic energy; in MX ionic crystals it is the crystal lattice energy $U(MX)$, which can be determined experimentally from the Born-Haber cycle or calculated theoretically from the known net charges of ions ($Z$, not to be confused with nuclear charges) and inter-ionic distances ($d$), as:

$$U(MX) = k_M \frac{Z^2}{d} \left(1 - \frac{1}{n}\right)$$

(2.1)

where $k_M$ is the Madelung constant and $n$ is the Born repulsion factor, in good agreement with the experiment. The ionic theory explains many facts of structural inorganic chemistry. Thus, in many ionic structures, larger ions (anions) form a close packing motif while smaller ions (cations) occupy the voids in it. As this motif contains only tetrahedral and octahedral voids, this explains why cations usually have the coordination number, $N_c$, of 4 or 6. Coulomb interactions being strong, ionic crystals have high fusion (melting) temperatures and high atomization energies, but dissolve in polar liquids (e.g. water) due to high solvation (hydration) heat. The absence of electrons in the inter-ionic space results in low refractive indices and high atomic polarizations, wide band gaps, and insulator properties.

Figure 2.9 Scheme for the electron transferring from Na to Cl and the formation of the typical ionic compounds NaCl.
As noted above, Kossel introduced the idea that the transition from ionic to covalent substances is gradual, the covalence increasing with the mutual polarizing influence of ions. This idea was developed by Fajans[78] and his school who defined the polarizabilities of ions and estimated the polarizing action of cations \((Z/r^2)\), but ultimately failed to create a quantitative theory. The reason is obvious: there are no completely ionic substances, only intermediate cases, more or less approaching this type. Hence the parameters of ideal ions are not available experimentally, the more so since ionic radii cannot be uniquely defined from interatomic distances, thus the polarization concept remained only qualitative. However, the contribution in the bond energy of the polarizing effect of atoms can be described in the form that has proven itself for the van der Waals interaction, where the deviation of the \(A \cdot \cdot \cdot B\) distance from the mean of \(A \cdot \cdot A\) and \(B \cdot \cdot B\) distances is a function of the difference of the atomic polarizabilities.

\[
p_{\alpha} = \left(\frac{\alpha_A - \alpha_B}{\alpha_A}\right)^2
\]  

(2.2)

turning from distances to volumes, this function takes the form

\[
p_{\alpha} = \left[\frac{\alpha_A - \alpha_B}{\alpha_A}\right]^2
\]  

(2.3)

Taking into account the interaction of effective charges of atoms, the total ‘energetic’ polarizing effect is

\[
q = p_{\alpha} \frac{(Z_i)^2}{d}
\]  

(2.4)

Evidently, the smaller the atom the stronger its polarizing effect. If the smaller ion is the cation (as is usually the case) then it reduces the total \(\alpha\) of the substance, if is the anion then \(\alpha\) increases. Such simple approach allows
calculating polarizability of inorganic compounds with good accuracy. [79] The detail for the energy scale will be discussed in the sub-chapter below.

2.2.2 Covalent Bond

Usually, a covalent bond between two atoms is formed by two electrons, one from each atom. These electrons tend to be partly localized in the region between the two nuclei. If the orbitals of these electrons are \( \Psi_1 \) and \( \Psi_2 \), the molecular orbital of the bonded atoms must be their linear combination, symmetric \( \Psi_b = \Psi_1 + \Psi_2 \) and antisymmetric \( \Psi_a = \Psi_1 - \Psi_2 \). The former orbital has a minimum of energy at certain distance and generally has lower energy than the latter, therefore the former orbital is bonding and the latter antibonding. Since an orbital can be occupied by no more than two electrons, this picture was in fact anticipated by the Lewis’ model[80] which regarded bonds as shared electron pairs. Lewis also noted that in stable molecules, each atom usually has 8 electrons in its valence shell (except H which has two), counting both the bonding and the unshared electron pairs and taking no account of the bond polarity. This octet rule for a long time was regarded as a law of chemistry, apparently resulting from the fact that there are only one s and three p orbitals in an electron shell, which can accommodate a maximum of 8 electrons between them. Compounds which did not conform to this rule were regarded as special classes of compounds, hypervalent (with\( >8 \) electrons) and hypovalent (with\( <8 \) electrons). Alternatively, exceptions were explained away by including d orbitals into hybridization, or by invoking bond polarity and net atomic charges and assuming that the octet rule applies to the effective number of electrons around each atom (contrary to Lewis’ own approach). Today it is clear that this rule, although pedagogically useful, has numerous exceptions which show no extraordinary properties.[81] Particularly, comparison of bonds in hypervalent molecules with those in octet molecules reveals no fundamental difference in their nature. Likewise, saving the octet rule by assigning net
charges to atoms, contributes nothing to understanding the structures and properties of molecules. Thus, the nitrogen atom in a protonated amine or pyridine has a formal charge of +1 but shows no corresponding contraction of the bond distances; in fact, this atom has a small negative charge.

It seems that the belief in the octet rule and in misread quantum-mechanical concepts helped for a long time to discourage the search for compounds of ‘inert’ gases, although von Antropoff [82] and Pauling[38] have predicted that these might be chemically awaken by powerful oxidizing agents with high electronegativity. This prediction was confirmed in 1962 when xenon compounds were discovered[83, 84]. Since then, over 500 compounds of the ‘rare’ (formerly ‘inert’ and later ‘noble’) gases were synthesized[85] and dozens of them characterized by X-ray diffraction. Finally, solid xenon was converted into metallic state under ultra-high pressure [86]

2.3 Effective charge in bulk materials.

The covalent and ionic bonds and their “mixture”, the “polar covalent” or “partial ionic” bonds, are shown in Figure 2.10, the wavefunction of the polar covalent bond, like H-F in the hydrogen fluoride molecule, presenting the in-between types compared with the covalent H2 and ionic NaCl. The ratio of ionic character versus covalent character of the same chemical bond could be understood and quantified with the help of definition of “electronegativity” first provided by Linus Pauling[38]. The larger the difference between the electronegativity between two atoms, the more ionic the nature character of the chemical bond can be expected. In traditional presentation, bonds could be recognized as ionic if the ionic ratio is much greater than the covalent counterpart in the same bond, and whenever the bonds that fall in between the two extremes, having numerical close ionic and covalent contribution, are recognized as materials with polar covalent bond or partial ionic bonds.
Speaking about electronegativity, we mention here that there exist several different electronegativity scales, e.g. Phillips scale[87], Jaffe scale[88, 89], Allen scale[76, 90, 91] etc. Throughout this thesis, the Pauling electronegativity is applied the Shannon’s ionic radii methodology is applied for all the elective ions.

2.4 Effective Charges of Atoms

The term ‘ionic substance’ is often used in inorganic chemistry, but although the reality of ions is manifest in the ionic conductivity in molten state, and in some cases in the solid state, in fact there are not many compounds which can be regarded even as practically ionic, and none with purely ionic bonding. Monoatomic cations are always smaller than anions (except for F$^-$ being smaller than K$^+$, Rb$^+$, Cs$^+$) and tend to polarize the latter, causing a displacement of the anion’s electron density towards the cation. The ionization potentials of metals being higher than the electron affinities of nonmetals has similar effect. Thus, even in the most ionic crystals the charges must be less than the oxidation numbers. How these can be determined? Dozens of

![Figure 2.10 Scheme of the electron cloud distribution among (a), Covalent bond in H$_2$, (b), Polar Covalent bond in HF, (c), Ionic bonds in NaCl](image)
experimental and theoretical methods have been suggested for the determination of atomic charges [92].

X-ray spectroscopy (XRS) gives important information on the bond polarity. Firing X-rays at molecules or ions and measuring the energy of the electrons given off can determine the charge distribution in molecules or ions. In a bond, when the charge distribution leads to unequal sharing of electrons between the atoms, as electrons will be drawn closer to an atom with another lead to the bond polarity. Experiments have shown that the binding energy of inner electrons of an atom ($E_{BIE}$) depends on the external electronic environment, i.e. on the effective charges of atoms: a positive net charge increases and negative one reduces $E_{BIE}$. Therefore, knowing the values of $E_{BIE}$ in different crystalline compounds, one can define the magnitudes and signs of the atomic charges, and how they vary with the composition and structure changes. Thus, effective atomic charges in MX crystals were found to increase with $N_e$ and $\Delta \chi$[93], while in the succession MnS, MnO, MnO$_2$, MnF$_2$, the MnKα-edge of the X-ray absorption band shifts to higher energies by 1, 3, and 3.6 eV, respectively[94].

The most reliable charge determinations by XRS[95-97] are compiled in Table 2.1 and Table 2.2 The effective charges decrease when the valence of the central atom increases or when the electronegativity of the ligands decreases. The effective charges of S, P, Si and Cl atoms in organic compounds were determined by the shifts of the Kα-line in comparison with the same atoms in the elemental solids.[98, 99] The drawback of this method is the smallness of Kα in comparison with the absolute binding energies, but its advantage is that the volume to which the charge refers is known precisely, as electronic transitions are localized within the atom; the values Kα can be scaled against the effective atomic charges calculated from electronegativities. [100]
Table 2.1  Effective charge from X-ray spectroscopy, for variant MX crystal structures. The units are electron charge e.

<table>
<thead>
<tr>
<th>MX&lt;sub&gt;an&lt;/sub&gt;</th>
<th>e&lt;sup&gt;*&lt;/sup&gt;(M)/v</th>
<th>MX&lt;sub&gt;n&lt;/sub&gt;</th>
<th>e&lt;sup&gt;*&lt;/sup&gt;(M)/v</th>
<th>MX&lt;sub&gt;an&lt;/sub&gt;</th>
<th>e&lt;sup&gt;*&lt;/sup&gt;(M)/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>0.95</td>
<td>SiF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.35</td>
<td>GeSe</td>
<td>0.17</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.92</td>
<td>SiCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.25</td>
<td>Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.54</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.83</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.23</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.25</td>
</tr>
<tr>
<td>NaI</td>
<td>0.75</td>
<td>SiC</td>
<td>0.12</td>
<td>Al(OH)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.26</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.90</td>
<td>SnF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.83</td>
<td>AIN</td>
<td>0.21</td>
</tr>
<tr>
<td>CuF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>SnCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.76</td>
<td>In&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.24</td>
</tr>
<tr>
<td>CuO</td>
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<td>Sn&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.42</td>
<td>In&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.17</td>
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<tr>
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<td>SnSe</td>
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<td>As&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
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Table 2.2  Effective charge from X-ray spectroscopy, for variant MX crystal structures. The units are electron charge e, another reference[101]

<table>
<thead>
<tr>
<th>MX&lt;sub&gt;n&lt;/sub&gt;</th>
<th>r&lt;sub&gt;M&lt;/sub&gt;</th>
<th>e&lt;sub&gt;m&lt;/sub&gt;/v</th>
<th>MX&lt;sub&gt;m&lt;/sub&gt;</th>
<th>r&lt;sub&gt;M&lt;/sub&gt;</th>
<th>e&lt;sub&gt;m&lt;/sub&gt;/v</th>
<th>MX&lt;sub&gt;n&lt;/sub&gt;</th>
<th>r&lt;sub&gt;M&lt;/sub&gt;</th>
<th>e&lt;sub&gt;m&lt;/sub&gt;/v</th>
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<td>0.74&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>KBr</td>
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<td></td>
<td>InAs</td>
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<td>0.5&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>TiO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.72&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.63&lt;sup&gt;d&lt;/sup&gt;</td>
<td>CaSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.0&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoF&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>BN</td>
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<td>0.15</td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>0.74&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
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<td>AIN</td>
<td>0.20</td>
<td></td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.13&lt;sup&gt;f&lt;/sup&gt;</td>
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<td></td>
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28
2.4.1 Methods for calculation effective charge and iconicity.

First of all, we will introduce several previous methods to calculate the effective charge and iconicity, it includes Pauling’s electronegativity methods, Coulson, Phillips, Sanderson and Szigeti’s methods.

2.4.2 Pauling’s electronegativity

Pauling defines electronegativity as “the power of an atom in molecule to attract electrons to itself.” The electronegativity (\( \chi \)) is a dimensionless number. A complete table for all elements is shown in Table 2.3. In a binary material, the important parameter is the amount of charge transfer between the two different atoms in the unit cell. This charge transfer is related to the differential value in the electronegativity between the two elements:

Where

\[
\Delta_{AB} = D(A - B) - \frac{1}{2}[D(AA) + D(BB)]
\]

(2.5)

The explanation for the fact that \( \Delta_{AB} > 0 \) is the following. One of the atoms (say A) has greater capability to attract electrons than the other. The term electronegativity \( \chi_A \) is a dimensionless number, which is defined the ability of a given atom A to attract electrons to atom A itself. Expand \( \Delta_{AB} \) in powers of \((\chi_A - \chi_B)\) and keep only the first non-vanishing term. By symmetry this gives to lowest order in \((\chi_A - \chi_B)\) the approximate result

\[
\Delta_{AB} = (\text{constant with dimensions of energy})(\chi_A - \chi_B)^2
\]

(2.6)

One can imagine that a certain number of electrons proportional to \((\chi_A - \chi_B)\) has been transferred from atom B to atom A. The Coulomb interaction between the remaining ionic charge and the transferred valence charge is proportional to
\((\chi_A - \chi_B)^2\), and this can be recognized as the origin of the extra-ionic energy. Some of the \(\chi\) value is listed in Table 2.3.

We see then that \(\chi_A - \chi_B\) is a measure of ionicity. But by definition \(f_i\) never exceeds one, and as \(\chi_A - \chi_B\) becomes large \(f_i\) tends to one. Moreover, ionicity of an A–B bond should be the same as ionicity of a B–A bond. This suggested to Pauling the definition of ionicity of a single bond,

\[
f_i = 1 - \exp \left[ - \frac{(\chi_A - \chi_B)^2}{4} \right]
\]

(2.7)

where the constant in (2.6) has been chosen so that \(\chi_A\) increases by 0.5 when \(Z\) changes by one in the first-row elements. The choice of (2.7) makes the NaCl single bond about 67% ionic on Pauling’s scale.

Table 2.3  
Electronegativity scale of some elements, according to Pauling

<table>
<thead>
<tr>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
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<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td>0.9</td>
<td>1.2</td>
<td>1.5</td>
<td>1.8</td>
<td>2.1</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
<td>Cu</td>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
</tr>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>1.9</td>
<td>1.6</td>
<td>1.6</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
<td>Ag</td>
<td>Cd</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
</tr>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>1.9</td>
<td>1.7</td>
<td>1.7</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.4.2.1  Extension of Pauling’s definition to crystals

In most molecular structures, the coordination number of an atom usually is less than or equal to its formal valence electrons numbers \(N\), which is equal to \(Z\) for \(Z \leq 4\) and to \(8 - Z\) for \(Z \geq 4\). In crystals, on the other hand, the coordination number generally exceeds \(N\). In \(A_NB_{8-N}\) crystals the coordination number is
usually four or six, so it is only in diamond-type crystals, where \( N \) equals four and the coordination is tetrahedral, that one has single bonds.

To resolve this conflict Pauling introduced the concept of resonating bonds. In each compound, there are \( N \) valence bonds per atom, and these are pictured as shared with all the four or six nearest neighbors of each atom. This means that the degree of covalency \( f_h = 1 - f_i \) is also shared, so that the single-bond ionicity \( f_i \) must be replaced by a resonating-bond ionicity \( f_i' \) defined by

\[
1 - f_i' = \frac{N(1 - f_i)}{M}
\]

(2.8)

where \( M \) is the number of nearest neighbors and \( f_i \) is defined by (2.7). One can rewrite (2.8) as

\[
f_i' = 1 - \frac{N}{M} + \frac{N f_i}{M}
\]

(2.9)

When \( N < M \), \( f_i' > 0 \) even when \( f_i = 0 \).

### 2.4.2.2 Limitation of Pauling’s ionicity

If one is concerned with heats of formation of diatomic molecules, then Pauling’s equations (2.5) and (2.6) are probably as good a definition of ionicity as any. Later workers showed that Pauling’s results could be improved somewhat by defining \( D_{AB} \) as the average bond energy of the polyatomic molecules \( AB_n \) or \( A_mB_m \), where \( n \) is the valence of atom A or \( m \) is the valence of atom B, thus making certain that as many electrons as possible of A or B, respectively, are actually bonded.

This improvement does not remove the central weaknesses of Pauling’s definition, the semiconductors are much simpler than diatomic or even polyatomic molecules, because all valence electrons are bonded, and all bonds are equivalent. (E.g., in the molecule \( AB_n \), the \( n \) valence electrons of A are all
bonded, but only one of the valence electrons of each B atom is bonded). However, in the crystalline case $D_{AB}$ refers to the heat of formation of the A–B crystal from A–A and B–B at STP (standard temperature and pressure). For example, the heat of formation of BN is measured relative to crystalline boron and gaseous nitrogen. The former has a complicated network structure which cannot be well described by hybridized orbitals, while the latter consists of sp-bonded diatomic molecules. These changes in structure make a significant contribution to $D_{AB}$.

