FIRST-PRINCIPLES STUDY OF STRUCTURAL AND RESPONSE PROPERTIES OF BARIUM TITANATE PHASES

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2017

FIRST-PRINCIPLES STUDY OF STRUCTURAL AND RESPONSE PROPERTIES OF BARIUM TITANATE PHASES

by

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Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

March 2017

ACKNOWLEDGEMENT

This Master thesis would not be completed successfully without the guidance and help of many people. I am grateful for the opportunity given in this study; and through the exposure in this research, my research skills have been greatly improved.

First and foremost, I would like to express my deepest appreciation to my supervisors, Dr. Yoon Tiem Leong and Prof. Dr. Ong Lye Hock. Thanks to Dr. Yoon Tiem Leong, my main academic supervisor, for initiating my foray into computational physics and providing the required resources for my computations. Being a man full of the spirit and adventurous, he allows full freedom for me to conduct my research, and bestows me the opportunity to set up a computer cluster myself. Despite our relationship as supervisor and students, Dr Yoon never utilize his status to strength his arguments, an humble act that I greatly grateful of. On the other hand, Prof. Dr. Ong Lye Hock, my co-supervisor, had been my mentor in my research journey, which I will certainly be quite lost without his guidance. Constantly steering me towards the correct direction, he ensures that I will be able to finish my Master on time. Despite being ready for retirement, he readily extent his help in correcting my draft research paper and happily shared his experiences in teaching and research. I would like to thank him again for his meticulous efforts in explaining things to me, and for providing me with financial assistance from his research grant.

The author also acknowledge the contributions of Universiti Sains Malaysia (USM) and School of Physics. Thanks to USM for providing financial support to me through Assoc. Prof. Ong's RU grant, without which is impossible for me to continue my study. I would also like to thank the School of Physics for providing the computer

KAJIAN PRINSIP-PERTAMA STRUKTUR DAN RESPONS SIFAT FASA BARIUM TITANATE

ABSTRAK

Sifat keadaan asas $BaTiO_3$ perovskite kristal dalam kedua-dua bentuk pukal dan kepingan telah dikaji dengan menggunakan prinsip pertama Teori Fungsian Ketumpatan (DFT) dan kaedah projektor gelombang imbuhan. Pengiraan kristal pukal $BaTiO_3$ dalam semua empat fasa telah dilakukan dengan penghampiran ketumpatan tempatan (LDA) dan penghampiran kecerunan umum (GGA). Dua keupayaan PAW yang berbeza berdasarkan set data yang diperkembangkan oleh Jollet-Torrent-Holzwarth (JTH) dan Garrity-Bennett-Rabe-Vanderbilt (GBRV) telah digunakan dalam pengiraan. Penekanan bahagian pertama diletakkan pada sifat elektronik, struktur dan sifat tindak balas semua fasa $BaTiO_3$ dengan menggunakan fungsian korelasi pertukaran (XC) dan keupayaan PAW yang berbeza. Pengiraan dengan GGA didapati menghasilkan sifat struktur yang lebih dekat dengan nilai eksperimen daripada LDA. Ciri-ciri getaran yang diramal dengan teori fungsian ketumpatan usikan adalah konsisten dengan kajian teori dan eksperimen terdahulu. Pengutuban spontan tiga fasa ferroelektrik yang dikira dengan menggunakan teknik fasa Berry berbeza secara ketaranya dibandingkan dengan nilai eksperimen tetapi selaras dengan keputusan teori lain. Fluktuasi parameter kekisi yang dikira menggunakan fungsian XC yang berbeza secara langsung mempengaruhi pengutuban spontan yang dikira. Kepingan $BaTiO_3$ simetri dengan ketebalan yang berbeza (6, 8 dan 10-unit-sel tebal) dan penamatan permukaan BaO (100) telah dikira dengan menggunakan DFT dalam rangka fungsian PBE-GGA dan keupayaan JTH-PAW.

Kesan-kesan pengenduran permukaan kepada perubahan parameter struktur telah dikaji. Berbeza dengan penemuan sastera dahulu, semua jarak antara lapisan individu telah berkembangan kecuali jarak antara permukaan dan lapisan yang berikutnya. Perbandingan ketiga-tiga kepingan dengan pelbagai ketebalan mendedahkan magnitud sesaran antara lapisan bagi kepingan dengan 8-unit-sel tebal adalah rendah daripada dua kepingan lain. Had penembusan praktikal kesan pengenduran permukaan dianggarkan pada lima lapisan daripad permukaan BaO (100), dan sesaran ferroelektrik satar setiap lapisan didapati tidak dipengeruhi olek ketebalan kepingan. Setara dengan penemuan sastera dahulu, kepingan simetri $BaTiO_3$ bersudut empat dengan penamatan permukaan BaO (100) diramalkan memiliki nilai pengutuban spontan satar yang lebih kecil berbanding dengan kes pukal. Ini menunjukkan kewujudan peranan faktor dominan lain dalam penindasan pengutuban kerana nilai yang dikira dengan teknik fasa Berry adalah terlalu kecil berbanding dengan sesaran ferroelektrik lapisan TiO_2.

