

Band Structure of Silver Chloride(AgCl) using LDA(linear density approximation with ABINIT)

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The band structure of compound silver chloride(AgCl) is studied using ABINIT package in the domain of density function theory(DFT).The approximation used is linear density approximation(LDA).For obtaining the band gap,TD-DFT calculation is done using ab-initio pseudopotentials which makes DFT a true ab-initio calculation.The obtained values of band gap are compared with the theoretical value and other approximations.

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I. INTRODUCTION

A. ABINIT

ABINIT is a package whose main program allows one to find the total energy, charge density and electronic structure of systems made of electrons and nuclei (molecules and periodic solids) within Density Functional Theory (DFT), using pseudopotentials (or PAW atomic data) and a planewave basis. ABINIT also optimize the geometry according to the DFT forces and stresses, or perform molecular dynamics simulations using these forces, or generate phonons, Born effective charges, and dielectric tensors, based on Density-Functional Perturbation Theory, and many more properties. Excited states and spectra can be computed within the Many-Body Perturbation Theory (the GW approximation and the Bethe-Salpeter equation). DFT+U and Dynamical mean-field theory are available for strongly correlated materials. In addition to the main ABINIT code, different utility programs are provided. ABINIT implements density functional theory by solving the KohnSham equations describing the electrons in a material, expanded in a plane wave basis set and using a self-consistent conjugate gradient method to determine the energy minimum. Computational efficiency is achieved through the use of fast Fourier transforms,[5] and pseudopotentials to describe core electrons. As an alternative to standard norm-conserving pseudopotentials, the projector augmented-wave method[6] may be used. In addition to total energy, forces and stresses are also calculated so that geometry optimizations and ab initio molecular dynamics may be carried out. Materials that can be treated by ABINIT include insulators, metals, and magnetically ordered systems including Mott-Hubbard insulators.

B. Density Functional theory(DFT)

Density functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. Using this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. DFT calculations allow the prediction and calculation of material behaviour on the basis of quantum mechanical considerations, without requiring higher order parameters such as fundamental material properties. In contemporary DFT techniques the electronic structure is evaluated using a potential acting on the systems electrons. This DFT potential is constructed as the sum of external potentials V_{ext} , which is determined solely by the structure and the elemental composition of the system, and an effective potential V_{eff} , which represents interelectronic interactions. Thus, a problem for a representative supercell of a material with n electrons can be studied as a set of n one-electron Schrödinger-like equations, which are also known as KohnSham equations.

1. Formalism

In many-body electronic structure calculations, the nuclei of the treated molecules or clusters are seen as fixed (the BornOppenheimer approximation), generating a static external potential V in which the electrons are moving. A stationary electronic state is then described by a wavefunction $\Psi(r_1, r_2, \dots, r_N)$ satisfying the many-electron time-independent Schrödinger equation

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U} \right] \Psi = \left[\sum_i^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) + \sum_i^N V(\vec{r}_i) + \sum_{i<j}^N U(\vec{r}_i, \vec{r}_j) \right] \Psi = E\Psi$$

where, for the N-electron system, \hat{H} is the Hamiltonian, E is the total energy, \hat{T} is the kinetic energy, \hat{V} is the potential energy from the external field due to positively charged nuclei, and \hat{U} is the electronelectron interaction energy. The operators \hat{T} and \hat{U} are called universal operators as they are the same for any N-electron system, while \hat{V} is system-dependent. This complicated many-particle equation is not separable into simpler single-particle equations because of the interaction term \hat{U} .

Here DFT provides an appealing alternative, being much more versatile as it provides a way to systematically map the many-body problem, with \hat{U} , onto a single-body problem without \hat{U} . In DFT the key variable is the electron density $n(\vec{r})$, which for a normalized Ψ is given by

$$n(\vec{r}) = N \int d^3r_2 \cdots \int d^3r_N \Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N).$$

This relation can be reversed, i.e., for a given ground-state density $n_0(\vec{r})$ it is possible, in principle, to calculate the corresponding ground-state wavefunction $\Psi_0(r_1, r_2, \dots, r_N)$. In other words, Ψ is a unique functional of n_0 .

$$\Psi_0 = \Psi[n_0]$$

and consequently the ground-state expectation value of an observable \hat{O} is also a functional of n_0 .

$$O[n_0] = \langle \Psi[n_0] | \hat{O} | \Psi[n_0] \rangle$$

In particular, the ground-state energy is a functional of n_0 .

$$E_0 = E[n_0] = \langle \Psi[n_0] | \hat{T} + \hat{V} + \hat{U} | \Psi[n_0] \rangle$$

where the contribution of the external potential $\langle \Psi[n_0] | \hat{V} | \Psi[n_0] \rangle$ can be written explicitly in terms of the ground-state density n_0

$$V[n_0] = \int V(\vec{r}) n_0(\vec{r}) d^3r. V[n_0] = \int V(\vec{r}) n_0(\vec{r}) d^3r.$$