Another problem in extending the molecular approach to crystals is the meaning of the valence $N$. For most non-transition atoms the choice $N = Z$ or $8 - Z$ works well. The IB atoms Cu, Ag, and Au often are divalent in molecules, however, which means that one of the $(n - 1) d^{10}$ core electrons is participating in the bonding along with the ns valence electrons. Thus in the silver halides Pauling suggested that $N$ was probably equal to two. However, the halogen ions are always monovalent, so that one could equally well argue that $N$ should be one. An ambiguity has arisen because the cation valence is one more than the anion valence.

### 2.4.3 Coulson’s ionicity

Coulson uses an explicit representation based on atomic orbitals. Each valence wave function is written in the form:

$$\psi_{\text{valence}} = \psi_{sp^3}(A) + \lambda \psi_{sp^3}(B)$$

(2.10)

where $\psi_{sp^3}$ (A, B) denotes a hybridized valence orbital centered on atom A or B, respectively. The trial wave function (2.10) is inserted in the wave equation and an estimate is made of the total energy. When the latter is minimized, the best value of $\lambda$ is obtained. Because the two atomic wave functions in (2.10) are
assumed to be orthogonal, the ionicity defined by (Prob. = probability of finding a valence electron)

\[ f_i = \frac{(\text{Prob. on A}) - (\text{Prob. on B})}{(\text{Prob. on A}) + (\text{Prob. on B})} \]

(2.11)

is given simply by

\[ f_i = \frac{1 - \lambda^2}{1 + \lambda^2} \]

(2.12)

Within the framework of quantum theory based on atomic orbitals, equations (2.10)–(2.12) probably give about as good a definition of ionicity as can be obtained. The trouble with this definition is that it suffers from two weaknesses. First, the restriction to a trial function of the form (2.10) is much too severe, because the formation of the bond changes the localized orbitals about each atom from what they were in the free atom, making (2.10) a poor choice for defining that bond’s ionicity. Second, the energy calculated does not give the cohesive energy of the crystal, or the observed lattice constant, so that varying \( \lambda \) to minimize that energy is a much less meaningful process than it might appear to be at first sight.

### 2.4.4 Phillip’s ionicity

Another method of measuring bond ionicity (fi) in solids was developed by Phillips and Van Vechten (PVV)[40, 102-104], as shown in Figure 2.11. \( \psi_a \) and \( \psi_b \) are atomic wavefunctions of anion and cation in AB crystal respectively, \( \psi_v \) and \( \psi_c \) are valence and conduction states wavefunctions. Eg is the effective band gap and C is the ionic component of Eg, fi is defined as \( f_i = C^2/Eg^2 \), from the wavefunction

\[ \psi_v = a\psi_a + b\psi_b \]

(2.13)

Which can result as:
\[ \sqrt{f_i} = \frac{(a^2 - b^2)}{(a^2 + b^2)} \]  

(2.14)

Using eigenvalue equation:

\[
\begin{vmatrix}
\frac{C}{2} - \varepsilon & h \\
-h^* & -\frac{C}{2} - \varepsilon
\end{vmatrix} = 0
\]

(2.15)

Where \( h = \frac{E_h}{2} \), \( E_h \) is the covalent part of \( E_g \) as defined by Phillips, this equation also provided the relationship about the band gap \( E_g \) as

\[ E_g^2 = C^2 + E_h^2 \]

Figure 2.11 Illustration for the Phillips’ ionicity

2.4.5 Szigeti’s effective charge

The effective charges of atoms in crystals, rather than molecules, can be determined by Szigeti’s spectroscopic method[42], using the formula

\[ \varepsilon_S = \varepsilon_\infty + \left[ \frac{\varepsilon_\infty + 2}{3} \right]^2 \left( \frac{s^2 (ze)^2 N}{\pi \mu v_t^2} \right) \]

(2.16)

Here \( z \) is the valence, \( e \) is the electron charge, \( N \) is the molecular number, \( v_t \) is the transverse optical frequency, \( \mu \) is the reduced mass. The first term on the
right of the Eq (2.16) \((\varepsilon_\infty)\) is the optical dielectric constant origin from the high energy polarization and the second term origins from infrared polarization. Szigeti’s methodology as shown in Eq (2.16) contains two additional factors which are not presented in Born’s relation \((\varepsilon_s = \varepsilon_\infty + (z^2 e^2 N / \pi \mu \nu t))\); both arise out of the electronic contribution to the infrared polarization. The coefficient \(((\varepsilon_\infty + 2)/3)^2\) origins from the fact that the long range interaction cannot be fully decayed for transverse waves. The other additional factor is “s” which includes the short-range Coulomb interaction for both the electronic and atomic displacements. The new term \(s(ze)\) is equivalent to replacing \(ze\) by an effective charge \(ze^*\); through some math variation, \(s(ze) = ze^*\) and \(s = (ze^*/ze)\). In historical literature, “s” has been defined as the ‘effective charge’ or the ‘Szigeti charge’. The results of some MX crystals are listed in Tables 2.4, in the conventional form \(e./v\) where \(v\) is the formal valence of the atom (i.e. the values are the relative bond ionicities).
Table 2.4  Szigeti charge for some MX crystal

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<th>M (ν = 1)</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
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</thead>
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<td>0.74</td>
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<td>Cu</td>
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<td>0.91</td>
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<th>S</th>
<th>Se</th>
<th>Te</th>
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<td></td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
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<table>
<thead>
<tr>
<th>M (ν = 3)</th>
<th>N</th>
<th>P</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.38</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.41</td>
<td>0.26</td>
<td>0.21</td>
<td>0.16</td>
</tr>
<tr>
<td>Ga</td>
<td>0.41</td>
<td>0.19</td>
<td>0.17</td>
<td>0.13</td>
</tr>
<tr>
<td>In</td>
<td>0.22</td>
<td>0.18</td>
<td>0.14</td>
<td></td>
</tr>
</tbody>
</table>

2.4.6  Sanderson’s effective charge

Another method of calculating the effective charge in molecule and crystal MX by Sanderson[105] as

\[ EC_{MX} = \sqrt{EC_M EC_X} \]

(2.17)

allows us to calculate the atomic charges in molecules by comparing the molecular and atomic covalent energy EC. Sanderson has postulated (assuming the bond ionicity q=0.75 in NaCl) that one positive or negative charge on atom
A will change its EC by the increment $\Delta q = \pm a\sqrt{EC_A}$. The coefficient was estimated as 2.08, later corrected to 1.56\([41]\). Thereby it is possible to calculate EC for any cations and anions, and from them to calculate bond ionicities

$$q_A = \frac{EC_{AB} - EC_A}{EC_{A^+} - EC_A}$$

(2.18)

Sanderson has applied this principle indiscriminately, assuming EC to equalize for all atoms even in such species as K2SO4, where K and S play quite different chemical roles and have different valences. Later it was suggested \([106]\) to equalize EC in separate bonded pairs of atoms, rather than throughout the entire molecule. It was also observed that total equalization in organic molecules would give different EC for isomers of the same composition, and a novel, rather efficient, method of calculating EC for isomers was proposed instead \([107, 108]\).

One big problem of Sanderson’s iconicity is that the fi value origins from the electronegativity difference of elements only thus makes no difference in the molecule and crystal phase.
Chapter 3

Calculation Methodology

This chapter introduces the background and theoretical methods and models are to be employed in this thesis, include some basic information about density functional theory, as well as Kohn-Sham equations, Nudged Elastic Band Method.
3.1 Density Functional Theory

DFT is a successful theory to predict the ground state properties of variant kinds of materials, such as metals, insulators and semiconductors. Normally, we can define a solid by electrons (e) at position \( [43] \) and nuclei (n) at position \( [43] \), and the conjugated momenta \( P \) and \( p \), the electrons and nuclei are coupled by coulomb interactions. Then the non-relativistic Hamiltonian of an N-electron system can be given by

\[
H = T_n (P) + T_e (p) + V_{nn} (R) + V_{ee} (r) + V_{ne} (R, r),
\]

(3.1)

Where \( T \) and \( V \) are the kinetic and coulomb interaction operators.

And the solution of equation of Eq. (3.1)

\[
H \Psi (r, R) = E \Psi (r, R)
\]

(3.2)

can totally describe all the properties of the system. However, it is impossible to get analytic solutions for most of the cases due to the huge complexity inside the equation; while in numeric, it is still difficult to get satisfying solutions of this equation because there is no general idea to decouple the 3N degrees of freedom. The adiabatic approach is a well-established method to decouple the electron and nuclei into two independent equations due to the fact that the motions of electrons and nuclei are of huge difference. The nuclei is fixed and has a zero kinetic energy in the electron’s dynamics. Then the whole wavefunction can be split into two products, electrons and nuclei, as Eq (3.2).

\[
\Psi (r, R) = \Psi (R) \Psi _e (r)
\]

(3.3)

Next we can only focus on the electron system with the nuclei fixed statically

\[
H_e (r) = -\frac{\alpha^2}{2m} \sum_{i=1}^{N_e} \nabla_i ^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \sum_{i=1}^{N_e} V_{ext} (r_i).
\]

(3.4)
is the external field induced by the interaction between the electrons and nuclei.

\[ V_{\text{ext}}(r) = \frac{1}{N_e} V_{\text{in}}(R) + V_{\text{ne}}(R, r), \]

(3.5)

By decreasing the degrees of freedom for the nuclei, it makes much advantage for solving the equations.

### 3.1.1 Two Theorem in DFT

DFT is a very successful theory to predict the ground state properties of variant kinds of materials, such as metals, insulators and semiconductors. Its main idea is that the ground state of an interacted many electron system in an external potential is only related with the electron density \( n(r) \). In history, Thomas and Fermi first use the electron density to get the total energy 1. They constructed the inhomogeneous system by the express of kinetic, exchange and correlation energies of the homogeneous system. In 1964 Hohenberg and Kohn\[109\] proved two important theorems and introduced the fundamental references for the DFT theory. The two theorems are:

**Theorem I:** The relation between any external potential and the electronic charge density is unique, i.e. no two different potentials acting on a given system can give the same ground state charge density.

**Theorem II:** The ground state energy can be determined by minimize the energy functions:

\[ E[n(r)] = F[n(r)] + \int V_{\text{ext}}(r')n(r')dr', \]

(3.6)
If and only if the charge density is exact the ground state charge density, the function is minimized. is independent on thus it is universal. Though is unknown, all ground state information can be completely got when minimize it.

### 3.1.2 Kohn-Sham equations

Theorem II introduced a universal function \( F[n(r)] \), Kohn and Sham[110] rewrite \( F[n(r)] \) in the following form:

\[
F[n] = T_0[n] + \frac{1}{2} \int n(r) V_H(r) dr + E_{xc}[n],
\]

(3.7)

In Eq (3.7), the first term \( T_0[n] \) is the kinetic energy; \( V_H \) is thehartree potential in the form of \( V_H(r) = e^2 \int \frac{n(r')}{|r-r'|} dr' \); the last term \( E_{xc}[n] \) is the exchange and correlation term.

As shown in Theorem II, Eq (3.7) is minimized like Eq (3.6) and all problems solved, and the problem can be transformed into a set of single particle Schrödinger equations:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r),
\]

(3.8)

\( \varepsilon \) is the i-th Kohn-Sham eigenvalue and is defined as

\[
V_{xc}(r) = \frac{\delta E_{xc}[n(r)]}{\delta n(r)}
\]

(3.9)

has a name “exchange correlation potential”.

In Eq (3.8), the wavefunction \( \psi_i \) yield the charge density \( n(r) \), and \( n(r) \) decided the value of \( V_H \) and \( V_{xc} \), thus Eq (3.8) only can be solved self-consistently with an initial guess until a final convergence is achieved.
3.2 Local Density Approximation

One of the main advantages of the DFT method is the introduction of the exchange and correlation function $E_{xc}$ to replace the many electron problems by single particle problem. However, the exact value of $E_{xc}$ is still unknown and it is necessary to define $E_{xc}$ by variant approximations. The most widely used form of $E_{xc}$ is the local density approximation (LDA). In the LDA, the exchange correlation energy at each point of the real space, $E_{xc}$ is assumed to be equal to that energy of a uniform electron gas with the same electronic density

$$E_{xc}^{LDA}[n(r)] = \int n(r) \varepsilon_{xc}^{hom} [n(r)] dr.$$  \hspace{1cm} (3.10)

In Eq (3.10) $\varepsilon_{xc}^{hom}$ is the exchange-correlation energy per electron in a homogeneous electron gas of density $n(r)$. Though this equation is exact for homogeneous system, it can also be extended to some inhomogeneous system, like low dimensional molecules or gas.

3.3 Nudged Elastic Band Method

The Nudged Elastic Band (NEB) method is widely applied in the research on finding the local maxima energy and saddle points energy barriers between two minima energies, usually it refers to the free energy of a reactant and a product in a whole reaction. The fundamental principle for the NEB method is based on linear interpolation for sets of intermediate images listed between the initial and final energies, an elastic band, called spring, is used to connect all of the intermediate images and the energy of each image is locally minimized. There are two problems which are suffered by the traditional elastic band methodology, the first one is the sliding-down issue and the second one is the corner-cutting issue. When the spring constant is chosen at a small value, like $k=0.1$, to describe the total spring force, it will cause the true potential force sliding away from the barrier region along the path, a low resolution oscillating around the
saddle point region will be provided, which is mistake. However, if the spring constant is chosen as a much high value, like k=1.0, it will make the elastic band too hard to decay to converged into the saddle point, and the spring force perpendicular to the reaction path will drive the images to deviate from the true track and thus the expected saddle point region cannot be reached. It is very obvious that the spring constant is dominate on the final result, thus it is of extreme impotence to choose the appropriate spring constant. However, there is no practical way to confidently set a spring constant to conquer both of the two problems with one method. Based on this fact, the “nudging elastic bond” method has been developed to solve the issues. The NEB method first proposes a force projection scheme, in which the perpendicular component of the spring force and the parallel parts of the potential force is projected out, then delete the competitive correlation parts between the two forces, in the end, the total force applied on each image in NEB method is actually the summation of the true potential force perpendicular to the local tangent and the spring force along the local tangent. Once the total energies of the interpolated images are fully minimized, which can be understood that the artificial elastic forces optimized to zero, the hypothetic elastic band lies in true minimal energy path. Figure. 3.1 illustrates the schematic of NEB method. The initial and final states are labeled as r₀ and rₙ, respectively. The linearly interpolated image rₘ(m=1, 2,...,N-1) is constructed by rₘ = r₀ + \frac{m}{n} (rₙ − r₀).
Figure 3.1 Illustration of the NEB method. Including the linear interpolation images connected by the initial and final states. Two optimization pathways are also shown.
Chapter 4

Lattice energy study on common inorganic components

This chapter introduced the key thinking, physics picture and the math formula of the theory prosed in this thesis. With benchmark with the previous theories and experimental data in the study of alkali metal halides, alkali earth metal oxides, and some transition metal compounds, providing a new physics picture for understand lattice energy. The new theory wide the coverages and narrows the limitations compared with the previous theories.
4.1 Introduction of Lattice energy

Lattice Energy is a literal defined as a form of potential energy that could be understood in two ways. In one kind of definition, the value of lattice energy indicates the minimal energy required to destroy the periodic lattice pattern in the ionic solid and transfer its elementary component atoms into the gaseous phases ions. Under this definition, the numerical value of lattice energy is absolutely positive, due to the fact that the reaction described above is always an endothermic one. The other kind of definition address lattice energy as the reverse process, defining it as the energy released when gaseous phases ions start to binding together to form the ionic solid. Either of the defined understanding is illustrated in the scheme shown in Figure 4.1. As mentioned in the second definition, the crystal structure creating process is always an exothermic one, and thus the value for lattice energy is negative. The lattice energy values are expressed with the energy units kJ/mol. The energy of Coulomb interactions between two charged ions, is presented by

\[ U_{\text{ion\ pair}} = C \frac{(n^+ e)(n^- e)}{d} \]  

(4.1)

The symbol C is a constant, d is the distance measure from the center of the positive and negative ions, e is the charge of an electron.
Lattice Energy can be widely used to investigate the stability of ionic crystal compounds. Due to the low entropy of such ion-pair system, it is reasonable to expect the instability in such an ordered structure, however, the strong Coulomb interaction between the positive and negative ions in the crystal produced ultra-high stability which causes a tremendous favorite in the enthalpy. It takes lots of energies to be broken the ordered ion-pair network, which causes most of the typical ionic solids are materials of extreme high melting point and high boiling point.

4.2 Thermodynamic approach, Born-Habor cycle

The value of the lattice energy can get from a thermodynamic cycling reaction, the Born–Haber cycle. The lattice enthalpy is defined as the enthalpy change related in the formation of an ionic crystal compound from gaseous phase ions (an exothermic process), or sometimes defined as the energy to break apart the ionic crystal compound into gaseous phase ions (an endothermic process), as
discussed in the previous session. The thermodynamic model for lattice energy will be first approached in terms of the enthalpy change, referenced to the energy in Figure. 4.2.

\[ \Delta H_{f} = V + \frac{1}{2} B + IE_{M} - EA_{X} + \Delta H_{latt} \]  

(4.6)

V: the enthalpy of sublimation for the lithium atoms  
B: the bond energy of F\(_2\)  
\(IE_{M}\): lithium’s first ionization energy  
\(EA_{X}\): fluorine’s electron affinity  
\(\Delta H_{latt}\): the lattice energy (also named \(E_{BH}\) in the next part in this thesis)

4.3 Electrostatic model, Madelung Energy

A crystal energy derived from thermodynamic parameters has a well-defined value, with a precision dependent upon those of its several components.
However, it does not reveal, or need, any knowledge of the nature of the chemical bonds. It is necessary, therefore, to construct a model based on the interaction of charged species, the simplest of such being a point charge electrostatic model.