FIRST-PRINCIPLES STUDY OF STRUCTURAL AND RESPONSE PROPERTIES OF BARIUM TITANATE PHASES

ABSTRACT

Ground state properties of $BaTiO_3$ perovskite crystal, both in bulk and slab form, were studied using first-principles density functional theory (DFT) using the projector-augmented wave methods. The computations on bulk $BaTiO_3$ crystals, in all four phases, were performed within the framework of local-density approximation (LDA) and generalized-gradient approximation (GGA). Two different PAW potentials based on the datasets developed by Jollet-Torrent-Holzwarth (JTH) and Garrity-Bennett-Rabe-Vanderbilt (GBRV) are employed in the calculations. The emphasis of the first part is placed on the electronic, structural and response properties of all phases of bulk $BaTiO_3$ using different exchange correlation (XC) functionals and PAW potentials. It is observed that calculations with GGA yields structural properties much closer to reported experimental values than LDA. The vibrational properties predicted from density functional perturbation theory are consistent with experimental and previous theoretical studies. Spontaneous polarization for the three ferroelectric phases, computed using Berry phase, differ considerably from experimental values but are consistent with other theoretical results. The fluctuation of lattice parameters computed using different XC functionals directly affects the computed spontaneous polarization. Symmetric $BaTiO_3$ slabs of different thickness (6, 8 and 10-unit-cell thick) with BaO (100) surface terminations were computed using DFT within PBE-GGA functionals using JTH-PAW potentials. The effects of surface relaxation on the structural parameters changes are

studied. In contrast to previous literature findings, all interlayer spacings between the individual layers were experiencing an expansion except of the spacing between the surface and subsequent deeper layer. A comparison across the three slabs with varying thickness revealed the expansion in interlayer spacings in the 8-unit-cell thick slab is smaller than the other two slabs. The practical penetration limit of the surface relaxation effects was estimated to be five layers from the BaO (100) surface, and the computed in-plane ferroelectric displacements of each layer were relatively independent of the slab thickness. In agreement with previous literature findings, symmetric tetragonal $BaTiO_3$ slab with BaO (100) surface terminations was predicted to possess a much smaller value of in-plane spontaneous polarization than the corresponding quantity in the bulk case. This suggests the role of another dominant factor in suppressing the polarization. For the computed value using Berry phase formalism, it is too small with regard to ferroelectric displacements in the TiO_2 layers.

CHAPTER 1

GENERAL BACKGROUND AND LITERATURE REVIEW

1.1 Introduction

Ferroelectricity is a classic scientific discovery that is continued to be studied to this day since its discovery in 1921 (Valasek, 1921). With the intensive research interest it is receiving, huge advancements have been made in the area from the identification of numerous ferroelectric materials to novel experimental works and theoretical understandings in various attempts to understand this phenomenon. In the simplest terms, ferroelectricity is the existence of spontaneous polarization in a material which can be reversed by the application of an electric field; the oscillations of electric field vectors will result in a polarization hysteresis loop. Nowadays, ferroelectricity have been revealed to exhibit complex interplay of dielectric and dynamical properties. In the course of history of ferroelectricity, one of the major event is the discovery of ferroelectricity in the perovskite crystals, where barium titanate (BTO) is the most well known example.

The objective of this thesis is to investigate the structural and response properties of the ferroelectric ceramic BTO from first-principles, and to make detailed studies and comparisons between the four phases of BTO both from the theoretical and computational perceptive. The thesis is mainly divided into 3 different part: theoretical, computational and results sections, which will be further discussed later.

1.2 Background of ferroelectricity

The subject of ferroelectricity began with the studies of sodium potassium tartrate tetrahydrate (Rochelle Salt) by Valasek (1921), whose works leads to the coining of the term ”ferroelectricity”, although it should be mentioned that the associated anamolous dielectric response had been identified by Pockels (1894) earlier as mentioned by Cross and Newnham (1987).

Nevertheless, it is found that Rochelle Salt is, among other major obstacles, structurally complex with 112 atoms per unit cell, which poses difficulties in investigation in that era. The discovery of ferroelectricity in potassium dihydrogen phosphate (KDP) (Busch & Scherrer, 1987) leads to the progress in understanding the phenomena in ferroelectrics, despite having constraint that ferroelectricity only manifests at temperature below $-150\,^{\circ}\mathrm{C}$. The origin of ferroelectricity in KDP lies in the ordering of hydrogen bonds at the corners of phosphate. The presence of hydrogen bond is then seen as a necessary condition for polar instabilities to occur in ferroelectric materials.