More generally, the contribution of the external potential $\langle \Psi[n_0] | \hat{V} | \Psi[n_0] \rangle$ can be written explicitly in terms of the density n ,

$$V[n] = \int V(\vec{r}) n(\vec{r}) d^3r.$$

The functionals $T[n]$ and $U[n]$ are called universal functionals, while $V[n]$ is called a non-universal functional, as it depends on the system under study. Having specified a system, i.e., having specified V , one then has to minimize the functional

$$E[n] = T[n] + U[n] + \int V(\vec{r}) n(\vec{r}) d^3r$$

with respect to $n(\vec{r})$, assuming one has reliable expressions for $T[n]$ and $U[n]$. A successful minimization of the energy functional will yield the ground-state density n_0 and thus all other ground-state observables.

The variational problems of minimizing the energy functional $E[n]$ can be solved by applying the Lagrangian method of undetermined multipliers. First, one considers an energy functional that does not explicitly have an electronelectron interaction energy term,

$$E_s[n] = \langle \Psi_s[n] | \hat{T} + \hat{V}_s | \Psi_s[n] \rangle$$

where \hat{T} denotes the kinetic energy operator and V_s is an external effective potential in which the particles are moving, so that $n_s(\vec{r}) = n_r(\vec{r})$

Thus, one can solve the so-called KohnSham equations of this auxiliary noninteracting system

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

which yields the orbitals φ that reproduce the density $n(\vec{r})$ of the original many-body system

$$n(\vec{r}) \stackrel{\text{def}}{=} n_s(\vec{r}) = \sum_i^N |\varphi_i(\vec{r})|^2.$$

The effective single-particle potential can be written in more detail as

$$V_s(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + V_{\text{XC}}[n_s(\vec{r})]$$

where the second term denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, while the last term V_{XC} is called the exchange-correlation potential. Here, V_{XC} includes all the many-particle interactions. Since the Hartree term and V_{XC} depend on $n(\vec{r})$, which depends on the φ_i , which in turn depend on V_s , the problem of solving the KohnSham equation has to be done in a self-consistent (i.e., iterative) way. Usually one starts with an initial guess for $n(\vec{r})$, then calculates the corresponding V_s and solves the KohnSham equations for the φ_i . From these one calculates a new density and starts again. This procedure is then repeated until convergence is reached. A non-iterative approximate formulation called Harris functional DFT is an alternative approach to this.

2. Approximations(exchange correlation functionals)

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. In physics the most widely used approximation is the local-density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated:

$$E_{\text{XC}}^{\text{LDA}}[n] = \int \varepsilon_{\text{XC}}(n) n(\vec{r}) d^3 r.$$

The local spin-density approximation (LSDA) is a straightforward generalization of the LDA to include electron spin:

$$E_{\text{XC}}^{\text{LSDA}}[n_{\uparrow}, n_{\downarrow}] = \int \varepsilon_{\text{XC}}(n_{\uparrow}, n_{\downarrow}) n(\vec{r}) d^3 r.$$

A simple first-principles correlation functional has been recently proposed as well. Although unrelated to the Monte Carlo simulation, the two variants provide compatible accuracy.

The LDA assumes that the density is the same everywhere. Because of this, the LDA has a tendency to underestimate the exchange energy and over-estimate the correlation energy. The errors due to the exchange and correlation parts tend to compensate each other to a certain degree. To correct for this tendency, it is common to expand in terms of the gradient of the density in order to account for the non-homogeneity of the true electron density. This allows for corrections based on the changes in density away from the coordinate. These expansions are referred to as generalized gradient approximations (GGA) and have the following form:

$$E_{\text{XC}}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int \varepsilon_{\text{XC}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}) n(\vec{r}) d^3 r.$$

Using the latter (GGA), very good results for molecular geometries and ground-state energies have been achieved.

C. Linear density Approximations(LDA)

Local-density approximations (LDA) are a class of approximations to the exchange-correlation (XC) energy functional in density functional theory (DFT) that depend solely upon the value of the electronic density at each point in space (and not, for example, derivatives of the density or the KohnSham orbitals). Many approaches can yield local approximations to the XC energy. However, overwhelmingly successful local approximations are those that have

been derived from the homogeneous electron gas (HEG) model. In this regard, LDA is generally synonymous with functionals based on the HEG approximation, which are then applied to realistic systems (molecules and solids).

In general, for a spin-unpolarized system, a local-density approximation for the exchange-correlation energy is written as

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho) \, d\mathbf{r} \, ,$$

where ρ is the electronic density and ϵ_{xc} is the exchange-correlation energy per particle of a homogeneous electron gas of charge density ρ . The exchange-correlation energy is decomposed into exchange and correlation terms linearly,

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