Equations for calculating the crystal lattice energy $\Delta H_{\text{lat}}$ here using in this chapter based on the simplest model in which considered the ions as point charges, occupying fixed positions in a regular geometric array, with coulombic forces acting between the ions (the Madelung Energy, $E_M$). Differences between various equations for the lattice energy arise from the way they take into account those interactions which result from the fact that ions are not motionless point charges: overlap repulsive forces, induced dipole forces, vibrational energy, etc.

### 4.3.1 Madelung Constant

For a typical ionic crystal, if knowing the crystal structure, it is routine calculations to calculate the released energy on condensing together the gas phase ions to form the solid crystal, following the equations based on the fundamental Coulomb interactions or electrostatics. The electrostatic energy of an Coulomb ion pair, $M^+$ and $X^-$, separated by a distance valued $r$, can be expressed as below:

$$
E = -\frac{e^2}{4\pi\varepsilon_0 r}
$$

(4.7)

and where the magnitudes of the charges on the ions are $Z^+$ and $Z^-:

$$
E = -\frac{Z^+Z^- e^2}{4\pi\varepsilon_0 r}
$$

(4.8)

(Here $e$ is the unit charge of an electron, equals to $1.6 \times 10^{-19}$ C and $\varepsilon_0$ is the vacuum permittivity, which values at $8.854 \times 10^{-12}$ F m$^{-1}$).
The energy origins from cumblic interactions in a crystal can be calculated for a particular structure by summing all the available ionic interactions, thereby it will produce an infinite series. The series contains terms origins from the attraction between the oppositely charged cations and anions, and also contains the repulsion terms origins from the cation-cation and anion-anion repulsive interactions. Figure 4.3 shows some of these interactions applied in the rocksalt NaCl structure: one Na\(^+\) ion at the center position is surrounded by other 6 Cl\(^-\) ions as next neighbors at a distance \(r\), then by other 12 Na\(^+\) cations at distance \(\sqrt{2}r\), then by other 8 Cl\(^-\) anions at distance \(\sqrt{3}r\), followed by another 6 Na\(^+\) cations at distance \(2r\) and so on. The total energy of the cumblic interaction is given by the summation of all the interactions discussed above:

\[
E_c = -\frac{e^2}{4\pi\varepsilon_0 r \left( 6 + \frac{12}{\sqrt{2}} - \frac{8}{\sqrt{3}} + \frac{6}{\sqrt{4}} - \frac{24}{\sqrt{5}} + \cdots \right)}
\]  
(4.9)

Figure 4.3  The calculation process for the Madelung constant, with the rocksalt lattice type.

The new term inside the brackets is traditionally defined as the Madelung constant \(M\), in this case, for the NaCl structure. The infinite series is difficult
to converge; nevertheless, by numerical treatments, the Madelung constant’s value can be computed numerical with high precision, not only for ionic NaCl crystal but also for almost all the ionic crystal structures. For one mole of NaCl crystal, we can write

\[ E_c = -\frac{N_A e^2}{4\pi\epsilon_0 r} \]

(4.10)

where \( N_A \) is the Avogadro constant, which is \( 6.022 \times 10^{23} \) mol\(^{-1}\) (to avoid counting every interaction twice, the expression is multiplied by \( N_A \) for every ion-pair,). The value of the Madelung constant is dependent only on the geometry types of the given lattice, not on the ion types; values for various structures are given in Table 4.1.

<table>
<thead>
<tr>
<th>Crystal (structure type)</th>
<th>Calculated Madelung constant</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (Rocksalt)</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>CsCl</td>
<td>1.77</td>
<td>1.76</td>
</tr>
<tr>
<td>ZnS (Zinkblende)</td>
<td>1.64</td>
<td>1.64</td>
</tr>
<tr>
<td>ZnS (Wurtzite)</td>
<td>1.65</td>
<td>1.65</td>
</tr>
<tr>
<td>Li(_2)O</td>
<td>2.52</td>
<td>1.62</td>
</tr>
<tr>
<td>MgF(_2)</td>
<td>2.41</td>
<td>2.38</td>
</tr>
<tr>
<td>FeS(_2) (Pyrite)</td>
<td>2.38</td>
<td>2.38</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>4.17</td>
<td>4.17</td>
</tr>
</tbody>
</table>

When the cation and anion are separated at small distances, the electron clouds will behavior to repel each other instead of attraction, and this dominant effect needs to be added in as a new energy form when it comes to the calculation of the lattice energy of the crystal. While distance is large, the repulsion energy can be negligible; however, as the ions approach one to another tightly, the repulsion term increases very quickly. Max Born[111] suggested that the repulsive interaction can be described in the equation as below:

\[ E_R = \frac{B}{r^n} \]

(4.11)
here B is a constant, n is denoted as the Born exponent, which is a constant and relative larger number. After the introduction of the repulsive energy, now we can now update the expression for the previous mentioned lattice energy combined by all the terms of the energies

\[ E_M = E_C + E_R = -\frac{N_A Me^2}{4\pi \varepsilon_0 r} + \frac{B}{r^n} \]  

(4.12)

The value of the lattice energy can reach the minimum energy point once the ionic crystal structure is at its equilibrium, which means when the inter-nuclear distance is also at its equilibrium value of \( r_0 \). After minimize the lattice energy, we can get

\[ E_M = -\frac{N_A M Z^+ Z^- e^2}{4\pi \varepsilon_0 r_0} \left(1 - \frac{1}{n}\right) \]  

(4.13)

This equation is defined as the famous Born–Landé equation: the values of \( r_0 \) and n can be acquired experimentally from X-ray crystallography and measurements for compressibility, respectively.

Pauling[38] showed that the values of constant n can be approximated with reasonable accuracy for crystal structures of typical ionic crystal as well as noble gas geometry structures, by averaging empirical constants for individual ion. Some selective values of the constants are listed in Table 4.2. For example, the n value for the rubidium chloride (RbCl) structure is 9.5 (average of 9 and 10) and for the crystal structure of strontium chloride (SrCl\(_2\)), n equals 9.33 (average of 9, 9 and 10).

Later another equation Born–Mayer equation is also used to calculate the lattice energy, it is a refinement of the Born–Landé equation by using an improved repulsion term, we can get

\[ E_M = -\frac{N_A M Z^+ Z^- e^2}{4\pi \varepsilon_0 r_0} \left(1 - \frac{\rho}{r_0}\right) \]  

(4.14)

Here \( \rho \) is a constant dependent on the compressibility of the crystal.
### Table 4.2 Values of n suggest by Pauling

<table>
<thead>
<tr>
<th>Ion Type</th>
<th>constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>[He]</td>
<td>5</td>
</tr>
<tr>
<td>[Ne]</td>
<td>7</td>
</tr>
<tr>
<td>[Ar]</td>
<td>9</td>
</tr>
<tr>
<td>[Kr]</td>
<td>10</td>
</tr>
<tr>
<td>[Xe]</td>
<td>12</td>
</tr>
</tbody>
</table>

#### 4.3.2 Polarization

The Coulomb interaction between ions is the largest energy term. Another energy term is due to the polarizability of the ions. If one ion has a charge $q$, it creates an electric field $E = qr / 4 \pi \varepsilon_0 r^3$, when this field acts on another atom or ion, it induces a dipole moment $p = 4 \pi \varepsilon_0 \alpha_d E$, where $\alpha_d$ the polarizability in units of volume, and $p$ is in the units of coulomb-meter. The physical picture of polarization is shown in Figure 4.4. This dipole moment creates an electric field that acts back on the original charge. Since this is a self-energy effect, the energy term is

\[
E_\alpha = -\frac{q^2 \alpha_d}{8 \pi \varepsilon_0 r^4}
\]

(4.15)

This interaction is found between an ion and an atom in gases. It is not a term that contributes to the ground-state energy of most ionic crystals. In NaCl, each Cl$^-$ has six Na$^+$ neighbors in an octahedral arrangement. This symmetrical arrangement does not produce an electric field, or a dipole moment, on the Cl$^-$ ion. There is no induced dipole moment. The moral is that, when dealing with polarization forces, one cannot just add up pairwise interactions.

The polarization will contribute corrections to the ground-state energy. The energy term in Eq. (4.15) is the first term of a multipole expansion:

\[
E_{pol} = -\frac{q^2}{8 \pi \varepsilon_0 r} \left( \frac{\alpha_d}{r^3} + \frac{\alpha_q}{r^5} + \frac{\alpha_o}{r^7} + \cdots \right)
\]
where $\alpha_q$ and $\alpha_o$ are the quadrupole and octupole polarizabilities of the ion. A quadrupole has the units of $qr^2$ and an octupole has the units of $qr^3$. They are induced in the atom by the first and second derivatives of the electric field. Because of the symmetrical arrangement of the six neighbors in rocksalt, there is no quadrupole or octupole field on any ion when at its equilibrium site.

![Figure 4.4](image)

**Figure 4.4** Scheme illustrating the polarization effects: (a) an ideal ion pair without any polarization effect, (b) mutually polarized ion pair, (c) sufficient polarization effects boost the covalent bond. Dashed lines represent hypothetical unpolarized ions.

The polarizing ability and polarizability that boost the formation and strength of the covalent bonds can be briefly affected by several factors: 1. The small cation will provide the high polarizing radiation origins from the greater concentration of positive charge restricted in a small area. This explains the fact that LiBr has more covalence character than KBr (the radius of Li$^+$ 90 pm, K$^+$ is 152 pm). 2. The large anion will provide the high polarizability origins from the larger size, in which the outer electrons are not tightly bonded and can be easily distorted by the cation. This explains the fact that for the common halides, iodides have the most covalence in nature (I$^-$ 206 pm). 3. The large charged ions provided large polarization ability for sure, due to the fact that the polarization effect is naturally a Columbic interaction, the large Columbic attraction in the cation will distort the electron cloud for the anion more efficiently. Figure 4.5 shows an insightful scheme for the charge dependent polarization.
Figure 4.5  Scheme for the charge dependent polarization effect. The cation charge is increased from Na\(^+\) to Al\(^{3+}\), the anion size increases from F\(^-\) to Br\(^-\). The covalent ability ranked in the order: [Na\(^+\)Cl\(^-\), NaCl] < [Mg\(^{2+}\)2Cl\(^-\), MgCl\(_2\)] < [Al\(^{3+}\)3Cl\(^-\), AlCl\(_3\)] and [Al\(^{3+}\)3F\(^-\), AlF\(_3\)] < [Al\(^{3+}\)3Cl\(^-\), AlCl\(_3\)] < [Al\(^{3+}\)3Br\(^-\), AlBr\(_3\)].

4.4 The general Born-Harbor circle methods.

As discussed above, the Madelung energy is in the form like

\[ E_M = -\frac{N_AMZ^+Z^-e^2}{4\pi\varepsilon_0\rho_0}(1 - \frac{\rho}{r_0}), \]

here \(q\) is the normal charge of the given crystal. \(r\) is the lattice parameter and \(\rho\) is a constant dependent on the bulk modulus of the crystal, it was supposed that a value of 30 pm works well for all alkali metal halides. If we take the crystal as partial ionic, the real charge on both the anion and cation are not of the exact value of their normal charge, we can try to make the Madelung energy \(E_m\) equals to the experimental BH energy \(E_{BH}\), and approach the solution of the real value of \(q\). However, as shown in Figure 4.6, and Table 4.6, It is obvious to find that for variant kinds of lattice type (from NaCl, CsCl to TiO\(_2\), from standard 3D to layer structures CdI\(_2\) as shown in Figure 4.6 and listed in Table 4.3), the electrostatic potential energy of these crystals always more negative than that of their Lattice energy obtain from the experiment result. The differences between electrostatic potential energy arise
from the way they take into account those interactions which result from the fact that ions are not motionless point charges: overlap repulsive forces, induced dipole forces, vibrational energy. This conclusion indicates the fact that Madelung energy and the Born-Harbor model are only rough methodologies for the purpose of acquiring the ionic charge in the ionic and polar covalent materials and the constant parameter $\rho$ is only applied to balance the theory working on different structures but not describe all the materials in a uniform way. For the previous work of effective charge or iconicity accomplished by Pauling,[38] Coulson,[39] Phillips,[40] Sanderson[41] and Szigeti,[42] they all have some limitations when applied to the universal understanding for the effective charge or iconicity among all the catalogue of crystal lattice and chemical bonds.
Figure 4.6 Energy calculated from the Madelung energy and B-H cycle respectively, among the NaCl, CsCl, CaF$_2$, CdCl$_2$, MgF$_2$, ZnS, TiO$_2$, SiO$_2$, CdI$_2$, CdS, Al$_2$O$_3$ and FeS$_2$, with different crystal type and iconicity, the atomic structures are shown in the below.
Table 4.3  Experimental Lattice energy (From Born-Harbor cycle) and Electrostatic potential energy (Madelung energy) of alkali metals compounds and alkaline earth metals compounds, all the energies are in the units of KJ/mol.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Experimental Lattice energy $E_{BH}$</th>
<th>Electrostatic potential energy $E_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>-1047.85</td>
<td>-1194.82</td>
</tr>
<tr>
<td>LiCl</td>
<td>-860.09</td>
<td>-943.15</td>
</tr>
<tr>
<td>LiBr</td>
<td>-817.33</td>
<td>-881.14</td>
</tr>
<tr>
<td>LiI</td>
<td>-761.4</td>
<td>-806.08</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>-2863.97</td>
<td>-3543.63</td>
</tr>
<tr>
<td>NaF</td>
<td>-930.128</td>
<td>-1049.08</td>
</tr>
<tr>
<td>NaCl</td>
<td>-786.768</td>
<td>-858.80</td>
</tr>
<tr>
<td>NaBr</td>
<td>-751.658</td>
<td>-808.76</td>
</tr>
<tr>
<td>NaI</td>
<td>-703.008</td>
<td>-746.56</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-2530.88</td>
<td>-2967.03</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>-2962.94</td>
<td>-3318.74</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>-2522.12</td>
<td>-2489.92</td>
</tr>
<tr>
<td>MgBr$_2$</td>
<td>-2433.96</td>
<td>-2283.59</td>
</tr>
<tr>
<td>MgI$_2$</td>
<td>-2326.44</td>
<td>-2069.06</td>
</tr>
<tr>
<td>MgO</td>
<td>-3843.34</td>
<td>-4584.25</td>
</tr>
<tr>
<td>MgS</td>
<td>-3398.82</td>
<td>-3720.70</td>
</tr>
<tr>
<td>ZnO</td>
<td>-4026.46</td>
<td>-4540.71</td>
</tr>
<tr>
<td>ZnS</td>
<td>-3693</td>
<td>-3886.5</td>
</tr>
</tbody>
</table>

We can see that the value of the Experimental $E_{BH}$ is always larger than that of the electrostatic potential energy $E_M$, indicating that the simple $\frac{q_1q_2}{r}$ like coulomb interaction is not well enough for the description of the total energy, other interaction information is expected to add in.

4.4.1  The limitations for the previous work.

As mentioned in the previous session, Pauling’s iconicity works major on the diatomic molecule due to its definition based on the whole molecular bond energy as below

$$\Delta = D(A - B) - \frac{1}{2} |D(AA) + D(BB)|$$
which means that if the bond order in the molecule and crystal phase are different (like diamond and C<sub>2</sub> molecule, it is C-C single bond in the former and double bond in the later structure), this method will be seriously challenged, especially for the structure with larger covalent character. For example, the LiF/LiCl/LiBr/LiI is about 0.98/0.94/0.93/0.91 respectively, and the Na halide serious NaF/NaCl/NaBr/NaI is 0.98/0.94/0.93/0.91, makes no difference compared with the Li serious. Even though the electronegativity difference between Li and Na is notable (0.05), the bond energy part from Eq.(4.7) introduces the additional errors from the molecule Li<sub>2</sub> or Na<sub>2</sub> structures and compensate the intrinsic energy difference caused by electronegativity.

Coulson’s method as shown below, is largely numerical, the trial function is

\[ \psi_{\text{valence}} = \psi_{sp^3}(A) + \lambda \psi_{sp^3}(B) \]

very important to achieve the converged results. One challenge of the Coulson’s method lies in the fact that the formation of the bond changes in a localized orbitals picture, in which each atom from what they were in the free atom, not a delocalized one, making it a poor choice for defining that bond’s ionicity.

