| CALCULATION OF ELECTRONIC PROPERTIES OF OXIDES MnO AND NiO | TÍNH TOÁN CÁC THAM SỐ ĐIỆN TỬ CỦA CÁC OXIT MnO VÀ NiO BẰNG |
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# USING DENSITY FUNCTIONAL THEORY (DFT) METHOD

## ABSTRACT

In this article, we used a Density Functional Theory (DFT) method for calculation of oxides NiO and MnO properties, such as: total energy, band dispersion, density of states (DOS), Mulliken charge, Voronoi charge, dipole moment, geometry optimization, etc. The results of this report also were compared with calculations of other authors and experimental data.

## TÓM TẮT

Trong bài báo này, chúng tôi sử dụng phương pháp lý thuyết hàm mật độ (DFT) để tính toán các tham số điện tử của các oxit NiO và MnO, chẳng hạn như: tổng năng lượng, giản đồ năng lượng, mật độ trạng thái (DOS), điện tích Mulliken, điện tích Voronoi, moment lưỡng cực, tối ưu hóa hình học , v.v…Các kết quả mô phỏng trong công trình này cũng được so sánh với các tính toán của các tác giả khác và các dữ liệu thực nghiệm.

## INTRODUCTION

The classical oxides MnO and NiO have been widely studied as a representative of the family of first-row transition-metal monoxides. These oxides are antiferromagnetic insulators and have occupied a special place in condensed-matter physics for a long-time [1, 6]. Their electronic properties have been the subject of recent theoretical solid state physics. There were many methods used to study these oxides. In this work, all calculations are performed using Density Functional Theory (DFT) method with the OpenMX (Open source package for

Material eXplorer) code. OpenMX is a program package for nano-scale material simulations based on DFT, norm-conserving pseudopotentials, and pseudoatomic localized basis functions [10].

METHOD
Since its first suggestion by Hohenberg, Kohn, and Sham, the DFT combined with local density approximation (LDA) or generalized gradient approximation (GGA) have made a great success in the description of ground state and related properties without any adjustable parameter. However, due to the simplification in their exchange-correlation (XC) functional form and other unphysical features like self-interactions, LDA and GGA fail to describe the system with strong Coulomb interactions such as transition metal oxides (MnO and NiO) and rare-earth compounds. Today, there were many good XC functional. We used Local Spin Density Approximation (LSDA) and LDA+U method [3, 4, 10] for calculation of electronic properties of oxides.

The DFT is presently the most successful (and also the most promising) approach to compute the electronic

structure of matter. Its applicability ranges from atoms, molecules and solids to nuclei and quantum and classical fluids [15].

The main objective of DFT is to replace the many-body electronic wave function with the electronic density as the basic quantity [9].

COMPUTATIONAL DETAIL

In calculation, a linear combination of localized pseudoatomic orbital method is employed and the core Coulomb potential in OpenMX is replaced by a tractable norm-conserving pseudopotential proposed by Troullier and Martine (see Ref. [1, 10]). Both pseudoatomic and pseudopotential can be downloaded from a website http://www.openmx-square.org. We used 5 x 5 x 5 k-points and the Ceperley-Alder exchange correlation energy functional (LSDA-CA) parameterized by Perdew and Zunger. The real space grid techniques were used with the energy cutoff of 250 Ry for MnO and 160 Ry for NiO. In numerical integrations and the solution of the Poisson equation, the fast Fourier transformations (FFT) were applied. In addition, the calculation of the ground state

http://www.openmx-square.org

properties, density of state (DOS) and band structure was refined using a denser 10 x 10 x 10 k-mesh. We used valence electron configuration 2s22p4, 3d54s2, 3d84s14f1 for O, Mn, Ni atoms, respectively.