When the ferroelectric properties of BTO were found, it was a significant breakthrough for BTO is a simple oxide material belongs to the perovskite family. The members of perovskite family ABO_3 have the metallic A elements occupying cubic lattice points, where each cubic unit cell in turns contains an embedded octahedron having oxygen at its vertex and another metallic B element at its centre. Contrary to KDP, BTO in cubic structure is paraelectric and it exhibits ferroelectric phase in tetragonal, orthogonal and rhombohedral structures. It is natural that the then research interests extend to other members of the perovskite family due to simplicity of the

structure of the ABO_3 family.

However, not all the phase transition occuring in ABO_3 perovskite structures are ferroelectric in nature, with some members exhibit non-polar structural phase transitions. One such perovskite structure is strontium titanate (STO), which undergoes an antiferrodistortive transition from cubic to tetragonal structure (Cowley & Shapiro, 2006). The particular phase transition in the form of relative rotations between the oxygen octahedrals in adjacent cells, in other words a Brillouin zone boundary type displacement.

Following the successes of experimental works and discovery, it is inevitable that the theoretical efforts to understand ferroelectricity were carried out. Major contributions were made by several prominent figures, including but not limited to Anderson (1960); Cochran (1960); Slater (1950) and Devonshire (1949, 1951). The role of the competition of long-range coulomb forces and short-range local forces in determining the ferroelectric instability, considered as conventional theoretical explanation nowadays, was proposed by Slater (1950). It is theorized that the long-range dipolar force associated with the Lorentz field is in competition with the local short-range forces which favour the high symmetry configuration, such as the paraelectric cubic phase of BTO. The structural phase transitions affect the balance of these two competing forces, determining which of the two forces will prevail and thus consequently the occurrence of ferroelectric instabilities. This explanation underlies the proposal of "displacive" type of phase transition for the perovskites, in contrast with the "order-disorder" description of phase transition in KDP-type. Another breakthrough occurs a decade later in 1960, when Cochran (1960), and also Anderson (1960) in another independent research,

incorporate the lattice dynamics in the description of ferroelectric phase transition. The formulation of soft-mode in the description of displacive phase transition is made by taking one of the lattice mode as variable. This dynamical model extends the picture of competing large-range and short-range force by considering it as the origin of the softening of a particular lattice mode.

On the other hand, the theoretical model on the macroscopic level using thermodynamic theory had been developed by Devonshire (1949, 1951). Devonshire's model is a phenomenological model built on the evaluation of free energy from the elastic, dielectric, structural and thermal properties of BTO. The model is based on the earlier work by Landau and Ginzberg and the resulting theory is now called Landau-Devonshire-Ginzberg Theory (LDGT). With the later inclusion of crystal lattice dynamics in the understanding of ferroelectric phase transition by Cochran (1960) and Anderson (1960), the static phenomenological description by Devonshire was linked with atomistic descriptions through atomic displacements and elementary crystal excitations.

Based on the foundational works by the pioneers, further experimental works and theoretical models were devised, during which the field of ferroelectricity advanced rapidly. Semi-empirical models were being used at this stage, following the realization of the roles of lattice dynamics and soft mode in ferroelectricity. With the advent of crystallography and spectroscopy methods and apparatus such as neutron scattering, Raman measurement, Rayleigh scattering, and conventional X-ray diffraction and scattering, the properties of soft modes of ABO_3 materials were studied extensively. The experimental data were studied and analysed by fitting into shell models. The work of Migoni, Bilz, and Bäuerle (1976), leading to the "polarizability model" later, sug-

gested the non-linearity and anisotropy of polarizability of oxygen atoms as the origin of ferroelectric behaviour of perovskites. In particular, the anisotropy of polarizability of oxygen atoms was suggested to be associated with the hybridization between O-p states and transition metal d-states. This explanation was supported by the first-principles calculations, as will be discussed later.

Despite the simplicity of the perovskite structure, the complexity of ferroelectric phase transitions were unexpectedly higher as more and more experimental data and different theoretical models were available. One of the most distracting, while intriguing, observation was that the phase transition is not purely displacive as envisaged by Cochran (1960), but somehow contains a mixture of displacive and order-disorder character especially near the transition temperature. In order to further investigate the properties of perovskite, the traditional analytical analysis are complemented and extended by various numerical computation methods with the advent and prevalence of more powerful and much cheaper computing machines.