Second, the energy calculated does not give the cohesive energy of the crystal, or the observed lattice constant, so that varying \( \lambda \) to minimize that energy is a much less meaningful process than it might appear to be at first sight. For example, the experimental value for the effective charge of AlN is about 0.21, the Coulson’s model provides a 0.36 value, which is 50% larger overestimated, more data compared with experiments are listed in Table 4.4

<table>
<thead>
<tr>
<th></th>
<th>Coulson[39]</th>
<th>Pauling[38]</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN</td>
<td>0.35</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>AlN</td>
<td>0.36</td>
<td>0.43</td>
<td>0.21[112]</td>
</tr>
<tr>
<td>CuBr</td>
<td>0.85</td>
<td>0.18</td>
<td></td>
</tr>
</tbody>
</table>
Similar to the Born effective charge, the Szigeti’s effective charge,

\[ \varepsilon_S = \varepsilon_\infty + \left( \frac{\varepsilon_\infty + 2}{3} \right) \left[ \frac{s^2(ze)^2N}{\pi \mu \nu_t^2} \right] \]

(4.19)
is derived from the dynamic vibration correlated with the static and optical dielectric constant \((\varepsilon_S, \varepsilon_\infty)\), though the Szigeti method could provide charge value agrees well with the experiment, as shown in Table 4.5. It is not a static charge, one obvious drawback of the Szigeti’s effective charge is that for the elementary substance like Sn, there is inequality \(\varepsilon_S \neq \varepsilon_\infty\), based on this condition, the Szigeti method will also provide a net charge for the elementary substance Sn, and other materials, which is supposed to be absolute zero due to the homo-nuclear bond types. This drawback prevent the Szigeti method widely applied in the analysis of the static and intrinsic property of variant materials, especially the elementary substance and other materials with high ratio of covalence.

**Table 4.5** Comparison between the Szigeti effective charge and the experimental data.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Szigeti[42]</th>
<th>Experiment</th>
<th>Structure</th>
<th>Szigeti</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>0.81</td>
<td>0.88[114]</td>
<td>MgO</td>
<td>0.59</td>
<td>0.68[101]</td>
</tr>
<tr>
<td>NaF</td>
<td>0.83</td>
<td>0.95[112]</td>
<td>CaO</td>
<td>0.62</td>
<td>1[101]</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.78</td>
<td>0.88[114]/0.92[112]</td>
<td>SrO</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>NaBr</td>
<td>0.75</td>
<td>0.83[112]</td>
<td>CuCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaI</td>
<td>0.74</td>
<td>0.75[112]</td>
<td>CuBr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>0.92</td>
<td></td>
<td>ZnS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Sanderson’s charge definition is much relied on the electronegativity, for a specific atom in the gas molecule or crystal; it doesn’t make the difference about the net charge the atom hold, even though the Sanderson’s effective charge and iconicity provided a reasonable numerical appearance, as shown in Table 4.6, this method is pure empirical, the charge $\delta$ can be scaled as $\sigma \propto \chi$, $\chi$ is the electronegativity. For the MX style crystal, the solution of the effective charge for cation M and anion X is actually can be scaled as $(\sqrt{\chi_X} - \sqrt{\chi_M})$ and $(\sqrt{\chi_M} - \sqrt{\chi_X})$. $\chi_X$ and $\chi_M$ is the Sanderson electronegativity respectively, this kind of formulism guarantees the total neutral condition in the binary MX crystal, however, for the MX$_2$ or other non-binary crystal structure, it needs the cube root for each atom, and the neutral condition is not analytic assured, however, the result happens to provide a “nearly neutral” condition. The Sanderson’s methodology relies on too much on the numerical approximation and empirical coincidence, lacks clear physical picture for understanding.

**Table 4.6** Sanderson’s effective charge for the alkali metal halide,

<table>
<thead>
<tr>
<th></th>
<th>LiF</th>
<th>NaF</th>
<th>KF</th>
<th>RbF</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.753</td>
<td>0.797</td>
<td>0.851</td>
<td>0.92</td>
</tr>
<tr>
<td>LiBr</td>
<td>0.666</td>
<td>0.711</td>
<td>0.764</td>
<td>0.833</td>
</tr>
<tr>
<td>LiI</td>
<td>0.621</td>
<td>0.666</td>
<td>0.719</td>
<td>0.789</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>0.585</td>
<td>0.638</td>
<td>0.711</td>
</tr>
</tbody>
</table>
4.4.2 The improved methodology

The previous session reviewed methods including Pauling, Coulson, Szigeti, Sanderson etc, all treat the electrostatic interaction within the Coulomb law, i.e. only the $\frac{1}{r}$ term is included, this kind of approach can well describe the systems of highly ionic character, like the rocksalt CsF, RbF, KF, in which cases the anion and cation are well separated the other high order interactions, like polarization, dipole-charge, dipole-dipole interactions are negligible, and the $\frac{1}{r}$ picture can almost dominate the electrostatic energies with a >99% ratio.

Figure 4.7 plots the polarization energy and the ration (the percentage of the polarization energy over the total Madelung energy) for the rocksalt structures composed by Na⁺, K⁺, Mg²⁺, Ca²⁺ with F⁻, Cl⁻, S²⁻, O²⁻. As introduced in the previous chapter, the ability of the polarization scales with the relationships as

\[
E_{pol} = -\frac{q^2 \alpha_d}{8\pi\varepsilon_0 r^4}
\]

(4.20)

It is $\frac{1}{r^4}$ scaled with the lattice parameter and square with the atomic effective charge q, we can expect that for the structure with +2 charged, like MgO, has much more significant polarization effect and higher polarization energy ($E_{pol}$). As shown in Figure 4.7, the value of $E_{pol}$ of +1 charged Na⁺ and K⁺ based structures (NaF/KF, NaCl/KCl) are around 125 KJ/mol, the $E_{pol}$ of +2 charged Mg²⁺ and Ca²⁺ based structures (MgO/CaO, MgS/CaS) are around 500 KJ/mol, almost 4 times as that for the +1 charged cases. Besides the remarkable charge effect, the ion size also shows influence on the polarization from the individual atomic polarizability $\alpha$, the polarizability of Na⁺, K⁺, Mg²⁺, Ca²⁺ cation is about 1 Å³, much smaller compared with that in the anion (around 5 Å³ based on the Pauling’s data), the anion is dominant on the polarization phenomena in these structures, we can see in Figure 4.7 that among the +2 charged O²⁻ and S²⁻ pair,
the larger $S^{2-}$ anion results a 60 KJ/mol and 65 KJ/mol, high $E_{pot}$ value in the Mg$^{2+}$ and Ca$^{2+}$ cation over the O$^{2-}$ anion, which can be recognized as a 5% total energy drop as shown in the down part of Figure 4.7, the same ratio for the +1 charged K$^+$ and Na$^+$ is within 1%.

Figure 4.7  Up, the polarization energy of several rocksalt structure composed by K$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$ and F, Cl, O$^{2-}$, S$^{2-}$. Down, the percentage of the polarization energy for the same crystal structures. This percentage can be recognized as the additional total energy drops from the polarization.

The Figure 4.7 and the above discussion provided an insightful solution for the improvement for the calculation of the effective charge based on the traditional Born-Harbor circle and Madelung energy, i.e. by introducing the polarization
energy of both the cation and anion which can affect 5% of the total energy. We define the improved charge balanced equation as

$$E_{BH} = \frac{Mq^+q^-}{4\pi\varepsilon_0 r_0} \left(1 - \frac{p}{r_0}\right) - \frac{q^+q^- (\alpha_+ + \alpha_-)}{8\pi\varepsilon_0 r_0^4}$$

(4.21)

The first item is the Born-Mayer equation, manifests the Madelung energy origins from the Coulomb’s law, the second term is the modified function based on the polarization energy induced by the additional anion and cation interactions, which scales $\frac{1}{r_0^4}$, of high order compared with the $\frac{1}{r_0}$ Coulomb’s law, the dipole-dipole interactions is on the even higher order $\frac{1}{r_0^6}$, it is comparable weaker than the polarization effect, and we find the modified formula (Eq 4.21) which including the polarization effect only, this improved Born-Mayer equation can work well for all the materials in this work, including all the I-VII, II-VI main group compounds, some transition metal compounds and the layer structures like transition metal dichalcogenides (TMDs). The polarization can be recognized as the extension of the electron cloud between the anion and cation, this kind of interaction has the similar picture of the covalent bonding character, however, the polarization origins from the electrostatic interaction (mostly dependent on the multiple of $q^+q^-$), it doesn’t have the same nature as the covalence, meanwhile, when the polarization is along the direction which happens to be along with the possible direction in which covalent bonds can be formed, the polarization effect will spontaneously enhance the covalent bonding as a side effect, take the LiI for example, the possible covalent bonding in this structure could be the sigma bond by Li’s 2s and I’s 6p orbitals, which is exactly along the Li-I direction in the crystal, the polarizability of I is around (7 Å³), which is significant compared with other halide anions as well as other anions like S²⁻, N³⁻, and a strong polarization effect is expected in the LiI crystal, due to the fact that this polarization effect is not directional, it covers radical Li-I direction as the covalent bonding, the weak covalent interaction could be well enhanced by the polarization. In some
other crystal with different lattice type or even amorphous phase, the directional covalent bonding may benefit very little from the polarization effect if the polarization favors the direction is less overlapping with the covalent orbital’s orientation. Figure 4.8 illustrated the example the polarization enhanced the σ bond much more rather than the π bond, due to the fact that the σ bond type can provide more space for overlapping with the polarization, while the π bond cannot. The other orbitals, like d or hybrid ones follow the same physical picture once interacted with the polarization, the enhancement of covalence due to the polarization can be directly analyzed through the orbital space.

Figure 4.8, Polarization interacted with the σ and π bonds. The polarization will enhance a lot to the σ bond due to the large overlapping, but will enhance a little to the π bond due to the limited overlapping.

4.5 The results of the new theory

To check the capability of the new theory, we start from the rocksalt alkali metal, which is typical ionic compound and well-studied by many previous research work. Here in our method, to solve he equation

\[
E_{BH} = \frac{Mq^+q^-}{4\pi\varepsilon_0r_0^3} \left(1 - \frac{\rho}{r_0}\right) - \frac{q^+q^- (\alpha_+ + \alpha_-)}{8\pi\varepsilon_0r_0^4}
\]

(4.22)
we need to know the expression of $E_{BH}$ from the Born-Harber cycle, the electron affinity (EA) and ionization potential (IP) are two charge dependent variables contributed to the $E_{BH}$.

$$E_{BH} = \Delta H_f - \Delta H_{at} - IP_1 - EA_1$$  \hspace{1cm} (4.23)

Here $\Delta H_f$ and $\Delta H_{at}$ are the formation energy and atomization energy, which can be acquired both experimentally and theoretically, the subscribe “1” in IP and EA means the first order IP and EA energy respectively.

The equation 4.22 is independent on the variable $q$, which makes it impossible to solve Eq. 4.23, therefore we provided an approximation method to get the linear relationship between $E_{BH}$ and the effective charge of the anion ($q^-$) and cation ($q^+$),

$$E_{BH} = \Delta H_f - \Delta H_{at} - q^+IP_1 - q^-EA_1$$  \hspace{1cm} (4.24)

And for the materials including second order IP and EA, it turns into the following equation

$$E_{BH} = \Delta H_f - \Delta H_{at} - IP_1 - EA_1 - (q^+ - 1)IP_2 - (q^- - 1)EA_2$$  \hspace{1cm} (4.25)

For this kind of materials, like MgO, the first order IP/EA is fully accomplished, with the coefficient equals to “1” in front of $IP_1$ and $EA_1$, the $q^+$ and $q^-$ in Eq.4.25 represent the first order charge, within the range [0,1], and the total effective charge in this condition equals to the sum of the events in these two orders, $q_{tot} = 1 + q_2$. When the IP/EA is higher than 3rd order, it follows the same procedure.

$$q_{tot} = (n - 1) + q_n$$

$n$ correlates with the $n^{th}$ order IP/EA energies.

By applying the above approximation, the equation 4.24-25 can be expressed in

$$\Delta H_f - \Delta H_{at} - q^+IP_1 - q^-EA_1 = \frac{Mq^+q^-}{4\pi\varepsilon_0 r_0} \left(1 - \frac{r_0}{\rho}\right) - \frac{q^+q^- (\alpha_+ + \alpha_-)}{8\pi\varepsilon_0 r_0^4}$$  \hspace{1cm} (4.26)
for the MX type crystal, like alkali metal halides, the neutral conditions require \( q^+ + q^- = 0 \), then equation 4.26 could be solved analytically and numerically. However, in order to look into the detail of the solution, we will choose the numerical methods to get the solution and further look into the necessarily of the new methods developed from the classic Born-Mayer equation.

Figure 4.9 illustrated the details for the solution of Eq. 4.24-25, the whole procedures can be realized by plotting the \(|z|\) dependent function of \( E_{BH} \) and \( E_M + E_{pol} \), and get the intersection. We can see in Figure 4.9 that without the polarization item \( E_{pol} \), there is no intersection between \( E_{BH} \) (the black line) and \( E_M \) (the red line) within the range \([0,1]\), since \( E_M \) is energetically higher than \( E_{BH} \) when \( q \) equals to 1, as discussed previously. Once the additional \( E_{pol} \) item joined in, the total energy (\( E_M + E_{pol} \), the blue line) dropped down and there comes up a solution at \( q = 0.943 \) for LiF, which is defined as the effective charge of LiF in our model. From Figure 4.9, we can realize that since the Born-Harbor Circle describes the whole energy system for each step inside, the classic Born-Mayer equation only consider the \( \frac{1}{r} \) scale Coulomb interaction, which is not full enough to quantize the whole energy related to the lattice formation, this is why there is a gap between the two theories, as shown in the dashed red circle in Figure 4.9. The introduction of the polarization events provided a vital correction to the Born-Mayer theory and in the next part we will check the capability and popularity for this new theory.
Figure 4.9  The illustration for the solution of effective charge $q$, take the LiF structure as an example. The black, red and blue line represents the Born-Harber energy ($E_{BH}$), the Madelung energy ($E_M$) and the Madelung energy plus the polarization energy ($E_M + E_{pol}$). The dashed red rectangular indicates that there is no intersection between the $E_{BH}$ and $E_M$, and once the $E_{pol}$ is added in, a solution equals 0.943 can be got for equation 4.26, which is the effective charge for Li+ in LiF crystal in our model.

4.5.1  The application to the alkali metal halides.

Following the calculation procedure in the previous session, we calculated the effective charge for the alkali metal halides, the raw data are shown below catalogued by alkali metal families, from Li to Rb, the black, red and blue lines represent the Born-Harbor energy ($E_{BH}$), the Madelung energy ($E_M$) and the Madelung energy plus the polarization energy ($E_M + E_{pol}$). The effective charge,
i.e., the intersection of the $E_{BH}$ curve and the $E_M + E_{pol}$ curves, are marked for each structure.
Table 4.7, summarize the effective charge (or ionicity) for the alkali metal halides plotted in all the figures above, from LiF to RbI, including the methods developed by Pauling[38], Phillips[40], Sanderson[41], Szigeti[42] and this work, also some experimental data are included for benchmark and reference. Figure 4.9 presents the graphic version. Compared with the previous works, our data is close to the Phillips’ ionicity (here, in alkali metal halides, we assume the concept of “ionicity” equals to the “effective charge”) and Sanderson and Szigeti’s effective charge, that means our methods can keep the merits of the previous works, and avoid the vital weakness. Also, our data are close to the available experimental value as shown in Table 4.7. It is noticeable in Figure 4.10 that there seem huge errors between Pauling’s data and the others, the hidden mechanism for such mismatch is due to the intrinsic definition as discussed in the previous sessions, which is expected to expand the errors in typical ionic crystals.

We can see from Figure 4.10 that our results pronounce periodic character for each alkali metal. Like Li, combined with variant anion, the effective charge is in the order like LiF>LiCl>LiBr>LiI, which indicates that the more electronegativity the anion is, the more effective charge, more ionic the compound will have, even though this regularity sounds reasonable, there is no numerical guarantee at all, because from equation 4.26 the electronegativity is not an input parameter in our model. The previous Pauling or Sanderson’s models are all based on the pre-defined electronegativity concepts, and the charge or ionicity calculation mainframe strictly derived from the linear or polynomial combinations of the relative electronegativity between two ions.(like $|\chi_A - \chi_B| \cdot |\sqrt{\chi_A} - \sqrt{\chi_B}|$ etc), the electronegativity is a universal parameter for the element in any chemical forms, including atom, molecule, crystal, etc, when this universal definition applied in the given typical ionic crystal, the inevitable errors come up in a systematic and expected way. In some extent those methods could be recognized as “pre-assumed”, not developed directly from the nature of the given crystal, i.e. once compared whether LiF or
LiI have more effective charge, people can think for granted that LiF will be the answer, because of the large electronegativity fluorine ion has, however, as discussed above, this kind of philosophy is just an empirical approach and cannot strictly be guaranteed scientifically. As shown in the data shown in Table 4.7 and Figure 4.10, we find that the introduced polarization effect could meanwhile cover the electronegativity picture, which proves that our model hits a more universal picture than the previous Pauling or Sanderson’s electronegativity guided effective charge scheme. For the fixed anion structures, like Cl, the effective charge orders in the sequence RbCl>KCl>NaCl>LiCl, decreases from 0.99 to 0.93, for the fixed cation structures, like Na, the effective charge orders in the sequence NaF>NaCl>NaBr>NaI, decreases from 0.98 to 0.94, all of the above structures are typical ionic crystal, with effective charge >0.90.

