

# DFT Theory and Application to Defect Cluster Concentration

Tigany Zarrouk

July 22, 2019

## Contents

<b>1</b>	<b>Introduction</b>	<b>2</b>
1.1	Born-Oppenheimer Approximation . . . . .	4
1.2	Self-Consistent Mean-Field Theory . . . . .	5
1.3	Density Functional Theory . . . . .	5
1.3.1	Theory . . . . .	5
1.3.2	Kohn-Sham Equations and Self-Consistency . . . . .	8
1.3.3	Practical steps towards accurate calculations . . . . .	8
<b>2</b>	<b>Defects in Materials</b>	<b>8</b>
2.1	Vacancies and Solutes . . . . .	8
2.2	Ti3Al Solutes and their effects. . . . .	8
2.3	Current research: Vacancy-Solute Complexes. . . . .	8
<b>3</b>	<b>Bibliography</b>	<b>8</b>
	<b>References</b>	<b>8</b>
	PLAN	

- Start with the theory of DFT with the HK theorem and KS equations to solve for the density.
- Talk a bit about the approximations that are made.
- Alloy theory and the structure of Ti3Al
- Look at literature to do with all of this. Go through why solutes are incredibly important and why it is necessary to do this research.

- How can solutes lead to failure and why is oxygen in particular bad for the alloy.
- Is it wavy or planar slip
- Go into the calculations and what I have done for them
- Cite the research about the Fe and C vacancy concentration and what the implications are for alloy research
- What can I add to the research.

## 1 Introduction

Since the discovery that quanta may accurately describe the phenomena of black body radiation, it has been known that atoms are governed by a different physical paradigm to that of matter on the macroscopic scale: quantum mechanics. To model the behaviour of atoms in a solid, we can use quantum mechanics.

The first postulate of quantum mechanics states that a quantum mechanical system can be described by a wavefunction, a function of the positions of the quantum mechanical entities, and time, which satisfies the Schrödinger equation. Bonding in materials is heavily dependent on how electrons arrange themselves upon the assembly of atoms to make a solid. By the first postulate, we would expect upon assembly, that the state of the system can be fully described by a *many body wavefunction*: a wavefunction which is a function of the positions of each of the electrons and nuclei in the system.

Assuming that we have non-relativistic electrons, the Schrödinger equation one must solve is then

$$\left( \sum_i -\frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_i \sum_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \sum_I \frac{-Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) \Psi(\{\mathbf{r}\}; t) = E \Psi(\{\mathbf{r}\}; t),$$

where  $\Psi(\{\mathbf{r}\}; t)$  is an eigenstate and Hartree units have been used ( $e = m = \hbar = 4\pi\epsilon_0 = 1$ ).

A time-independent observable is the expectation value of a given operator,

$$\langle \hat{O} \rangle = \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle},$$

this is an integral over all of the coordinates.

The electronic density operator is defined as

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\rho(\mathbf{r}) = \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

The total energy is the expectation value of the Hamiltonian:

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1)$$

$$= \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3V_{\text{ext}} \rho(\mathbf{r}) + E_{II}, \quad (2)$$

where

$$V_{\text{ext}}(\mathbf{r}) = \sum_I -\frac{eZ_I}{|\mathbf{r} - \mathbf{R}_I|}$$

is the external potential due to the coulomb interaction acting on the electrons from the nuclei—the expectation value has been explicitly written as an integral over the local electron density,  $E_{II}$  is the classical electrostatic nucleus-nucleus interaction energy,  $V_{\text{int}}$  is the electron-electron interaction energy and  $\langle \hat{T} \rangle$  is the expectation value of the electronic kinetic energy.

Stationary points in the total energy correspond to eigenstates of the many-body Hamiltonian. One can vary the ratio, or the numerator, in (2). The latter must be subjected to the constraint of orthonormality ( $\langle \Psi | \Psi \rangle = 1$ ), which is possible with the use of Lagrange multipliers. One finds that upon variation of the bra  $\langle \Psi |$  that the ket must satisfy the time-independent Schrödinger equation:

$$\hat{H} |\Psi_m\rangle = E |\Psi\rangle,$$

where  $|\Psi_m\rangle$  is an eigenstate.