1.3 First-principles ab-initio approach

First-principles method, as performed by the density functional theory (DFT) (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), is based on the established law of physics unlike an empirical model requiring fitting of experimental data. Since the introduction of the Noble prize winning DFT in about 1964, the properties of condensed matter system can be investigated at the atomistic level by solving the fundamental equations of quantum mechanics. While the formulation of DFT is exact in itself, its practical application is hindered by the unknown exchange and correlation terms, and the amount

of numerical computation is restricted by the limited efficient computing resources. The application of DFT is observed to increase exponentially during the last two decades in which computational power has improved dramatically leading to emergence of new theoretical computing method.

The capability of DFT is well demonstrated in an influential work by Cohen (1992) on the origin of ferroelectricity in perovskite oxides. The ferroelectric behaviours of perovskites were not completely understood, where perovskites which are structurally similar but chemically different exhibit different behaviours. One of the obvious discrepancy is between BTO and lead titanate (LTO) where both have similar unit cell volumes, but BTO undergoes three structural phase transitions (from cubic to tetragonal, orthogonal and rhombohedral), whereas LTO has only one phase transition from cubic to tetragonal phase. Using electronic structures calculations with the local density approximation (LDA), Cohen managed to show that hybridization between Ti 3d states and O 2p states are essential for ferroelectric, which is in line with that suggested by Migoni et al. (1976). The different structural phase transitions between the two materials are resolved by noting that LTO tetragonal phase contains large strains from the hybridization of Pb and O states, whereas in BTO the Ba-O interaction is almost ionic in nature, causing BTO to prefer a rhombohedral structure as its most stable form.

Unfortunately, the macroscopic polarization, a fundamental quantity for ferroelectric material, cannot be directly computed using the conventional definition of polarization. This difficulties had been resolved by King-Smith and Vanderbilt (1993); Resta (1994); Vanderbilt and King-Smith (1993) with the modern theory of polarization. It is realized that polarization is quantum phenomenon which cannot be expressed in the classical

definition of charge dipole per unit space. Rather than the absolute value of polarization, the difference in polarization with respect to a referenced state is found to be the more basic quantity. In the new approach, the ionic polarization is still derived using the established electromagnetic theory, but the remaining electronic part of the polarization is obtained from the Berry phase of the electronic wavefunctions. The Berry phase formalism had been implemented in the framework of DFT.

The functionality of DFT is further extended to calculate additional response properties apart from the structural properties through the use of linear response theory. Various physical properties can be computed from the second derivatives of total energy with respect to different perturbations, where the perturbations can be phonons, static homogeneous electric field or strain. The second derivatives of total energy are collectively called the response functions. The linear responses connected to derivatives of energy, implemented within density functional perturbation theory (DFPT), include phonon dynamical matrices, dielectric tensor, Born effective charges, elastic constant, internal strain and piezoelectricity constant. Non-linear response connected to the third-order derivatives of the energy can also be calculated, which is an extension to the linear response method.

1.4 Thesis outline

This thesis is divided into two main portions: i) theoretical and computational methods part and ii) results and discussion part. Excluding this chapter which is concerned with general background and basic existing literature review, the first part covers from Chapter 2 to Chapter 5 whereas the second part of this thesis covers two

chapters: Chapter 6 and Chapter 7. The last Chapter 8 is about the conclusion made from interpretations of the obtained results.

The main computation methods used in this work, which are density functional theory (DFT) and its extension, density function perturbation theory (DFPT), are discussed in Chapter 2 and Chapter 3 respectively. The response properties are calculated by the use of DFPT, of which basic principles are discussed in Chapter 3. Chapter 4 concerns with the computation method for spontaneous polarization, an essential quantity in a ferroelectric. The polarization from a microscopic perceptive is discussed, including the limitations of conventional definition of macroscopic polarization leading the formulation of modern theory of polarization. The computational flow chart is then illustrated in Chapter 5. The detailed aspect of computations in this work including the potentials, XC functionals and various convergence parameters are given. Both computational work flows for the bulk and slab calculations are given.

The results of computations for the bulk $BaTiO_3$ are presented in Chapter 6. Structural properties and electronic structure are first given for bulk $BaTiO_3$ of all four phases with comparisons to those of existing literatures, in addition to quantities essential for the characterization of a ferroelectric such as the Born effective charge, spontaneous polarization and the phonon modes and frequencies. On the other hand, Chapter 7 contains the results from structural relaxation of $BaTiO_3$ of various thickness. The polarization variation with respect to variation in three different slab thickness is then presented. Finally, the last Chapter 8 is about the conclusions derived from this work and some possible future works are suggested.