Table 4.7  Summary of the effective charge for the alkali metal halides, from Li⁺ to Rb⁺, F⁻ to I⁻, including the methods from Pauling[38], Phillips[40], Sanderson[41], Szigeti[42] and this work, some experimental data are also attached from reference.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pauling</th>
<th>Phillips</th>
<th>Sanderson</th>
<th>Szigeti</th>
<th>This work</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>0.89</td>
<td>0.915</td>
<td>0.753</td>
<td>0.81</td>
<td>0.943</td>
<td>0.88</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.63</td>
<td>0.903</td>
<td>0.666</td>
<td>0.77</td>
<td>0.912</td>
<td></td>
</tr>
<tr>
<td>LiBr</td>
<td>0.55</td>
<td>0.899</td>
<td>0.621</td>
<td>0.74</td>
<td>0.911</td>
<td></td>
</tr>
<tr>
<td>LiI</td>
<td>0.43</td>
<td>0.89</td>
<td>0.54</td>
<td>0.54</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>0.91</td>
<td>0.946</td>
<td>0.797</td>
<td>0.83</td>
<td>0.959</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>0.67</td>
<td>0.935</td>
<td>0.711</td>
<td>0.78</td>
<td>0.93</td>
<td>0.88</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.59</td>
<td>0.934</td>
<td>0.666</td>
<td>0.75</td>
<td>0.926</td>
<td></td>
</tr>
<tr>
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<td>0.47</td>
<td>0.927</td>
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<td>0.75</td>
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<td>KF</td>
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<td>0.851</td>
<td>0.92</td>
<td>0.964</td>
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</tr>
<tr>
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<td>0.947</td>
<td>0.97</td>
</tr>
<tr>
<td>KBr</td>
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<td>0.952</td>
<td>0.719</td>
<td>0.77</td>
<td>0.944</td>
<td>0.80</td>
</tr>
<tr>
<td>KI</td>
<td>0.5</td>
<td>0.95</td>
<td>0.638</td>
<td>0.75</td>
<td>0.931</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.10  The graph presentation for the summary of the effective charge or iconicity for the alkali metal halides.

The numerical effective charge listed in Table 4.7 and Figure 4.10 provided a vision impression about the ionic character and the benchmark with the other methods and experiments, the data demonstrates the polarization effect can present a reasonable figure of the effective charge, however, it didn’t involve the picture from the real space wavefunction or charge density distribution. If the polarization effect leading picture is real and can hold the whole system, it should grasp more than the figure of the effective charge only, this effect can show up and be measured in variant intrinsic properties or response to the
external perturbation, like dielectric properties, optical properties, transport properties, etc.

Figure 4.11  Potential surface plot for lithium halides and potassium halides. The iso-value is 8.5 eV/Å³. The Alkali metal cations are on the corner of the primitive cell, the halide anions are in the center. The red circle in the LiI structure indicates the
The green rectangular indicates the “ionic disconnection” between the alkali metal and the halides in other structures.

Figure 4.11 shows the total potential surface for the lithium and potassium halides crystal structures, from which we can derive the bonding information between the anion and cation, for the lithium halides systems, the LiF is much more ionic than the LiI, which indicates the lithium and fluorine ion should be well separated without any bonding character, as highlighted by the green rectangular in Figure 4.11, for the potassium halides structures, the ionic character is much dominant than the lithium halides, from KI to KF, this isolated potential surface for the anion and cations is more obvious than that in the corresponding lithium halides with the same anion. This isolated “ionic disconnection” phenomena appear in all the typical ionic crystals unless the polarization effect boost the covalence in much further extent which can induce directly inter-atomic wavefunction overlapping, as shown in the LiI case in Figure 4.11, the effective charge of LiI is 0.91, the least among all the alkali metal halides, in other way of expression, the LiI crystal possess the largest covalence and it is the most possible structure to show the polarization promoted covalence in the typical ionic crystal structures, as shown in Figure 4.11, highlighted by the red circle in the LiI case, we can see a clearly potential surface overlapping between the lithium cation and the nearby iodine anion, illustrating the existence of the covalence, there are many factors for the emergence for the covalence, here we suggest that the most decisive condition comes from the capability of polarizability, which makes covalence comes up in the iodine anion structures. For the KI crystal, the summation of the polarizability from (K\(^+\), I\(^-\)) pair is actually larger than the (Li\(^+\), I\(^-\)) pair, however, this doesn’t hint the polarization capability of KI is over LiI, because the polarization origins from the Coulomb interaction and it scales \(\frac{1}{r_0}\), \(r_0\) is the inter-atomic distance, which is half of the lattice parameter, the lattice parameters of LiI and KI are 6.00 Å and 7.05 Å, the Coulomb interaction distance of KI is much longer than that of LiI, which decrease the polarization effect much than
the increase benefits from the atomic polarizability, which results the effective charge 0.9 in LiI and 0.931 in KI.

Another analysis on the covalent bonding character is from the electron localization function (ELF), this data provides insightful information about the distribution of the bonding electrons. For example, in the typical covalent crystal diamond, the ELF lie on the center of each \( sp^3 \) C-C bonds, indicating the classic covalent bonding between the two C atoms. Figure 4.12 plots the ELF for the lithium halides crystal structures we can see that from LiF to LiI, the size of ELF significantly increases with the decrease of effective charge from 0.98, 0.94, 0.93, 0.91 in LiF, LiCl, LiBr, LiI, indicating the strong capability for bonding formation in the LiI crystal structures.

![Electron Localization Function](Image)

**Figure 4.12** The electron location function (ELF) plot for the lithium halides. The iso-value is 0.3. The purple atom represents the Li, the other color represents the halide in each structure.

To summarize, from our modified methods, we can predict the effective charge for the alkali metal halide, the data trend agrees well with the previous work driven by the electronegativity assumptions, and can benchmark well with the
experimental investigation. By studying the real space potential surface and the ELF distribution, the polarization effect can be understood in visualization way and the polarization enhanced covalence can be well observed from the weak inter-atomic bonding formation happens gradually from LiF to LiI structures. Even though the atomic polarizability in KI is larger than that in LiI, the shorter Coulomb interaction length in LiI assures a more dominant polarization effect and a relative smaller effective charge.

4.5.2 The application to the alkali earth metal oxides chalcogenides.

The alkali earth metal oxides and chalcogenides, like MgO, CaO, CaS, have the same rocksalt crystal structure as the alkali metal halides, however, the noticeable difference lies on the charge states, the formal charge of the cation in alkali earth metal oxides and chalcogenides are +2, which includes two process for the ionization potential (IP) and electron affinity (EA), firstly the system reaches the transient state when IP1 and EA1 are full achieved, after the balance , start on the second processing, the effective charges defined in our model thus only matters with the second IP/EA events summers the charges in the two processing.

Figure 4.13 illustrated the calculation procedures for the effective charges in the two steps IP/EA events in the alkali earth metal oxide and chalcogenides, takes the BeO for example. A brief scheme in Figure 4.14 shows the intermediate states. We assume hat in the first order ionization events, the Be and O atom first reach the Be⁺O⁻ states with IP₁/EA₁ fully accomplished, however, as shown in the green rectangular in Figure 4.13, when q=1, the $E_{BH}$ is still deeper than $E_M + E_{pol}$, which indicates that only 1 charge ionization cannot make the system to the balance state, i.e, due to the less value of the Coulomb interaction, even though the polarization energy already contributes around 500 KJ/mol. Since the system is still motivated to low the total energy, and there are still one more available electron in the Be⁺⁺ cation to be lost, the system starts the
second order ionization, as briefed in Figure 4.14. In the second order stage, the \( \text{Be}^{1+}\text{O}^{1-} \) structure turns into the \( \text{Be}^{2+}\text{O}^{2-} \) after the IP/EA energy released, however, similar to the alike metal halides case in the previous session, the polarization effect will enhance the covalent \( \sigma \) bond along the inter-atomic direction, which lower the ionic character and the effective charge. Here in BeO we can see the intersection between the \( E_{BH} \) and \( E_{M} + E_{pol} \), results a 1.315 effective charge value, can converts to 0.66 ionicity value, which is much lower than the same periodic element composed LiF structures (0.94).

**Figure 4.13** The illustration for the solution of effective charge \( q \) for the alike earth metal oxide and chalcogenides, take the BeO structure as an example. The black, red and blue line represents the Born-Harber energy (\( E_{BH} \)), the Madelung energy (\( E_{M} \)) and the Madelung energy plus the polarization energy (\( E_{M} + E_{pol} \)). The dashed red rectangular indicates that there is no intersection between the \( E_{BH} \) and \( E_{M} \), and once the \( E_{pol} \) is added in, a solution equals 1.315 can be got for equation 4.26, which is the effective charge for \( \text{Be}^{2+} \) in BeO crystal in our model. The dashed line indicates the boundary for the first and second order IP/EA energies.
Figure 4.14  Brief scheme for the Be"O" through several steps strategies. First the Be and O atoms forms the Be"O" intermediate phase through IP₁ and EA₁ energies, second the Be"O" transforms into the Be"O" phases once the IP₂/EA₂ applied, at last the system converged to the final states Be"O" by releasing the additional energies.

The calculation details for all the alkali earth metal oxide and chalcogenides are plotted in the below figures, the anion elements include O, S, the cation elements include Be, Mg, Ca, Sr.
Table 4.8 summarize the effective charge (or ionicity) for the alkali earth metal oxides and chalcogenides plotted in all the figures above, from BeO to SrS, including the previous work done by Pauling, Phillips, Sanderson, Szigeti and this work, also some experimental data are included for benchmark and reference. Figure 4.15 presents the graphic version. Compared with the previous works, very similar to the alkali metal halides data in the previous session, the main group (II-VI) data is also close to the Phillips’ ionicity (here, in alkali earth metal oxides and chalcogenides, the formal charge is 2, we assume the concept of “ionicity” equals to the half of the “effective charge”) and can benchmark well with the experimental observation. Our data for the alkali earth metal oxides and chalcogenides also product the effective charge follow the electronegativity order as defined by the Pauling and Sanderson’s methods.

Table 4.8   Summary of the effective charge for the alkali earth metal oxides and chalcogenides, from Be$^{2+}$ to Sr$^{2+}$, O$^{2-}$ to S$^{2-}$, including the methods from Pauling[38], Phillips[40], Sanderson[41], Szigeti[42] and this work, some experimental data are also attached form reference.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pauling</th>
<th>Phillips</th>
<th>Sanderson</th>
<th>Szigeti</th>
<th>This work</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>0.63</td>
<td>0.602</td>
<td>0.361</td>
<td>0.55</td>
<td>0.6575</td>
<td>0.88</td>
</tr>
<tr>
<td>BeS</td>
<td>0.22</td>
<td>0.312</td>
<td>0.24</td>
<td>--</td>
<td>0.597</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.73</td>
<td>0.841</td>
<td>0.486</td>
<td>0.59</td>
<td>0.7745</td>
<td></td>
</tr>
<tr>
<td>MgS</td>
<td>0.34</td>
<td>0.786</td>
<td>0.366</td>
<td>0.49</td>
<td>0.752</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.79</td>
<td>0.913</td>
<td>0.598</td>
<td>0.62</td>
<td>0.819</td>
<td></td>
</tr>
<tr>
<td>CaS</td>
<td>0.43</td>
<td>0.902</td>
<td>0.479</td>
<td>0.52</td>
<td>0.805</td>
<td>0.88</td>
</tr>
<tr>
<td>SrO</td>
<td>0.79</td>
<td>0.926</td>
<td>0.677</td>
<td>0.64</td>
<td>0.8225</td>
<td></td>
</tr>
<tr>
<td>SrS</td>
<td>0.43</td>
<td>0.914</td>
<td>0.558</td>
<td>0.54</td>
<td>0.8185</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Figure 4.15 The graph presentation for the summary of the effective charge or iconicity for the alkali metal halides.

Figure 4.16 plots the potential surface for the LiF/LiI, BeO/CaO rocksalt crystal structures. The CaO and BeO crystal structures are composed from the same anions however, due to the difference between the radius of the cations, the polarization effect in BeO is much dominant than that in the CaO, with the effective charge (ionicity) 1.31 (0.65) and 1.64 (0.82) in the two structures, which indicates that the covalent character in the BeO is significant, as illustrated by the red circle in Figure 4.16, there are more distinct covalent interactions in the BeO crystal structures. This scenario is very similar to the LiF/LiI case as discussed in the previous session.
Figure 4.16  Potential surface plot for LiF, BeO, LiI and CaO crystal structures. The iso-value is 5 eV/Å³. The metal cations are on the corner of the primitive cell, the anions are in the center. The red circle in the LiI structure indicates the covalent-style energy surface. The green rectangular indicates the “ionic disconnection” between the cations and the anions in other structures.
Figure 4.17  Summary of the ionicity for some transition metal compounds, including the Phillips, Pauling, Sanderson and Szigeti’s previous work.

Besides the I-VII, II-VI main group ionic compounds, our method also can work well for the transition metal compounds as shown in Figure 4.17, similar to the previous results, the data derived from our method are close to the Phillips’ ionicity, the relationships between our methods and Phillips’ will be continued to discuss in the next chapter. Since the transition metal compounds include more complicated factors, like d-orbital penetration, this part of research will keep modified and improved in the future work.

To summarize, our methods can well extend to the alkali earth metal oxides and chalcogenides, which system has formal charge 2. We have divided the whole converged balance status into three step strategies, including the fully ionized first step with IP₁/E₀₁ energy events, the fully ionized second step with IP₂/E₀₂ energy events, and the last step including the additional energy releasing to reach the balance, due to the fact that there is overflow for the electrostatic energy required for the crystal formation viewed from the Born-Harber cycle. The data trend we got agrees well with the previous work and can benchmark
well with the experimental investigation. Follow the same procedure as applied in the alkali metal halides session, by studying the real space potential distribution, the polarization effect can be understood in visualization way and the polarization enhanced covalence can be well observed from the weak interatomic bonding formation. Compared with the alkali metal halide compounds, the ionicity of this II-VI main group compounds are significantly reduced within the range between 0.65~0.75, which can be explained due to the enhanced polarization effects due to the larger formal charge and large anion radius compared to the alkali metal cation or halide anion in the same row of the periodic table.

4.5.3 The influence with the electronic band structures.

The effective charge and ionicity have influence with the electronic band structures together with the distance between ions. Take three of material with same structure type and similar lattice parameter as reference, the band structure of LiBr(a=5.5 Å), NaCl(a=5.62 Å), RbF(a=5.64 Å) are calculated and shows in Figure 4.18.

![Figure 4.18](image)

**Figure 4.18** Band structure of a) LiBr crystal, b) NaCl crystal, c) RbF crystal. Red dash line indicate the fermi level and the blue line point out the position of lowest unoccupied molecular orbital of LiBr.
It can be observed that with the effective charge getting bigger, the band gap of the crystal also became bigger with similar lattice parameter. The tendency of this influence is indicated in Figure 4.19. That mainly because that when the effective charge getting bigger, the crystal is more ionic and as we know the ionicity $f_i = \frac{E_c^2}{E_g^2}$, here $E_g$ is energy of band gap, and $E_g^2 = E_c^2 + E_h^2$, and $E_h$ here is constant, so the increase of ionicity result the increase of energy band gap.

![Figure 4.19](image1.png)  

**Figure 4.19**  Band gap of crystal with different effective charge.

When consider with the material with significant difference with lattice parameter, it need to balance the influence of both two effect on band structure. Figure 4.20 shows the band gap of NaF, NaCl, NaBr, NaI.

![Figure 4.20](image2.png)  

**Figure 4.20**  Band gap of NaF, NaCl, NaBr, NaI from left to right.
Chapter 5

Lattice energy and the effective charge of the 2D layer transition metal dichalcogenides

This chapter extended the new theory to the quasi 2D layered materials, which is beyond the capability of the previous theories, also applied the methodology on calculating the effective charge between monolayer MoS$_2$ and WS$_2$, providing reasonable explanation to the higher Raman frequency in mono WS$_2$, the layer dependent and stacking dependent effective charge also been calculated.
5.1 The new model towards the low dimensions

The previous chapter, we have reviewed the formal work about the calculation of effective charge and ionicity of Pauling, Phillips, Sanderson and Szigeti, and also provided suggestions about the characteristic and weakness of the above-mentioned methods. Except the dynamic Szigeti charge, the previous work calculating the static charge are all based on the electronegativity which is an elementary property whatever the studied element in which kinds of substance formation, atom, gas molecule or condensed states. Those kinds of methods are pure universal and works pretty well for some systems, however, due to the complexity and multi-functional properties of the atomic orbital combination in the solid states, sometimes the unneglectable errors will come up, for example, Pauling’s ionicity origins from the diatomic molecule, which is proved to be poor on predict the effective charge in typical ionic crystal with slight covalent character, like LiI. Inspired by the universal polarization effects in the polar ionic crystals, we have developed a new methodology based on the energy scale for the individual crystal instead of the elementary scale, the energy from the Born-Harbor Cycle, Madelung energy, and the polarization effect inside, as shown in the previous session, the physics picture for this new model is based on the question

“How many energies it needs to form the stable crystal and where can the energy come from?”