Quite often, the state we would most like to find is the lowest energy state (*ground state*) of the system, as this is the fundamental state from which other mechanisms return to or start from. This necessarily occurs at

zero kelvin by the third law of thermodynamics. To find this state for the full system, one must minimise the energy with respect to the parameters of the many-body wavefunction that satisfies the Schrödinger equation and appropriate symmetry constraints (e.g. for electrons,  $\Psi$  must be antisymmetric). This quickly leads to a problem of computation: each electron has four degrees of freedom (the quantum numbers  $n, m, l$  and  $s$ ), and each nucleus will have  $n_I^d$  degrees of freedom; given a collection of just  $M$  atoms, we would have  $4M + Mn_I^d$  variables to minimise with respect to energy. To make the problem tractable, we must make a few approximations.

## 1.1 Born-Oppenheimer Approximation

The first approximation that we make allows us to separate nuclear and electronic motion: this is the Born-Oppenheimer approximation. One must first make the assumption that the wavefunction which describes the system is a product state between the nuclear and electronic portions of the system.

$$\psi(\mathbf{R}, \mathbf{r}) = \Phi(\mathbf{R}) \cdot \psi_{\mathbf{R}}(\mathbf{r}),$$

where  $\psi_{\mathbf{R}}(\mathbf{r})$  is the electronic wavefunction and  $\Phi(\mathbf{R})$  is the nuclear portion of the wavefunction.

Due to the large disparity in mass between an electron and the nucleus of an atom ( $M_{\text{Nuc}} \sim 2000m_e$ ) we can neglect the contribution to the Hamiltonian that comes from the nuclear kinetic energy operator acting on the electronic wavefunction, as the resulting term is far smaller than the electronic kinetic energy operator acting on the electronic wavefunction.

$$T_{\text{Nuclear}}(\mathbf{R})\psi_{\mathbf{R}}(\mathbf{r}) = \sum_{I=1}^M -\frac{1}{2M_I} \nabla_{\mathbf{R}_I}^2 \psi_{\mathbf{R}}(\mathbf{r})$$

$$T_{\text{Electronic}}(\mathbf{r})\psi_{\mathbf{R}}(\mathbf{r}) = \sum_{i=1}^M -\frac{1}{2m_i} \nabla_{\mathbf{r}_i}^2 \psi_{\mathbf{R}}(\mathbf{r})$$

This results in the motion of the electrons being instantaneous with regard to the motion of the ions in the system and that the electrons relax into their ground state with respect to any configuration of the ions. This results in the total energy being a function of only the nuclear coordinates [1].

To obtain the total energy, we can solve for the electronic part of the wavefunction and then solve for the nuclear wavefunction,

$$\left(T_{\text{Nuclear}} + E_{\mathbf{R}}\right)\Phi(\mathbf{R}) = E_{\text{Total}}\Phi(\mathbf{R}),$$

where  $E_{\mathbf{R}}$  contains all of the information of the configuration of the electrons in the system.

## 1.2 Self-Consistent Mean-Field Theory

## 1.3 Density Functional Theory

### 1.3.1 Theory

Now that the electronic motion has been decoupled from that of the nucleus, we can now try to find the ground-state solution for a given configuration of ions. A computationally tractable way of doing this for a many-body solid describing all of the electrons is via the *Density Functional Theory*.

Hohenburg and Kohn's seminal paper in 1964 proved that there exists an energy functional of the electron density which can provide the exact ground-state energy and density upon minimisation. This reduces the number of variables from  $3N$  to that of only 3 for any number of electrons  $N$  in the system of interest.

In 1965, Kohn and Sham then developed a formalism to practically calculate this ground-state density via a set of self-consistent equations: the Kohn-Sham equations.

The main tenet of Density Functional Theory is: given a system that consists of  $N$  electrons, there exists an energy functional of the local electron density  $E[\rho(\mathbf{r})]$ , which corresponds to an antisymmetric wavefunction  $|\Psi\rangle$ ; upon minimisation by variation of the electron density, subject to the constraint that the number of electrons is conserved,

$$\int_{\text{all space}} \rho(\mathbf{r}) = N,$$

the resulting density is unique and the value of the functional is the ground-state energy. To obtain this result we can go through the following theory.

Assuming  $\rho(\mathbf{r})$  is the exact ground state density, and  $|\Psi\rangle$  is the ground-state, by the variational principle we can write,

$$\langle\Psi|\hat{\mathcal{T}} + \frac{1}{2}\sum_i\sum_j\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|\Psi\rangle + \int \rho(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} \geq E_0.$$

The state  $\langle\Psi|$  may not be unique. To make it so, one can subject equation 1.3.1 to the constraints that the number of electrons is conserved and that  $\rho$  is constant.