CHAPTER 2

DENSITY FUNCTIONAL THEORY

2.1 The Schrödinger Equation

The DFT can be understood through a review of the quantum mechanics of a many body system. In most cases the ultimate aim of solid state physics and quantum chemistry is the solution of the Schrödinger equation. Consider the basic time-independent, non-relativistic Schrödinger equation:

$$\hat{H}\Psi = E\Psi, \tag{2.1}$$

where Ψ is the wave function of some collection of atoms in a well-defined boundary region. The time-independent Schrödinger equation describes the evolution of energy as a function of position of the constituting atoms, subjected to a background potential and inter-particles interaction described by the Hamiltonian of the system, H. In the description of the quantum mechanics, the position of an atom is not a absolute unit, but rather the positions of both nucleus and its electrons.

Subjected to the charge neutrality of an atom, the forces acting on the nucleus and electrons are of the same order of magnitude. Consequently the changes in momentum due to these forces must be about the same. Considering the huge differences between the mass of nucleus and electrons, the nucleus must have much smaller velocity compared to electrons due to its relative massive size. It follows that the motions of nucleus and electrons have different time scales, and that it can be assumed that at

the time scale of the nucleus the electrons will relax to their lowest energy (ground state) almost instantly. Hence, the solution of a quantum mechanical system can be divided into nucleus and electrons components. The separation of motions of nuclear and electrons into two mathematical problems is known as the Born-Oppenheimer approximation (Born & Oppenheimer, 1927).

Born-Oppenheimer approximation thus enables us to solve the equations that describe the electron motion for fixed positions of the atomic nuclei. The eigenfunction of the Hamiltonian is then assumed to take the following form:

$$\Psi(\{\mathbf{r}_i\},\{\mathbf{R}_\alpha\}) = \psi(\{\mathbf{r}_i\};\{\mathbf{R}_\alpha\}) \cdot \Phi\{\mathbf{R}_\alpha\}, \tag{2.2}$$

where $\mathbf{r_i}$ is the position of ith electron and $\mathbf{R}_\alpha$ is the position of αth nuclei. ψ is the electronic wave function whereas Φ is that of the nuclei part. From Eq. (2.2), $\psi(\{\mathbf{r}_i\};\{\mathbf{R}_\alpha\})$ is a wave function dependent only on $\mathbf{r}_i$ with $\mathbf{R}_\alpha$ as parameters. The ground state energy can then be expressed as a function of positions of the nuclei $E(\mathbf{R}_1,\ldots,\mathbf{R}_M)$, where M is the number of nuclei. The resulting energy function is known as the adiabatic potential energy surface of the system, describing the changes in energy with respect to positions of atoms.

Following the separation of nuclear and electronic motion, Eq. (2.1) can be simplified into

$$\hat{H}\psi = E\psi, \tag{2.3}$$

ψ is a set of quantum mechanical solutions of the electronic wave function corresponding to the Hamiltonian H. Each of the solution ψ_n is associated to their eigenvalue E_n,

which is a real number. In the case of a system with multiple nuclei with their respective electrons interacting with each other, the minimal description of the Schrödinger Equation, which ignores the contributions from the spins of electrons, will be:

$$\left[-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2+\sum_{i=1}^{N}V_{\text{ext}}(\mathbf{r}_i)+\sum_{i=1}^{N}\sum_{j<i}U(\mathbf{r}_i,\mathbf{r}_j)\right]\psi=E\psi, \tag{2.4}$$

where m is the mass of electron. The first term in the bracket is the kinetic energy of the electrons. V is the external potential energy, mainly due to the interaction between electrons and the electrostatic potential of the nuclei, which are fixed in position according to the Born-Oppenheimer approximation. The last term U refers to the potential energy due to interaction between the electrons themselves. In the context of Eq. (2.4), E corresponds to the ground state energy of the electrons of a particular instant of configuration of the system.

2.2 Computation complexities

For a many-body system, the electronic wave function is shown to be a function of the spatial coordinates of each of N electrons $\psi=\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$. The implication is that for a N-electrons system there are $3N$ variables to be determined. The number of electrons N is considerably larger than the number of nuclei M. The wave function is thus a $3N$ dimensional function, which makes the solving of the Schrödinger equation impractical except for a few exceptionally small systems. The ab-initio approach assumes that the wave function of the system can be decomposed into combinations of single individual electron wave functions. The wave function ψ is then approximated as $\psi=\psi_1(\mathbf{r})\psi_2(\mathbf{r})\ldots\psi_N(\mathbf{r})$, a product of one-electron wave functions of the constituting

electrons. The resulting expression is known as Hartree product.

An examination of the expression of the Hamiltonian of Eq. (2.4) will reveal that the third terms U is the main obstacle to solving the equation. The electron-electron interactions is expressed as the summation of the pair-wise inter-electron interaction potential. The presence of this electron-electron interaction term makes the electronic wave function a coupled equation. In other words, the individual wave function $\psi_i(\mathbf{r})$ cannot be defined without considering the positions of all other electrons at the same time. This indicates exceptional difficulties in solving the wave function of a many-body system, due to the presence of terms corresponding to interacting electrons.