So clearly there are two answers to the above question. ‘how many” and “where”. Our new model responses the answer to the first question from the Born-Harber Cycle and the answer to the second question from the electrostatic interactions.

The Born-Harber Cycle provided a full scenario about the energy scale required to form the stable crystal, which exactly describes the energy amount (\(E_{BH}\)) to
reach the static status of the given crystal, which can be a reasonable answer to the first question. The electrostatic interaction exists in all the crystals except the elementary substance, in which case we don’t have to worry about the static effective charge which analytically equals to 0. The traditional Born-Mayer equation only includes the $\frac{1}{r}$ like Coulomb interactions (Madelung energy $E_M$) with a repulsive item. However, as shown in Figure 4.9, the energy $E_M$ provided is not enough to touch the requirement from $E_{BH}$, which means that even for the perfect ionic crystal with the effective charges reaches the formal charge, there is still more additional energy needed. The “additional energy” item indicates that some other interactions, like polarization, dipole-dipole interaction, quadric dipole interactions etc. cannot be ignored, the polarization energy scales with $\frac{1}{r^4}$ is the most dominant one and we add in the polarization energy ($E_{pol}$) as the additional term and the new electrostatic energy is $E_M + E_{pol}$ and the solution for the effective charge becomes to solve the equation $E_{BH} = E_M + E_{pol}$, which results the effective charge for the given polar ionic crystals.

As discussed in the previous chapter, the data from our model of bulk ionic materials agree well with the previous works, especially the work of Phillips. In this chapter, we will conclude that our model has superiority over Phillips’ model since our model can well describe the quasi two-dimensional (2D) layer and quantum cluster structures as well.

5.2 The improvements over Phillip’s ionicity theory

The monolayer MoS$_2$ is a quasi 2D semiconductor which attracts tremendous research interest both in fundamental scientific investigation and advanced industry application, due to its quasi 2D character with direct band gap types and strong spin orbital coupling strength, the mono layer MoS$_2$ is expected as one of the most promising materials candidates for the next optoelectronics and
spintronics. The structure of mono-layer MoS$_2$ is shown in Figure 5.1, different from the traditional bulk materials, the structure of the mono-layer MoS$_2$ terminated at a surface S atom, which is connected to the nearby Mo atom by three bonds on one side and leaving the other side bared towards the vacuum. This geometry truncated structure makes the electric un-balanced statues for all the surface S atoms and generated the discrete potential surface gradient on the surface areas. As shown in Figure 5.1, by perturbing the surficial S atoms up and down with displacement shift $\Delta d$, we can get the difference of the site potential, as defined as $\Delta V = V_1 - V_2$, we can get the amplitude of the electric field as $E = \Delta V/2\Delta d$, the simulated electric field distribution is plotted in Figure 5.1. (b), we can see the net electric field effects starts from the Mo cation in the center and ended in the surface S atoms, since there is no mirror symmetry on the upside, this kind of electric will have practical affection on the intrinsic properties of the whole structure. This effect is still a polarization effect which is covered by the $E_{pol}$ term in our model. Since in the bulk materials, due to the symmetry protection, the intrinsic electric field sums equals to zero and what we can do is just turn to measure the size of the polarizability instead of the electric field itself, even though the polarizability is actually resulting from the electric field inside, this part of polarization energy can be described as $E_{pol}^1 = \frac{2}{3} \frac{q^2 \alpha}{8 \pi \varepsilon_0 r^4}$, since the 3 dimension is reduced to 2 now, the coefficient $\frac{2}{3}$ is applied here, the rest dimension responds to the electric filed affecting ones. For the 2D materials, besides the intrinsic polarizability, this symmetry-broken induced electric field is revoked and it joins the polarization events in a straightforward way, and this part of energy can be described as $E_{pol}^2 = \frac{1}{2} E^2 \alpha$, here $E$ is the amplitude of the electric filed defined above and $\alpha$ is the polarizability for the corresponding atoms, it is the surface S atom in the mono-layer MoS$_2$ structure, this energy part takes responsibility for the truncated dimension (the $\frac{1}{3}$ coefficient) in the $E_{pol}^1$ part, and now the total expression for the polarization energy now becomes
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\[ E_{pot} = E_{pot}^1 + E_{pot}^2. \]

(5.1)

Even though the Phillips’ methods also can provide reasonable ionicity value for most of the \( ANB^{8-N} \) (N is the number of valence electrons) inorganic crystals, here again, we recall its definition

\[ f_i = \frac{C_{AB}^2}{E_g^2} \]

(5.2)

Where \( E_g \) is the band gap and \( C_{AB} \) is the ionic part contribution to the band gap. \( C_{AB} \) is defined as,

\[ C_{AB} = b \left[ \left( \frac{Z_A}{r_A} \right) - \left( \frac{Z_B}{r_B} \right) \right] e^{-k_sR} \]

(5.3)

Here \( Z_A, Z_B \) represents the valence electron numbers, \( N \) and \( 8-N \) are the valence electrons in the cation and anion, respectively. \( r_A, r_B \) are defined as 1/2 of the bond length of the Group IV element with the same rows of periodic table as atoms A and B. \( k_s \) is the Thomas-Fermi screening wave number and \( R \) equals the half sum of \( r_A \) and \( r_B \).

We can see that Phillips’ definition of ionic part \( C_{AB} \) relies much on the covalent information especially the group IV elements, like the previous electronegativity driven model, this part is not from the given materials itself, and most seriously, even Phillips’ ionicity picture works perfect for the bulk materials, the theory itself lacks the supports for the inter-layer interactions in the low dimensional materials, like mono or multi-layer quasi 2D materials. However, our new methodologies, combined with the symmetry-broken induced \( E_{pot}^2 \) term, theoretically it still can cover the low dimensional materials.
Figure 5.1 (a), the atomic structure of the mono-layer MoS$_2$ and the scheme of the origin of the surface electric field. (b), the electric field distribution around the surface S atoms.
5.3 The effective charge for the monolayer MoS$_2$

Following the similar procedure as the case of alkali metal halides, alkali earth metal oxides, and update the contents of $E_{pol}$, we calculated the effective charge of mono-layer MoS$_2$, the result is shown in Figure 5.2. Different from the typical ionic alkali metal halides, the ionicity of MoS$_2$ is unknown and since the formal charge of Mo is 4, we start from the ionization events one by one, by the second ionization process, there is an intersection between the $E_{BH}$ and the $E_M + E_{pol}$ curves, as shown in the left part of Figure 5.2, if we keep on adding in the third or fourth ionization process, there are still no solutions for the equations, thus the 1.392 value is the reasonable effective charge for the Mo in the MoS$_2$, the ionicity is then given by $1.392/4 = 0.348$, which is very small compared with the alkali metal halides, indicating a pretty strong covalent bonding character for the MoS$_2$ crystal, which agrees well with the previous studies.[115]

![Figure 5.2](image)

**Figure 5.2** Left: The solution for the effective charge of monolayer MoS$_2$, as indicated by the intersection of the $E_{BH}$ and $E_M + E_{pol}$, which is 1.392 for Mo. There are no other intersections in other areas. Right: the components of the $E_{pol}$ energy.
The right part in Figure 5.2 plots the $E_{pol}$ term divided by the individual $E_{pol}^1$ and $E_{pol}^2$, it is obvious that the ratio of $E_{pol}^2$ takes more percentage of the $E_{pol}$, when the charge value approaches the formal charge, the contribution of $E_{pol}^1$ even can be ignored. This phenomenon means in the 2D monolayer MoS$_2$, the electric field induced from the truncated dimension takes more effect on the polarization energy compared with the intrinsic polarizability dominant items $E_{pol}$, which makes these kinds of materials different from the 3D bulk materials. Following the same computational procedure as above, the ionicity for some more quasi 2D TMDs are plotted in Figure 5.3 and the corresponding ionicity data are summarized in Figure 5.4, along with the data derived from Pauling and Philipps’ theories.

![Figure 5.3](image_url)  
**Figure 5.3**  Summarize of the ionicity for selective TMDs materials, the data from Phillips, Pauling and our methods are listed together.
The effective charge calculation details for some group VB and VIB elements, the value of the solved effective charges is remarked by the dashed circle in each figure.

We can pay more attention to the ionicity of the mono-layer MoS$_2$ and WS$_2$ structures, both the metal-sulfur bond length and the lattice parameter for these two structures are almost the same, and one distinct property between this two structures is the $A'_1$ Raman active mode as shown in Figure 5.5, which is around 405.6 cm$^{-1}$ in MoS$_2$ and 411.5 cm$^{-1}$ in WS$_2$, there is argument about why the $A'_1$ frequency of WS$_2$ is higher than that of MoS$_2$, since for the $A'_1$ mode, the metal atom keeps unmoved, and since the bond lengths are the same in these two structures, the ionic character may be the reason causes the
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difference, but there is no self-confident evidence for this arguments. Herein, by our new model, we get the effective charge for the metal in MoS$_2$ and WS$_2$ are 1.392 and 1.491 individually, which proves that the Coulomb interaction is slightly intensive in the WS$_2$ structure, which results a higher energy vibrational mode. Here we have to strength that this analysis is based on the fact that the metal-sulfur bond length in MoS$_2$ and WS$_2$ are of the same, thus the traditional covalent strength is theoretically close, thus the Coulomb interaction could be the key factor making the difference. For other materials which are not of the same bond length, the vibrational $A'_1$ mode energy could be well affected by both the covalent and electrostatic interactions, which is hard to analysis by the quantity of effective charge only.

**Figure 5.5** Raman spectrum for the monolayer MoS$_2$ and WS$_2$ structures, the frequency of $A'_1$ mode for MoS$_2$ and WS$_2$ are 405.6 cm$^{-1}$ and 411.5 cm$^{-1}$ respectively.
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5.4. The layer dependent and stacking dependent charge

As discussed on the initial parts of this chapter, our effective charge calculation model is individual energy based, which means this method can be applied to any real system as long as the total energy can be achieved, whether experimentally or theoretically or numerically, as an approximated theory, our method can be used to calculate complicated systems, which is beyond Phillips theory’s coverage, like the layer dependent effective charges.

For the multi-layer MoS$_2$ structures, when the number layer increase, the $E_{pol}^1$ term in the periodic X-Y plane makes no noticeable difference due to the relative weak inter-layer interactions, however, the perpendicular $E_{pol}^2$ term is more sensitive to the number of layers due to the appearance of the screening effects, which can affect the amplitude of the intrinsic electric field. When the number of layer increase, the center atoms gradually approach to the bulk status, to well investigate the layer dependent effect on the charge, we select the top surficial sulfur atoms and calculate the effective charge, the results are shown in Figure 5.6.

The most significant conclusion from Figure 5.6 is that, with the number of layer increase, the effective charge of the top surficial sulfur atoms increases as well, and is expected to be converged at the bulk phase. This picture can be understood in the way of the enhanced screening effect from the collective layers, i.e. more layers introduces more electric field as well as the induced charge on the top surficial sulfur atoms.
Figure 5.6  Layer dependent effective charge on multi-layer MoS$_2$ structures. The charge is calculated for the top surficial sulfur atoms.

Figure 5.7  the relationship between the frequency of the $A'_1$ mode and the effective charge derived from Figure 5.6. The experimental layer dependent frequency is got from ref.[116].
To double check the validity of the layer dependent effective charge, we plot the relationships between the frequency of the $A'_{1}$ mode and the effective charge derived from Figure 5.6 for each number of layers. We find a proportional relationship between the charge and the frequency, since all the layer dependent structures are of the covalent environments, it is the endorsement from the electrostatic interaction which makes the $A'_{1}$ mode vibrates into higher energy.

We can also validate the effective charge from the stacking configurations, as shown in Figure 5.8, the AB stacking is the ground state patterns and the AA stacking is of higher energy due to the “head to head” interaction of the two sulfur atoms from different layers. The calculated effective charge for the AB and AA stacking are 0.696 and 0.697 respectively, the frequency of the nt effective charge, we plot the relationships between the frequency of the $A'_{1}$ mode in these two patterns are 405.5 cm$^{-1}$ and 407 cm$^{-1}$, the trend agrees well with the layer dependent cases.

![AB and AA stacking configuration for the double layer MoS$_2$](image)

To summarize, by including the symmetry-broken induced electric field effect into the polarization energy, our model can work well for the dimension
truncated quasi 2D structures, combined with the Raman frequency analysis, the model can provide insightful picture for the layer dependent and stacking dependent charge distributions. Our agile model has significant benefits over Phillip’s theory on study the ionicity inside the low dimensional materials and predict the properties which are mainly determined by weak interactions.
Chapter 6

Study the morphology of MoS2 using charge driving Line Tension

This chapter keep on extending the new theory to the MoS$_2$ nanoclusters, concluded both the quantum size dependent and the edge geometry dependent effective charge distribution regularity. Translate the center-edge charge gradient into the concept "line tension", which can well describe the chemical potential changing in the non-stoichiometry nanoclusters. The effective charge also can be used to describe and predict the shape dependent edge stability and the growth direction of the nanoclusters.
6.1 Introduction

In this chapter, first, by using the improved formula in the application of the 2D materials, we extend our new methodology to the calculation of the effective charge on the MoS$_2$ quantum clusters, which is beyond the capability of the previous theories. We find that the effective charge distribution shows a radial like function, the edge atoms possess larger value of effective charge than the center bulk type atoms, which indicating that the un-saturated edge atoms are more chemical active due to their un-balance charge states, which affect a lot on the nanocrystal growth conditions. Next, we focus most on the growing mechanism of the MoS$_2$ layer structure. We discuss a comprehensive theoretical investigation for the role of edge configuration and environment chemical potential in tuning the structure and morphology of monolayer MoS$_2$ by using first-principles calculation. Our results present an evolution of MoS$_2$ morphology from the hexagonal shape to the triangular shape by investigate into the line tension of different kind of MoS$_2$ edge structure and with the variation of the elemental chemical potential of Mo and S which will further influence the edge free energy. The edge structure of MoS$_2$ is found to change correspondingly from mixed Mo/S edges to one kind of edges dependent on the concentrations of gas supplement. The results suggest the possibility to guide for experiment to prepare expected morphology, edge structure, and electronic properties of monolayer MoS$_2$ by adjusting the chemical potential during growth. By using the Nudge Elastic Band (NEB) calculation, we also investigate the possible energy barriers during the edge growth events lead by the add-in Mo or S atoms respectively.

6.2 The effective charge for the MoS$_2$ quantum clusters.

In the previous chapters, we already introduced the detail of our new theory on calculating the effective charge in both the bulk materials and the quasi 2D
materials, compared with the previous work, the key improvement is the introduction of the polarization energy ($E_{pol}$) as the correction to the Madelung energy ($E_M$). This method is full of agility and it can be applied into the quantum clusters structures, by following the same procedure as mentioned in Chapter 5, by considering the displacement along all the 3 non-periodic directions, we can get the amplitude of the electric filed and eventually the effective charge for any given atom. For the MoS$_2$ quantum cluster, it has two kinds of edge states, the S-S dimer edges (marked by the black rectangular) and the S edges (marked by the blue rectangular), as shown in Figure 6.1, these two kinds of edges have different S-S bonding structures thus the charge states should be different as well. Based on our methods as discussed in the previous chapter, we calculate the effective charge distribution on the hexagonal MoS$_2$ cluster; the size effect is also included.

The predicted effective charge for the S atom is listed near the individual S atom as shown in Figure 6.1, the effective charge in the center part of the two structures are almost the same, it is 0.65 in the smaller structure (a) and 0.64 in the larger structure (b), which is very close the value in the quasi 2D structure (0.635), the decreasing size in the cluster induced increase of the effective charge in the fully bonded atoms in the center part, based on our methodology, increase the effective charge from the balanced value will increase the gap between the $E_{BH}$ and $E_M + E_{pol}$ in the way as following:

$$E_M + E_{pol} > E_{BH}$$

as shown in Figure 6.2, which means the electrostatic energy is overflow and it can destroy the lattice structure, thus the fact that effective charge increasing in the smaller structure (b) indicates that the enhancement of the size effect will cause the structure instability, which can be understood in other way that the smaller size cluster is motivated for the growth, in order to require the stability from size increasing.

In the edge states of the cluster, the two kinds of edge show distinct charge states, as shown in Figure 6.1 (a), in the S-S dimer edges, the effective charge
of S atom is 1.335, and it is 0.968 in the S edge. For the S atom in the S-S dimer edge, the S atom only connects to only one Mo atom nearby, the number is 3 for the center S atom and 2 for the S edge atom, the decrease of the cation-anion coordination number requires more effective charges for the balance with the Mo cation. The high charge value for the S-S dimer edge also indicates that the unsaturated edge of the quantum cluster is expected to be more active in reactions, including the cluster growth, as discussed above, one driven force for the structure growth is to release the overflow energy gap between $E_{BH}$ and $E_M + E_{Pol}$, due to the highly stray-away-from-balance effective charge, the S-S dimer edge is keen to favor the growth events, especially for the attaching Mo atoms from the real experiments.