RESULT AND DISCUSSION
A.Band gaps and Density of states

Table I lists the band gaps for transition-metal monoxide bulk systems of MnO, NiO, as calculated by employing LSDA and LDA+U within the dual formalism (occupation number operator – see Ref. [16] for the details). Obviously, the band gaps of these oxides increase with increasing of effective Coulomb on-site repression U values. The magnitudes of the gaps and the effective U values are well compared in a reasonable agreement with experimental results (MnO [12, 13] and NiO [14]) as well as the previous calculations [1]. Since the effect of the U values depends on the calculation methods in detail, then, the direct comparison of the results at a fixed value of U may not be appropriate.

Table I. Calculated band gaps of MnO and NiO bulk as function of U values. Here we use the dual representation for the description of the on-site

Fig. 1. The influence of on-site Coulomb interaction on total density of states DOS of bulk MnO and NiO: (a) and (c) correspond to U =0 eV; (b) and (d) correspond to U =5 eV, respectively. Fermi level is set to be zero (vertical dashed line)

Fig 1. showed that the total density of state (DOS) of MnO and NiO for different values of effective Coulomb on-site repulsionU . The band gaps become wider with increasing the strength of on-site Coulomb interaction. We noted that there is no gap for MnO but a gap with magnitude 0.36eV for NiO, when U = 0. It means that without including of Coulomb repulsionU , MnO can be thought to have metallic behavior

B. Band structures and charge analysis

To calculate Band structures of MnO we used a periodic unit cell type rocksalt structure (see Fig. 2a). The rocksalt or sodium-choloride structure consists of two interpenetrating fcc lattices of metal and ligand atoms which are displaced relative to one another by 1/2a along <100> directions (a – is lattice parameter of cubic unit cell) [5].

Fig. 2. (a) Cubic unit cell of the rocksalt structure with dashed lines indicating the octahedral coordination of the central metal atom with its six neighboring ligands.
(b) Brillouin zone for the fcc bravais lattice. (c) Position of Mn and O atoms in a MnO bulk.
Fig. 3. Band structure of MnO (solid lines), effective Coulomb repulsion U = 5 eV is used. Fermi level is set to be zero (horizontal dotted line)

Fig. 3. illustrates the band structure of MnO along X Z W K Σ Γ Δ line in Brillouin zone. It was clearly see that MnO system is insulator with band gap around 2.37 eV when U = 5 eV.

Table II:     Voronoi charges

Table III: Mulliken populations
To analyze the charge state of each atom in a MnO bulk, We study their Voronoi charges and Muliken population.

The Voronoi charge of each atom is calculated by integrating electron and spin densities in a Voronoi polyhedron. The Voronoi polyhedron is constructed from smeared surfaces which are defined by a Fuzzy cell

partitioning method (see Ref. [17] for details). It should be noted that this Voronoi analysis gives often overestimated or underestimated charge, since Voronoi polyhedron is determined by only the structure without taking of atomic radius [10].

The Muliken population is decomposed to contributions of each atom. Table III. illustrates contributions of each atom in MnO, NiO bulk (Fig. 2. (c) shows visualization for MnO bulk)

Table II and III lists the charge density on atom in Δ Voronoi or Mulliken sense. Both types of spin densities show zero total spin for NiO case.

Table IV illustrates contribution to the total dipole moment of MnO and NiO. We note that the electron polarization dominates in these compounds.

Table IV: Dipole moment (Debye)

C.    Total energy and lattice parameter

According to our calculation the total energies for MnO and NiO are -198.39 and -283.90 eV, respectively.

Table V: Lattice parameter (Angstrom) (HF is Hartree-Fock method and PBE is Perdew-Burke-Ernzerhof

exchange-correlation functional)

Table V. lists the lattice parameters for studying oxides derived from DFT calculation. These obtained values are in good agreement with experiment [7, 11] and results given in [2, 5]

CONCLUSION

In this article, we have investigated the electronic properties of transition-metal monoxides MnO and NiO based on Density functional theory with the OpenMX code. We have calculated the band gaps, density of states (DOS), band structure, charge analysis (Voronoi charge, Mulliken populations), dipole moment, lattice parameter, total energy, etc. One can see that the role of effective Coulomb repulsion is very important to understand electronic properties of these oxides. The results in this study are in good agreement with the experimental value and others' calculations.