It should be noted that the wave function is dependent on the positions of electrons, the variables themselves are not exactly defined as a consequence of the position-momentum uncertainty theorem. This make the definition of wave function of a system of electrons at particular exact coordinates meaningless. According to the Copenhagen interpretation, the measurable quantity is the probability that the N electrons are at a particular set of position $\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$ instead, and this probability is proportional to $\psi^*(\mathbf{r}_1, \ldots, \mathbf{r}_N)\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Coupling with the notion of indistinguishable electrons in quantum mechanics, where electrons in a system are considered as identical, the interested quantity is the probability of a set of electrons at locations $\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$ without considering the order of elements in the set.

2.3 Electronic density

While the wave function contains all possible information of a system, its complexity is overwhelming; a $3N$-dimensional function ($4N$-dimensional if spin of electron is

condidered). The problem shall be resolved through the use of electronic density, as we have no direct use of the wave function. The solution can be brought back to 3-dimensional space, as will be shown later.

In quantum mechanics, electronic density is the probability of occupation of an electron at an infinitesimal element of space surrounding a given point; a scalar quantity depending upon three spatial variables. The definition of electron density is clear cut for a system of one electron:

$$n(\mathbf{r}) = |\psi(\mathbf{r})|^2, \tag{2.5}$$

which is known as Born's statistical interpretation, absolute square of wave function.

This simple probabilistic interpretation does not directly hold for an ensemble of electrons. Electron density is a 3D function about the expectation value of the density of electrons. Using the conventional interpretation of observables from wave function, we can write:

$$n(\mathbf{r}) = \langle \psi | \hat{n}(\mathbf{r}) | \psi \rangle, \tag{2.6}$$

where $\hat{n}(\mathbf{r})$ is an operator referring to electron number density.

Taken into account that electrons are point particles, the electronic density is defined to be

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\hat{\mathbf{r}}_i - \mathbf{r}), \tag{2.7}$$

where the direct delta function is used and $\mathbf{r}_i$ is the position operator for the ith electron. The operator $\hat{n}(\mathbf{r})$ is then the summation of density of electron i at $\mathbf{r}$ over the number of electrons.

The expectation value of the electronic density, without considering electron spin, is then:

$$\begin{aligned} n(\mathbf{r}) &= \int \cdots \int \psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \hat{n}(\mathbf{r}) \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N \\ &= \sum_{i=1}^{N} \int \cdots \int \psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \delta(\hat{\mathbf{r}}_i - \mathbf{r}) \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N \\ &= \sum_{i=1}^{N} \int \cdots \int \psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \delta(\hat{\mathbf{r}}_1 - \mathbf{r}) \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N \\ &= \sum_{i=1}^{N} \int \cdots \int \psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d\mathbf{r}_2 \ldots d\mathbf{r}_N \\ &= N \int \cdots \int |\psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2\, d\mathbf{r}_2 \ldots d\mathbf{r}_N. \end{aligned} \tag{2.8}$$

The substitution of $\mathbf{r}_i$ by $\mathbf{r}_1$ in the third step of Eq. (2.8) is a consequence of Pauli exclusion principle; all electrons are indistinguishable that an arbitrary electron can be selected. The presence of N is from the sum over identical numbers.

Eq. (2.8) shows that the electronic density at a particular point reduces to the density probability of a single electron, taken into account all possible configurations of the rest of electrons. The constant number of electrons N ensures that the electronic density over all space is preserved, which is equal to the N itself. This can be shown by an integration of Eq. (2.8) over all space:

$$\int n(\mathbf{r})\, d\mathbf{r} = N. \tag{2.9}$$

In Hatree Fock and DFT method the electronic density is typical expressed in terms of one-electron representation. Under the assumption of non-interacting electrons, the

total wave function can be approximated as a Slater determinant for N electrons. In this case, Eq. (2.8) can be simplified to, in terms of orbital wave functions and assuming doubly occupied spatial orbitals,:

$$n(\mathbf{r}) = 2\sum_{i}^{N/2} |\psi_i(\mathbf{r})|^2, \tag{2.10}$$

where the density of electron at a point is the summation of the squares of the orbital wave functions. The presence of the factor 2 takes into account that the fact that two electrons with different spin can occupy the same orbital, as stated by the Pauli exclusion principle. The density of electrons thus encodes information obtainable from the complex $3N$ dimensional solution of the Schrödinger equation, which is exploited by the method of density functional theory.

2.4 The Hohenberg-Kohn theorems

The remarkable achievement of DFT lies in its ability to reduce the complexities of many-body problem back to normal 3-dimensional space, without having to deal with many-electron state directly. The core principles behind DFT is stated by the Hohenberg-Kohn theorems (Hohenberg & Kohn, 1964).