Here in this chapter, addressed from the methodology in the previous chapter, we first extended our model to the quantum cluster structure and calculated the charge distribution with the size dependence and edge dependence, we conclude that one of the driven force for the nanocluster growth is to acquire the stability by balancing the overflow electrostatic energy in the form of growing, we propose that this kind of quantum confinement effect induced radial charge distribution driven growth can be understood as a line tension driven event as well.
Figure 6.1  (a) and (b) shows the two MoS$_2$ hexagonal quantum clusters with different size. The effective charge distribution on hexagonal MoS$_2$ clusters with different size, the two kinds of edges are marked by the blue and black rectangular, the effective charge in some select edge atoms are listed near the given atom respectively. The S-S dimer edge and the S edge are marked by the black and blue rectangular. (c) is the scheme for the effective charge distribution for the typical hexagonal MoS$_2$ cluster and the language “line tension” can help understand the growth events more vivid than the charge.
Figure 6.2  The calculation model for the effective charge of MoS2 structures, variants with the charge of S atoms; the balanced effective charge is marked by the dash circle line, the green up arrow shows the increase of the gap between $E_{BH}$ and $E_M + E_{Pol}$ when the charges moved up away from the balanced one.

6.3 Line tension in 2D

By analogy with surface tension, as shown in Figure 6.3, which defines the change of energy per unit surface by separating a whole material into two interfaces, line tension is the free energy get per unit length of a contact line where distinct phases coexist in the interface area. The concept of “line tension” which sometimes called edge free energy is extremely important in low dimensional material, which will always occur on the edge site of this kind of material and will determine many properties like terminate edge configuration and stability. In the last session, we have proposed the origin of the line tension is related to the charge gradient between the center and edge part which provided the motivation for the size increases from growth, and the line tension could be a vivid description for this hidden driving force. We thus try to using line tension to explain the observation in experiments of varies kinds morphology of TMDs, represented by MoS2. Figure 6.4 shows the typical scheme of the line tension generation in the MoS2 cluster’s edges, the red dashed line indicated the truncation of the structure which generated the charge radial gradient and form the line tension in the boundary area.
**Line tension**

The free energy cost for the formation of the nanodroplets on the substrate can be written as

\[ \Delta \Omega = V_i (\omega_i - \omega_v) + A_{li}(L - (\gamma_{ls} - \gamma_{lv})) + A_{lv}\gamma_{lv} + \tau L \]

- \( V_i \): the volume of the droplet
- \( A_{li} \): the area for different interfaces
- \( L \): the length of the contact line
- \( \omega_i \): the bulk free energy density of liquid or vapor

**Figure 6.3** Some basic concepts about the traditional surface tension, line tension in the vapor-liquid-solid interfaces.

**Figure 6.4** The schema of the line tension generation in the quasi 2D MoS\(_2\) structures, where a MoS\(_2\) cluster is cut from the perfect 2D plan. The red dashed line illustrated the location of the line tension.
6.3.1 Calculation Methodology

In previous works, edge free energy is studied in order to investigate the relative stability of the edge terminations under different thermodynamic conditions using DFT calculation under finite temperatures. Several Mo-terminated and S-terminated edge MoS$_2$ ribbon (as shown in Figure 6.5) are considered and define its line tension $\gamma$ as:

$$\gamma = \frac{1}{2L} [G_{\text{ribbon}}(\text{MoS}_2) - N_{\text{Mo}}\mu_{\text{Mo}} - N_{\text{S}}\mu_{\text{S}}]$$

(6.1)

where $G_{\text{ribbon}}(\text{MoS}_2 + N_{\text{H}}\text{H})$ is the typical Gibbs free energy for the ribbon unit cell. $N_i$ refers to the number of elementary atoms of element $i$ in the unit cell, $\mu_i$ refers to the chemical potential of element $i$, $L$ represents the edge length. The factor of 2 in Eq. 6.1 illustrates that the ribbon exposes two edges. It should be noted that both the Mo edge and the S edge will have exposed when MoS$_2$ form a nanoribbon, hence here $\gamma$ represents the average line tension of both edges. This indicates that just the relative stability of edge configurations can be studied while that the opposite edge shares the same configurations pattern, the stable structure geometry will be the one that minimizes the value of $\gamma$. That means the exact line tension of an individual edge cannot be calculated in nanoribbon and hence the model provides no useful information on the relative stability between the Mo edge and S edge.
Figure 6.5 Atomic structure of single layer MoS2 ribbon from top view, where the yellow balls indicate the S atom and the blue balls indicate the Mo atom. The left side of the ribbon is terminated by Mo-100% edge, while the right side is terminated by S-100% edge. Length of the edge L is indicated in figure using red dash line.

If the MoS2 stripe is large enough in size, then the edges structure will be in thermodynamic equilibrium state with the bulk MoS2 structure, then,

$$g_{\text{MoS}_2}^{\text{bulk}} = \mu_{\text{Mo}} + 2\mu_{\text{S}}$$

(6.2)

where $g_{\text{MoS}_2}^{\text{bulk}}$ is the Gibbs free energy of a formula unit of bulk MoS2 sheet. Hence the chemical potentials $\mu_{\text{Mo}}$ and $\mu_{\text{S}}$ cannot be varied independently and inserting this in Eq. 6.1 yields,

$$\gamma = \frac{1}{2L} \left[ G_{\text{ribbon}}(\text{MoS}_2) - N_{\text{Mo}} g_{\text{MoS}_2}^{\text{bulk}} + (2N_{\text{Mo}} - N_{\text{S}}) \mu_{\text{S}} \right]$$

(6.3)
Generally speaking, the Gibbs free energy can be alternatively re-written in the forms of the Helmholtz free energy \( f \) as \( g = f + pV \), in this formula, \( p \) presents the pressure, \( V \) presents the volume. For crystal solids, the last term is very small and can be neglected. For the practical temperatures in question, since \( T \ll T_F \), the degrees of freedom of electrons has been completely frozen out, which makes \( f_{elec} \approx E_{elec} \) is a fair well approximation. We can then re-write the free energy in the crystal solid as: \( g_{solid} \approx E_{elec} + f_{vib} \) here the electrostatic interaction energy is included in \( E_{solid} \) and \( f_{vib} \) is the Helmholtz free energy origins from the vibrations. We can assume \( g_{solid} \approx E_{solid} \), the vibrational contributions are neglected. The free energy in the edge can be defined as follow

\[
\gamma = \frac{1}{2L} \left[ E_{ribbon}(MoS_2) - N_{Mo}E_{MoS_2}^{bulk} + (2N_{Mo} - N_{S})\mu_{S} \right]
\]

(6.4)

### 6.3.2 Range of chemical potentials

Previous work [117] illustrated the relationship between the chemical potential and the edge geometry, as shown in Figure 6.6, it was found that specific up-triangle, down triangle or hexagonal edge shape are close dependent on the combination of the chemical potential of \( S \) and the surface energy ratio \( \frac{\sigma_{Mo}^{0\%}}{\sigma_{S}^{100\%}} \). This model well described the energy dependent edge shape formation and provide a general result, however, in the real system, the whole system is far from the equilibrium status and the lowest energy never secures the high growth rate in the reactions, this work is challenged once we need to know more about the realistic growth mechanism.
Figure 6.6  Scheme shown the stability for the Mo-terminated edge and S-terminated edge for the non-promoted crystallite dependent on the chemical potential of sulfur (in eV) and of the ratio of the surface energy $\sigma_{Mo}^{0\%}/\sigma_{S}^{100\%}$.

Here should examine the range of the chemical potential of every element. Use sulfur, $\mu_S$, for example. When it becomes large enough, the sulfur can form into the bulk phase, the solid state of MoS2 then turns into the unstable state. This upper limit thus can be written as

$$\mu_S \leq \mu_S^{(bulk)} \approx E_S^{(bulk)}$$  \hspace{1cm} (6.5)

A similar argument also applies to bulk molybdenum and leads to the lower limit. The free energy of formation for MoS2, $\Delta G_f^{MoS_2}$, is given by

$$\Delta G_f^{MoS_2} = g_{MoS_2}^{(bulk)} - \mu_{Mo}^{(bulk)} - 2\mu_S^{(bulk)}$$  \hspace{1cm} (6.6)

Combining Eq.(6.6) with Eq. (6.2) yields
\[
\mu_S - \mu_S^{(bulk)} = \frac{\Delta G_f^{MoS_2}}{2} - \frac{1}{2} [\mu_{Mo} - \mu_{Mo^{(bulk)}}]
\]

(6.7)

to form stable MoS\(_2\) against the formation of Mo, it requires that
\[\mu_{Mo} - \mu_{Mo^{(bulk)}} \geq 0\] and the down limit then,
\[
\mu_S - \mu_S^{(bulk)} \geq \frac{\Delta G_f^{MoS_2}}{2}
\]

(6.8)

An estimate for \(\Delta G_f^{MoS_2}\) is obtained by approximating it with the energy of formation, \(\Delta E_f^{MoS_2}\),
\[
\Delta G_f^{MoS_2} \approx \Delta E_f^{MoS_2} = E_{Mo^{(bulk)}} - E_{Mo^{(bulk)}} - 2E_{S^{(bulk)}}
\]

(6.9)

Using the \(\alpha\) phase of sulfur to the calculation of \(E_{S^{(bulk)}}\) we find \(\Delta E_f^{MoS_2} = -2.58\) eV, \(\mu S\) are estimated to be:
\[-1.3 eV \leq \mu_S - \mu_S^{(bulk)} \leq 0\]

(6.10)

A graphic plot in shown in Figure 6.7, the shadow areas boundaries the available areas for the MoS\(_2\) growth restricted by the chemical potentials.
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Figure 6.7 Possible chemical potential range to form MoS$_2$, indicate by black shadow. Here $\mu_{\text{Mo}}, \mu_{\text{S}}$ is the chemical potential of Mo and S, $\Delta_G^{\text{MoS}_2} = \Delta E_f^{\text{MoS}_2} = -2.58$ eV, the green and the blue boundary mean the chemical potential of the elements cannot lower than the chemical potential of bulk to avoid form bulk Mo and bulk S. The red boundary is determined by Eq (6.7).

6.3.3 Line tension of nanocluster

In many reported experiments [6, 8, 14], TMDs samples are usually found to be of variant sized triangle shapes as products. Different from the traditional nanoribbon-like geometry, the single layer TMD sheet often exits in a quantum cluster configuration, by considering the symmetry of the bulk TMDs, we can get an identical configuration on all three possible edge shapes of the cluster once cut the 2D sheets (see Figure 6.8) in order to understand the dynamical ways during the growth, we can study the line tension as the driven factor for each edge configuration. From the previous chapter we already know that both
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of the two types of edge atoms will possess higher effective charges and motivated for growth, in this chapter, instead of investigating the effective charge itself, we will focus on how the edge variation affect the growth, including the line tension benefits and the reaction barriers.

![Figure 6.8](image)

**Figure 6.8** The atomic structure of two kinds of edges occurred in cluster, the picture under each structure shows the side view of the structure. (a) 100% S covered Mo-edge. (b) 100% S covered S-edge. It can obviously notice that in triangular shaped nanocluster, we can get identical edge on each side of the cluster. The red dash line shows the measurement of length of the edge, using the Mo atom as the reference vertex.

As shown in Figure 6.8, the hexagonal and triangle shaped clusters have both Mo edge and S edge, and should be discussed in different condition. One important thing should take into consideration is that when come to the situation of small size nanoclusters, for example Mo$_6$S$_{24}$, the equation $g_{MoS_2}^{bulk} = \mu_{Mo} + 2\mu_{S}$ does not work, which causes inappropriate for the chemical potential calculation, and the line tension cannot directly obtain from the calculation results using Eq. (6.4). Some work[118] [119] has done on graphene to calculate line free energy using bond energy, define line tension as half of the work of rupture in a graphene nano-sheet along the single line per unit line length in vacuum at 0K.
Herein, we introduce a more effective method to calculate the energy changes scheme through the bond energies in any given structure. As illustrated in Figure 6.9. In order to quantize the energy scale in the diamond crystal, instead of from the Gibbs free energy, we try to understand it by the C-C single bond energies, which can be approximately derived from the ethane molecule, which is 349 kJ/mol based on the DFT calculation, the exact value for the C-C bond energy in diamond is 331.8 kJ/mol, agrees well with the previous one, which indicate that the bond energy is a good measurement for the energy pictures in the reactions. Here the bond energy of MoS$_2$ with both the center and surficial atoms are derived from the DFT calculation, and the reaction energy is defined as the bond breaking energy rather than then total energy difference between the products and reactants.

![Figure 6.9](image.png)

**Figure 6.9** Illustration of the definition of bond energy definition and benchmark. The upper part of the figure shows the common definition of C-C single energy, experimentally get the energy by breaking up the carbon-carbon bond in ethane result 349kJ/mol. The lower part shows the method used to get C-C single bond in this work, remove one carbon atom in diamond and break four surrounding bonds which get 331.84kJ/mol.
By considering bond energy instead of just using chemical potential of each element, we modified Eq. (6.4) to

\[ \gamma = \frac{1}{2L} \left[ E_{\text{ribbon}}(\text{MoS}_2) - N_{\text{Mo}}E_{\text{MoS}_2}^{\text{bulk}} - (2N_{\text{Mo}} - N_S)E_S - N_{\text{bond}}E_{\text{Mo-S}} \right] \]

Here \( N_{\text{bond}} \) is the number of extra Mo-S bond on the site position, and \( E_{\text{Mo-S}} \) is the bond energy of Mo-S.

### 6.3. Line tension barriers in the growth

Next we will investigate some possible energy barriers during a specific growth event, by DFT and NEB methodology. The DFT calculation is carried with the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) \([120]\) functional form and plane wave basis sets, which are implemented in the Vienna Ab Initio Simulation Package (VASP)\([121]\). The energy cutoff is 400 eV, a \( 10^{-4} \) eV/Å force convergence condition is reached for the criterion of SCF loops.

Figure 6.10 shows a hexagonal MoS\(_2\) cluster with sulfur full covered each edge. Here two different kind of edge configuration is marked by different colors of rectangle, the yellow one indicates a S-terminated edge (S edge), where the outmost row of the zigzag edge is S atom, each of the S atom is coordinated with two inner Mo atoms. Here in the yellow part of Figure 6.10 (a), each of the Mo atoms in the row behind the exposed S atom is fully coordinated with 6 S atoms, we define this a S 100% cover S-edge as the same in the previous work\([72]\). On the other hand, the blue one presents a Mo-terminated edge (Mo edge), where the outmost row of the zigzag shape is Mo atom, each of the Mo atom is coordinated with at least four inner S atoms, and is apt to be saturated with additional external S atoms. Here in the blue part of Figure 6.10 (a), each of the Mo atoms in the outmost row is coordinated saturated by two extra S atoms, which usually forms a S dimer in the extended direction. This fully coordinated Mo edge with S dimer are notated a S 100% cover Mo-edge. To investigate the critical factors in the edge grow direction, we demonstrate an
atomic structure as shown in Figure 6.10 (b), at the corner of the original hexagonal MoS$_2$ cluster (indicate in a red dash line rectangle), we move off one of the S atom from both S 100% cover S-edge and S 100% cover Mo-edge, which makes 2 Mo atoms unsaturated, one coordinated with 5 sulfur atoms and the other coordinated with 4 sulfur atoms. We then add additional S atom into this model to mimic the growth events in the micro scale, and investigate the line tension evolution during the growth process.

**Figure 6.10** (a) a hexagon MoS$_2$ cluster with sulfur full covered each edge. Here two different kind of edge configuration is indicating with different colors of rectangle, the yellow one indicates a S 100% cover S-terminated edge (S 100% edge), the blue one indicates a S 100% cover Mo-terminated edge (Mo 100% edge); (b) proposed an atomic structure, the red dash line rectangle indicate the corner part of the original hexagon MoS$_2$ cluster in (a), move off one of the S atom from both S 100% edge and Mo 100% edge

There are two possible edge configurations for the additional S atoms added in, as illustrated in Figure 6.11 (a), due to the different chemical environments, when one additional S atom is introduced in and added onto the S edge, there are two options to form the chemical bonds with the nearby Mo atoms, the first option (Figure 6.11 (a1)) is to form two bonds with two inner Mo atoms in the edge states, the second option (Figure 6.11 (a2)) is to add onto Mo edge and bonded with one out most Mo atom and form a S-S dimer bond with the other
S atom on the same edge, these two options determined different coordinated numbers. By using the DFT methodology, we study the energy scale of these two options and find out that the reaction energy of the situation that S atom connect on Mo edge (structure a1) is 0.47eV, which is larger than that of S atom connecting on the S edge (structure a2), this means that the a1 configuration is more energy stable and S atom is much like to grow in the direction of S edge. This energy difference can be understood by the effective charge balancing picture as discussed in the previous session of this chapter, the added in S atom in structure a1 lowers the total effective charge about 0.5 and the counter number in the structure a2 is only about 0.3, which means that by forming structure a1, the system releases more edge line tension and electrostatic energies, even though a1 is more stable than a2, the structure a2 may also dominate in the reactants if there is huge line tension barrier to overcome preventing a2 converted to a1, since this chapter is focus on the application on the effective charge based line tension driven structure growth, we use the line tension as the measurement of the energy scale. We then set the structure (a1) and (a2) as final and initio structure respectively to investigate the transition process of the additional S atom. Figure 6.12 (a) show there is a line tension barrier about 0.46eV/nm during the transfer pathway. This barrier is not very large, which can be overcome under normal experiment synthesize condition (which is usually above 800°C), that means S atom prefer the site coordinate with 2 Mo to form S 100% edge, and when it come to the situation that S atom absorb on the Mo edge site, it is usually easy for it to transfer to the S edge site to form S 100% edge.
Figure 6.11  Atomic structure for the added in atoms to the MoS$_2$ hexagonal structure, (a1) the optimized atom structure of additional S atom added onto S edge, (a2) the optimized atom structure of additional S atom added onto Mo edge, (b1) the optimized atom structure of additional Mo atom added onto S edge, (b2) the optimized atom structure of additional Mo atom added onto Mo edge. The blue circle remarks the added atoms in each figure.

