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- 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 solid. By the first postulate we would expect upon assembly, 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

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

where we have used Hartree units ($e = m = \hbar = 4\pi\epsilon_0 = 1$).

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 many-body wavefunction state that satisfies the Schrödinger equation with respect to energy. This quickly leads to a problem of computation. Each electron and nucleus each have three spatial coordinates, so even given a collection of a few atoms, we would struggle in being able to accurately determine the ground state. So we can make a few approximations.

1.1 Born-Oppenheimer Approximation

The first approximation that we make is the Born-Oppenheimer approximation, which allows us to separate nuclear and electronic motion. 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 the masses of the electron compared to the nucleus ($\sim 2000m_e$) 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.

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

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

Due to this, we can say that the motion of the electrons is 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 means that the total energy is 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 is via the *Density Functional Theory*.

The main tenet of Density Functional Theory is: given a system that consists of N electrons, there exists an energy functional $E[\rho(\mathbf{r})]$, which is a

functional of a local electron density $\rho(\mathbf{r})$; upon minimising the energy with respect to the changes in 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 corresponds to the ground-state energy.

A functional is an entity that maps a function to a value, similar as how a function maps a variable to a value. The Hohenberg-Kohn theorem states that there exists a functional of the electron density which has the correct ground state energy upon minimising with respect to energy [2].

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

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_{ext}) and the exchange-correlation potential V_{xc} . The Schrödinger equation is subsequently solved, and a new electron density is found. This density can be

1.3.2 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

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