2.4.1 Hohenberg-Kohn first theorem

Hohenberg-Kohn first theorem: *The external potential $V_{\text{ext}}(\mathbf{r})$ is uniquely determined by the corresponding ground-state electronic density, to within an additive constant.*

Before the proof is given, the definition of the external potential $V_{\text{ext}}(\mathbf{r})$ needs

to be first given based on the previous discussion. The problem concerned here is a simplified system of N electrons under a static external potential. Following the Born-Oppenheimer approximation, the static external potential $V_{\text{ext}}(\mathbf{r})$, assumed to be mainly the electrostatic Coulomb potential imposed by the surrounding nuclei, is

$$V_{\text{ext}}(\mathbf{r}) = -\sum_{\alpha} \frac{Z_\alpha}{|\mathbf{r}-\mathbf{r}_\alpha|}. \tag{2.11}$$

In the context of Eq. (2.4), the Hamiltonian operator $\hat{H}$ is made up of three parts: $\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{U}$, where $\hat{T}$ is the kinetic energy operator, $\hat{V}_{\text{ext}}$ is the potential energy operator and $\hat{U}$ is the interaction energy operators. The potential energy operator is then $\hat{V}_{\text{ext}} = \sum_i V_{\text{ext}}(\mathbf{r}_i)$.

Let $n_0(\mathbf{r})$ be the non-degenerate ground state density of N electrons in the potential $V_{\text{ext}}(\mathbf{r})$, with the wave function ψ_0 and energy E_0. Assume a second external potential $V'_{\text{ext}}(\mathbf{r})$, not equal to $V_{\text{ext}}(\mathbf{r})$ + constant, giving rise to a ground state ψ' not different from ψ_0 with a phase factor, but having the same electron density $n_0(\mathbf{r})$. Then the ground state energy can be expressed as

$$E_0 = \langle \psi_0 | \hat{H}_0 | \psi_0 \rangle = \langle \psi_0 | \hat{T} + \hat{V}_{\text{ext}} + \hat{U} | \psi_0 \rangle ,$$
$$E' = \langle \psi' | \hat{H}' | \psi' \rangle = \langle \psi' | \hat{T} + \hat{V}'_{\text{ext}} + \hat{U} | \psi' \rangle .$$

The $\hat{T}$ and $\hat{U}$ are the same for all N electrons systems as evident in the formulation of the Hamiltonian operator, so the a state ψ is completely determined by N and $V_{\text{ext}}(\mathbf{r})$.

Taking advantage of indistinguishability of electrons again, it is observed that the

expectation value of external potential operator is:

$$
\begin{aligned}
&\langle\psi|\hat{V}_{\text{ext}}|\psi\rangle \\
&= \int\cdots\int \psi^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i)\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ldots\mathrm{d}\mathbf{r}_N \\
&= \sum_{i=1}^{N}\int\cdots\int \psi^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)V_{\text{ext}}(\mathbf{r}_1)\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ldots\mathrm{d}\mathbf{r}_N \\
&= N\int V_{\text{ext}}(\mathbf{r}_1)\left[\int\cdots\int \psi^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\ldots\mathrm{d}\mathbf{r}_N\right]\mathrm{d}\mathbf{r}_1 \\
&= \int V_{\text{ext}}(\mathbf{r}_1)n_0(\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1 \\
&= \int V_{\text{ext}}(\mathbf{r})n_0(\mathbf{r})\,\mathrm{d}\mathbf{r}\,.
\end{aligned}
$$

Since ψ_0 is defined to be non-degenerate, the application of the variational principle, which E_0 is the minimal energy, will give rise to the following inequality:

$$
\begin{aligned}
E_0 < \langle\psi'|\hat{H}_0|\psi'\rangle &= \langle\psi'|\hat{H}'|\psi'\rangle + \langle\psi'|\big(\hat{H}_0-\hat{H}'\big)|\psi'\rangle \\
&= E' + \int n_0(\mathbf{r})\big[V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})\big]\,\mathrm{d}\mathbf{r}\,. \qquad (2.12)
\end{aligned}
$$

Similarly for the second Hamiltonian $\hat{H}'$,

$$
\begin{aligned}
E' < \langle\psi_0|\hat{H}'|\psi_0\rangle &= \langle\psi_0|\hat{H}_0|\psi_0\rangle - \langle\psi_0|\big(\hat{H}_0-\hat{H}'\big)|\psi_0\rangle \\
&= E_0 - \int n_0(\mathbf{r})\big[V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})\big]\,\mathrm{d}\mathbf{r}\,. \qquad (2.13)
\end{aligned}
$$

Adding Eq. (2.12) and Eq. (2.13) together results in the contradiction:

$$E_0 + E' < E' + E_0.$$

The assumption that the second potential $V'_{\text{ext}}(\mathbf{r})$, which is not equal to $V_{\text{ext}}(\mathbf{r}) + constant$ but have the same electron density $n_0(\mathbf{r})$ must be wrong.