For the Mo atom, we then add additional Mo atom into the same atomic structure. Similar to those of the add-in S atom cases, there are two available configurations of edge as illustrated in Figure 6.11 (b1) and (b2), in case (b1), the Mo atom added onto S edge and initially coordinate with three exposed S atoms and move a bit inside and form metal-metal bond with the inner Mo atoms after structure optimization. And another optional case (b2) is that, Mo atom added onto Mo edge and form bonds with the nearby three S atoms which is connect with the outmost Mo atom on the Mo edge, it also moves a bit inside approaching the Mo atom on the edge after structure optimization. Following the same analysis procedure as above, by studying the line tension picture of these two configurations, we find that the energy of the one that Mo atom connect on to Mo edge is much smaller than that of Mo atom connect on S edge, the energy difference is about 2.35eV, this means that the Mo atom add to Mo edge is more energetically stable than the case adding to S edge and Mo atom is much like to grow in the direction of Mo edge. We then set the up panel and down panel in two structures b1 and b2 as initio and final structure respectively.
to investigate the transfer process of the additional Mo atom. Figure 3(b) shows there is an energy barrier about 1.9 eV/nm during the transfer pathway. This energy barrier is very large for the two structures to transfer.

![Figure 6.12](image)

**Figure 6.12** NEB calculation for the transitions between the structures in Figure 6.11, the energy barriers are calculated about 0.46 eV/nm and 1.9 eV/nm.

Based on the discussion above, we find that when adding an additional S atom, it is more likely to grow in the S edge direction due to the more decrease in the line tension; while when for the additional Mo atom case, it will grow in the direction of Mo edge instead. Herein we provided a more universal law on the edge growth in TMDs system that the S atom is dominate the growth of the direction of S edge and Mo atom is dominate the growth of the Mo edge.

### 6.4 Size and shape dependent line tension

If we ignore the error influence of the experiment methods and sulfur concentration, once there are sufficient supplements of sulfur gas to the furnace during the CVD process, it is found that different kinds of morphology of TMD can be observed at different stage in the process of experiment. STM images were recorded different size of nanoclusters with carefully measuring the edge length, shape and edge configuration also can be roughly recognized. It is find
that the cluster form in a different shape and edge structure in different size of nanocluster. We conclude that MoS$_2$ nanoclusters are formed with an edge structure that is dependent on the actual size of the clusters.

To understand the origin of the size determined effect in the MoS$_2$ nano clusters, we study the atomic structure models of the MoS$_2$ nanocrystals. Three ordinary kinds of shape: triangle, hexagon and parallelogram are considered, especially here triangle shape nanocluster contain three different types edge configurations, S 100% edge, Mo 100% edge and Mo 50% edge, show in Figure 6.12, hexagon and triangle shaped nanocluster has both S 100% edge and Mo 100% edge. For whatever the geometry of the cluster is, our methodology introduced this thesis can provides the effective charge for any given atoms, and based on the effective charge difference compared with the edge S atom with dangling bonds and the 3-fold coordinated S atom in the quasi 2D MoS2 structure, we can develop the effective charge density gradient origin line tension, which can be applied on the understand the stability for the structures with variant edge geometry and bonding characters. The effective charge value for the presented MoS2 cluster structures in Figure 6.12 are listed besides the corresponding structures, which are marked in the black rectangular in the left figure.
Figure 6.12 Calculated line tension dependent of nanocluster size of three different kinds of shape: triangle, hexagon and parallelogram, and triangle contain three types; each line in different color represents one kind of shape which indicate in the small picture on the right side of the graph with a same color. Here N is the number of the Mo atom at each side of the cluster.

Line tension of different size of each type of cluster is calculated using Eq. (6.7) explained in the previous section. In Figure 6.12, the line tension of clusters is plotted as a function of the cluster size for several most ordinary MoS$_2$ nanocluster, N is the number of the molybdenum atom on each edge of the nanocluster.

Obviously, triangle shaped Mo 100% edge (S-S dimer structure) always is the most stable configuration regardless of size, due to the largest effective charge (1.48) of the dangling edge S atom, the Coulomb interaction is maximized among all the configurations by providing a lowest $E_M + E_{Pol}$ energy, however, since the S atom in the S-S dimer is dangling without affecting the inner crystallized atoms, this kind of enhanced Coulomb interactions didn’t
contribute any destroy to break the whole structure, and the direction of the Mo-S bonds in this condition is actually perpendicular to the line tension, with 90 degree, which didn’t contribute to any amount to the line tension at all. However, for the S 100% edge (S edge) structure, due to the lowest effective charge (0.95), gains smaller energy from the Coulomb interaction and due to the small angle between the S-Mo bonds and the edge line, the Coulomb interaction contributes to the adding amount of the line tension, which reduced the stability for this structure. The other structures have edge geometry between the two limit structures of the S-S dimer and S edge, the amplitude of the line tension depended on the ratio of the two edge options, for example, for the structure marked in purple outline, it has larger ratio of the S-S dimer structures, the structure marked in green outline has the larger ratio of the S edge, we can predict that the line tension of the structure marked in purple outline is smaller than the counterpart marked in green outline, which agrees well with the numerical results in Figure 6.12.

To summarize, in this chapter, we first extent our effective charge calculation methodology to the MoS$_2$ quantum cluster, and based on the effective charge distribution model, we provide new insights into the understanding for the quantum size effect and edge geometry effect determined stability in this system, and defined the charge gradient decided line tension as a vivid term to describe the structure stability and structure growth mechanism. For the size dependent line tension, the picture provided by our model aggress well with the traditional one based on the energy scale. Besides the capability for determining the ionic charge in bulk or quasi 2D materials, as introduced in previous chapters, our method also can work on the static (geometry) and dynamic (growth) property of nano-clusters.
Summary and Future Work

This chapter summarizes the accomplishments and highlights of this thesis and research plan for the future work extended on the available results, raise some possible work can been done latter based on the theory used in this work, include calculation of the effective charge in ternary materials, organics, metal organic frameworks (MOF), and the seconders with dopants and defects.
As discussed in all the contained chapters and sections, the objectivity of this thesis is to develop a universal methodology to describe the effective charge of materials with multiple dimensions, and the application on the materials property. It includes the comparison and benchmark between the new methodology with amounts of the classic work done by Pauling, Phillips, etc, in the study of the ionicity and effective charge in ionic crystals, the extension to the quasi 2D materials and nanoclusters, and the application on both static and dynamic property of the nanoclusters. The objectivity is fully accomplished and the important finding in each chapter can be summarized below.

### 7.1.1 Effective charges in bulk materials.

In this chapter, the previous works on studying the effective charges or iconicity are carefully reviewed, some classic terms, like Born-Harbor Cycle, Madelung constant, Pauling’s electronegativity, Phillip’s ionicity, Szigeti’s dynamic charge etc, as with as the strength and limitations for the previous methodologies are systematically reviewed. By introducing the polarization energy ($E_{pol}$) as a measure for the high order electrostatic interaction which is critical to providing the additional energy required for the crystallization, which can be experimental or computational realized from the Born-Harber cycle. The new scenario we proposed for the charge balancing during crystallization is: the effective charge is defined in which the energy required by Born-Harber cycle ($E_{BH}$) equals to the energy provided by electrostatic interaction ($E_M + E_{pol}$), i.e.

\[ E_{BH} = E_M + E_{pol} \]

(7.1)

The $E_{pol}$ term is essential because the $E_M$ term only cannot provide enough energy to satisfy the requirement from $E_{BH}$.

The definition of $E_{pol}$ in the bulk materials with centre-symmetry is
\[ E_{\text{Pot}} = -\frac{q^+q^-}{8\pi\varepsilon_0\sigma^4}, \]  
(7.2)

Which is derived from the pure electrostatic interaction, however, since the polarization effect will increase the orbital overlapping of anion and cation nondirectionally, this effect will enhance the σ bond covalence character objectively and reduce the ionicity eventually, in which condition even the effective charge is lower than the formal charge, the total electrostatic interaction energy is enforced, which can satisfy the required crystallized lattice energy \( E_{BH} \).

Following this new methodology and the new crystallization picture, we calculated the effective charge for the alkali metal halide, alkali earth metal oxides, and some transition metal compounds, the results agrees well with the merits part of the previous work and some experimental results. Our new methodology overcomes the significant drawbacks of Pauling, Sanderson and Szigeti’s methods, works comparable well with Phillip’s ionicity theory.

### 7.1.2 Effective charges in quasi 2D materials.

In this chapter, the new methodology is well extended to the quasi 2D materials, which is totally beyond the coverage of Phillip’s ionicity theory. Due to the truncated dimension, the symmetry prohibited internal electric field is recovered in the surface of the quasi 2D materials, this additional electrostatic interaction can be described by an extra supplementary term

\[ E_{\text{Pot}}^2 = \frac{1}{2} \alpha E^2 \]  
(7.3)

The total polarization energy turns into

\[ E_{\text{Pot}} = E_{\text{Pot}}^1 + E_{\text{Pot}}^2 \]  
(7.4)

The amplitude of \( E_{\text{Pot}}^2 \) is more than 5 times larger than the \( E_{\text{Pot}}^1 \) term in the
quasi 2D systems.

Following the new methodology supplemented by (eq 7.3), we systematically investigate the effective charge for several TMDs materials, we provide solid explanation for the $A_1'$ frequency issue in the mono-layer MoS$_2$ and WS$_2$ structure, since the lattice parameter and the metal-sulfur bond length are almost the same in these two structures, the difference between the two frequency could origin from the ionic character, but till now no conceivable evident available, because the previous model cannot cover the quasi 2D system. Here based on our new methodology, by comparing the effective charge on the metal, we conclude that the higher $A_1'$ vibration frequency in WS$_2$ is due to the higher ionicity of W compared with Mo.

We also investigate the layer dependent and stacking dependent effective charge distribution, by benchmark with the experimental Raman frequency data, we concluded a proportional relationship between the effective charge and $A_1'$ frequency in the layer dependent scheme, which agrees well with the experimental observation, which is solidly convincing that our methodology works quite well for the quasi 2D materials. The Phillips’ ionicity works pretty well in the bulk materials; however, it is surpassed by our mythology when it goes into the low dimension.

### 7.1.3 Application in nanoclusters

The previous two chapters provided details about the background, formulism and expression in bulk and quasi 2D structures, and the methodology can also extend the application in quantum clusters, like MoS$_2$ quantum cluster. Since all the dimensions are truncated in the nano-cluster structure, the effective charges are summed over all the total electric field in three dimensions, for the MoS$_2$ nanocluster, the edge state possess larger charge density than the center ones and due to the distinct bonding environments, the S-S dimer edge and the S edge show different charge character respectively, which results variable
chemical reactivity during the growth events and bonding strength. It can conclude that the new methodology are still robust in dealing with nanoclusters and can be of substantial efficient for investigating both the static (geometry, morphology) and dynamic (growth) properties. By conceptualizing the term “line tension” as the gradient of the charge density difference between the center and the edge, by choosing the chemical bond energy instead of the total energy, the chemical potential can be well described in the non-stoichiometric nanocluster, and a new scheme for the shape and size dependent growth model of MoS$_2$ quantum cluster is developed for understanding the experimental samples for the reactants with hexagonal and triangle morphology. This chapter concluded that besides the effective charge calculation, the new methodology can be widely applied in nano materials.

7.2 Future works

The previous works in the thesis stressed the successful application of the methodology in effective charge calculation from 3D bulk materials to low dimensional nanoclusters, and some combination with line tension for the description of the geometry and size dependent characters. Herein, by keeping improving the formulism based on the study objective, a more general form of the methodology could be applied in more complicated materials, like ternary compounds, organic compounds, metal organic frameworks (MOF) and other complex systems.

7.2.1 Effective charge for the complex stoichiometry structures

For the structures composed more than binary elements, ternary systems for example, like NaOH, the formulism $E_{BH} = E_{M} + E_{Pol}$ still can work if take the OH$^-$ group as whole and equalize an effective anion X, with effective charge, effective polarizability and effective radius, then problem is simplified to solve
the effective charge of structure NaX, here the parameters about X are all known from the effective approximation and it becomes an ordinary case as discussed in the previous chapters.

However, it is still challenging for the effective charge calculation inside the effective quasi anion X, because it is essential to get the value $E_{BH}$ and $E_M$ for the whole calculation procedure, here a new scheme for the modified Born-Harber cycle is proposed as shown in Figure 7.1, the expression of $E'_{BH}$ is

$$E'_{BH} = -IP_{OH} - \Delta H_{at} - IP_H - EA_O$$

(7.5)

The terms $IP_{OH}$, $\Delta H_{at}$, $IP_H$ and $EA_O$ all can be obtained from first principle DFT calculation, and for the electrostatic part $E_M$, since the $OH^-$ group is not of the crystal structure, the Madelung constant is invalid and $E'_M$ is in the form like

$$E'_M = \frac{q + q -}{4\pi\varepsilon_0 r_0}$$

(7.6)

For the polarization part $E_{Pol}$ is only dependent on the ion itself, this term can be kept unchanged, so the new equation for the solution of the effective charge in $OH^-$ is

$$E'_{BH} = E'_M + E_{Pol}$$

(7.7)
The modified Born-Harber cycle proposed for the OH\(^-\) anion, here IP\(_{\text{OH}^-}\) is the ionization potential for the OH\(^-\) anion, \(\Delta H_{\text{at}}\) is the atomization energy, IP\(_H\) is the ionization potential for H, EA\(_O\) is the electron affinity for O (second order).

By solving Eq (7.7), we can get the effective charge for all the charged ions, for some ions in low dimension, we can also include the electric field determined item inside and investigate the more general effective charge determined properties from bulk materials to nano materials.

7.2.2 Effective charge for structures with dopants and defects

In real materials, the dopants and defects are always part of the structures and most of applied semiconducts have dopants and defects, thus it is critical important to investigate the doped and defected structures, one of the most important character for the dopants and defects is the on site effective charge, which affect the spin states, screening strength, mobility etc. Our model can be applied to explore the charging states in those structures as well.

As presented by our methodology:

\[
E_{BH} = E_M + E_{pol}
\]

(7.8)
In the doped and defects structures, the value of $E_{BH}$ can be updated by the following scheme as shown in Figure 7.2

\[ 63\text{Zn}^{2+}(g) + \text{Al}^{2+}(g) + 64\text{O}(g) \]

\[ 63\text{Zn}(g) + \text{Al}(g) + 64\text{O}(g) \]

\[ 63\text{Zn}(s) + \text{Al}(s) + 32\text{O}_2(g) \]

\[ \text{Zn}_{63}\text{AlO}_{64}(s) \]

\[ E_{BH} = \Delta H_f - \Delta H_{at} - \text{IP}_{\text{Zn}} - \text{IP}_{\text{Al}} - E_{A_O} \]

**Figure 7.2** The modified Born-Harbor cycle proposed for the Al doped ZnO, here Hf is the formation energy of solid Zn, solid Al and Oxygen to form Al doped ZnO crystal, $\Delta H_{at}$ is the atomization energy for each element, $\text{IP}_{\text{Zn}}$, $\text{IP}_{\text{Al}}$ is the ionization potential for Zn and Al atom (first and second order), $E_{A_O}$ is the electron affinity for O (first and second order)

We can see from Figure 7.2 that the only difference lies the item $\Delta H_f$ and $\Delta H_{at}$, in the doped or defect cases, the energy related to the dopants or defects can be obtained by Ab initio DFT calculation, by updating the $\Delta H_f$ and $\Delta H_{at}$, we get the corresponding $E_{BH}'$. The $E_M$ part also can be updated accordingly to the definition, as shown in Figure 7.3, if it is the dopant case, the formal charge and the distance can be updated in the primitive calculation formula, if it is the defect case, the corresponding term should be set as zero, by such strategy, we can get the updated Madelung energy $E_M'$, the polarization energy $E_{Pol}$ origins from the individual ions, which can be used here directly.

The above strategy provided a reasonable approximation to obtain the effective
charge in the doped and defected semiconductor crystals, however, different from the perfect crystal, many other corrections have to be included, like dipole-dipole interaction, we will try to improve and extend our methodology applicable to the doped and defected materials as well.

![Image of calculation strategy](image)

**Figure 7.3** The calculation strategy for the structures with dopants and defects, based on the rocksalt lattice as an example. The dopant or defect site are highlighted by the red circle, the corresponding term in the calculation formula are marked by the red circle as well.
Reference


Appendix


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Appendix