This defines the functional:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \frac{1}{2} \sum_i \sum_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi \rangle = T[\rho] + E_{ee}[\rho],$$

where the notation  $\Psi \rightarrow \rho$  is to show that the minimisation is with respect to all  $\Psi$  that can make the density  $\rho$ .

One can see the functional with the minimum value as the ground-state energy is then

$$E[\rho] = F[\rho] + E_{\text{ext}}[\rho],$$

where

$$E_{\text{ext}}[\rho] = E_{\text{ext}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}),$$

of which its functional derivative is  $V_{\text{ext}}$ .

By the Euler-Lagrange equations, one finds that the ground state must satisfy

$$\frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} + V_{\text{ext}} = \mu.$$

A functional is an entity that maps a function to a value, similar as how a function maps a variable to a value. The Hohenburg-Kohn theorem states that there exists a functional of the electron density which has the correct ground state energy upon minimising the energy with respect to the electron density [2]. Thus all the information of the system is contained in the electron density, which reduces the minimisation problem from  $4M$  variables to one of just 3 for any number of electrons in the system.

To actually find this density, one can use the Kohn-Sham equations to find a self-consistent solution for the electron density [3].

To actually find the eigenvalues, one can replace the problem of solving a fully-interacting electronic system with a given electronic density with an auxiliary non-interacting electronic system which has the same electronic density. The resulting eigenvalues can be used to find the expectation value of the kinetic energy functional,  $T_s[\rho(\mathbf{r})]$ .

The Hohenburg-Kohn-Sham functional can be defined as

$$E^{\text{HKS}}[\rho] = T_s[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho] + E_{\text{ext}}[\rho] + E_{\text{ZZ}},$$

where  $T_s[\rho]$  is the kinetic energy of the fictitious non-interacting auxiliary system acting in the same effective potential  $V_{\text{eff}}[\rho]$ . The assumption made here is that the ground state density of the non-interacting, auxiliary system is equal to that of the system with full electronic interactions.

This definition of the functional redefines the exchange-correlation functional: the difference between the true kinetic energy and that of the non-interacting system is added to it. Such that the true exchange-correlation functional has the form of

$$E_{\text{xc}}[\rho] = (\langle \hat{T} \rangle - T_{\text{s}}[\rho]) + (\langle \hat{V}_{\text{int}} \rangle - E_{\text{H}}[\rho])$$

where we can interpret the first term as being the increase in kinetic energy from electronic correlation in a fully interacting system, compared to a non-interacting one—correlations cause electrons to move to more energetically favourable areas of the potential—and the second term is the change in the potential of a fully interacting system, with exchange and correlation included, and an electron density acting through the

The difference between the true kinetic energy  $\Delta T = T - T_{\text{s}}$  is now approximated by the exchange-correlation functional  $E_{\text{xc}}[\rho]$ . This is a reasonable approximation. Separating the kinetic energy from the long-range coulomb interactions means that the exchange-correlation potential can be approximated by an approximately local functional. Is this due to the fact that correlations basically lead to a screening of the coulomb potential?

The process by which this happens are as follows: one solves for the Hartree potential first with a given input density (the solution of Poisson's equation), then one finds the total effective potential for the system which is the sum of the Hartree potential, the potential from the nuclei ( $V_{\text{ext}}$ ) and the exchange-correlation potential  $V_{\text{xc}}$ . The Schrödinger equation is subsequently solved, and a new electron density is found. This density can be put back into the Poisson's equation to find the hartree potential and start the cycle again. These equations must be solved self-consistently as the electron density that one puts into Poisson's equation is the quantity that one solves for. Once the input and output densities are within some tolerance of each other, then one can say that the  $\rho^{\text{out}}(\mathbf{r}) = \rho^{\text{exact}}(\mathbf{r})$ , and the resulting Kohn-Sham eigenvalues are the ground state energies.

The Kohn-Sham eigenvalues are not strictly correct.

### 1.3.2 Kohn-Sham Equations and Self-Consistency

### 1.3.3 Practical steps towards accurate calculations

## 2 Defects in Materials

### 2.1 Vacancies and Solutes

### 2.2 Ti3Al Solutes and their effects.

### 2.3 Current research: Vacancy-Solute Complexes.

## 3 Bibliography

### References

- [1] M. W. Finnis, A. T. Paxton, M. Methfessel, and M van Schilfgaarde. Self-consistent tight-binding approximation including polarisable ions. *MRS Proceedings*, 491, jan 1997.
- [2] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136:B864–B871, Nov 1964.
- [3] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140:A1133–A1138, Nov 1965.