The ground-state density hence determine, to within a constant, the external potential term in the Schrödinger Equation. Since the Hamiltonian is determined only by the external potential and number of electrons (which is also determined by the electronic density, see Eq. (2.9)), the electron density $n(\mathbf{r})$ implicitly determines all properties of the system, including the wave function ψ.

Since the wave function, and hence all the properties of the system, is a functional of electronic density, it can be asserted that the kinetic energy and electron-electron interaction energy are functionals of the density as well: $T[n]$ and $U[n]$. Collectively these two terms are grouped together into

$$\hat{F} = \hat{T} + \hat{U}, \tag{2.14}$$

due to their independence of the potential and determined only by the forms of $\hat{T}$ and $\hat{U}$; they are universal for a N-electrons system.

The total energy of the system can be expressed in terms of the density in principle:

$$E_V[n] = T[n] + U[n] + V[n] = F[n] + \int V(\mathbf{r}) n(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \tag{2.15}$$

where V is an arbitrary external potential in the general case.

2.4.2 Hohenberg-Kohn second theorem

Hohenberg-Kohn second theorem: *The electron density that minimizes the energy of the overall functional is the exact ground state density.*

The proof of this theorem is straightforward by the use of the variational principle. Let E_0 be the ground state energy for N-electrons system in the external potential $V(\mathbf{r})$ with ground state density $n_0(\mathbf{r})$ in the Hamiltonian H. By the first theorem, an arbitrary v-representable density $n(\mathbf{r})$, which is a density that is ground state of an external potential, determines its own $V(\mathbf{r})$ and therefore a different wave function $|\psi'\rangle$.

By variational principle,

$$\begin{aligned}
\left\langle \psi' \middle| \hat{H} \middle| \psi' \right\rangle &> \langle \psi | \hat{H} | \psi \rangle \\
\left\langle \psi' \middle| \hat{F} \middle| \psi' \right\rangle + \left\langle \psi' \middle| \hat{V} \middle| \psi' \right\rangle &> \langle \psi | \hat{F} | \psi \rangle + \langle \psi | \hat{V} | \psi \rangle \\
F[n] + \int V(\mathbf{r}) n(\mathbf{r}) \, \mathrm{d}\mathbf{r} &> F[n] + \int V(\mathbf{r}) n_0(\mathbf{r}) \, \mathrm{d}\mathbf{r} \\
E_V[n] &> E_V[n_0] = E_0. \qquad (2.16)
\end{aligned}$$

By the Hohenberg-Kohn theorems, the problem of solving the Schrödinger equation reduces to the minimization of the energy functional $E_V[n]$. In non-degenerate case the ground state density corresponds to a unique ground state wave function, which is not true for the general degenerate case. The generalization to the degenerate case can be done, but will not covered in our scope of work.

2.5 Basic equation for DFT

Hohenberg-Kohn second theorem establishes a minimum principle for the energy functional concerning electronic density. Specifically, $E_V[n]$ (see Eq. (2.15)) needs to be minimized with the underlying constraint of constant number of electrons from the integration of electronic density, $\int n(\mathbf{r})\,d\mathbf{r} = N$ (see Eq. (2.9)).

Using the method of Lagrange multiplier, the following Lagrangian needs to be minimized:

$$L_{V,N}[n] = E_V[n] - \mu\left[\int n(\mathbf{r})\,d\mathbf{r} - N\right], \tag{2.17}$$

where μ is a Lagrange multiplier corresponding to the constraint imposed.

A routine minimization procedure will result in

$$0 = \frac{\delta L_{V,N}[n]}{\delta n(\mathbf{r})} = \frac{\delta E_V[n]}{\delta n(\mathbf{r})} - \mu = \frac{\delta F[n]}{\delta n(\mathbf{r})} + V(\mathbf{r}) - \mu,$$

or

$$\mu = \frac{\delta F[n]}{\delta n(\mathbf{r})} + V(\mathbf{r}). \tag{2.18}$$

This is the basic equation for DFT.

It can be immediately recognised that the approximation for the universal functional $F[n]$ determines the accuracy of the calculation. While the formulation is exact in principle, the accuracy of the approximation serves as a bottleneck to the accuracy of the whole calculation, thus compromising the reliability of the results. An alternative approach is proposed by Kohn and Sham, which overcame the necessity of finding an approximation for the universal functional by creating a system of non-interacting