Application of Density Functional Theory(DFT) in Soil and Geo Science

Dr.J. Karpagam
Asst. Professor, Department of Physics
Periyar Arts College, Cuddalore
Tamilnadu, India.

Abstract : Soil is the basis for life and soil science is regarded as the final frontier; however, as compared to chemistry, physics, biology, and other disciplines, soil science undergoes an obviously slower development and remains almost stagnant in the past few decades, mainly due to two reasons: (1) wrong and outdated perceptions for a large portion of soil researchers; (2) complexity of soil systems that are difficult to characterize by current experimental tech- niques. Computer simulations have unique advantages to handle complex systems while currently, its role during soil researches is far from being recognized. In this chapter, several examples are given with respect to application of density functional theory (DFT) calculations to soil science, focusing on the adsorption of uranyl ion and SO2 onto mineral surfaces and reaction mechanisms to form acid rain. In this way, insightful clues at the atomic level are provided for the adsorption, interaction, and reactions regarding soil systems. We believe that computer simulations including DFT are the right key to unravel the complicated processes occurring in soils. More efforts of computer simulations are anticipated for soil science with aim to decipher the experimental results and probe the uncharted principles that may result in a revolutionary in the near future.

IndexTerms **- soil science, computer simulations, density functional theory, interfacial adsorption, reaction mechanism, complex systems**

I. INTRODUCTION

The surface of the Earth exhibits many features and processes that directly reflect processes originating in the Earth's interior. Volcanic eruptions and earthquakes, for instance, are the violent and impressive manifestations of large-scale convective processes that occur because the Earth cannot release its heat by conduction alone. The magnetic field that, among other things, protects us from harmful solar rays and provides a navigational tool is also the result of large-scale convection, in this case in the Earth's liquid outer core. The time scale of these processes is far longer than the sudden events (earthquakes, volcanic eruptions) that have such an impact on humans, but nevertheless, to understand them properly we must understand the underlying properties and processes causing them. There is no realistic chance of ever directly sampling much of the interior of the Earth and certainly no chance of visiting it. All of our understanding of the inner regions of the planet is, therefore, the result of interpreting remote measurements. Of these, seismology has certainly had the greatest impact and continues to provide increasingly detailed and precise data on the seismic structure of the mantle and core. But taken alone, seismic data are of little use without the mineral physics data to interpret them. To do this, the elastic properties of all the possible minerals across the full range of pressures and temperatures in the Earth must be known. The interior could then be mapped out in terms of mineralogy, composition, and temperature (Figure 1). But to go further, transport properties such as diffusion, viscosity, and thermal-conductivity data are needed to make inferences about the dynamical behavior of the planet. And, to make things even more complex, a large range of chemical composition must be considered. Mineral physics data are very hard to obtain through experiment alone, simply because the pressures and temperatures are so extreme. This is particularly true of the lower mantle and core, where experimental pressures can only be achieved in diamond anvil cells or shock experiments (see a review by Mao and Hemley1). First of all, it is very difficult to achieve simultaneously the pressures and temperatures with the desired precision using these techniques; second, the sample must be probed at the same time with x-rays, infrared, Raman, or some other spectroscopic measurements. Although some techniques have become more achievable in the last few years using large national facilities with very bright sources, measuring transport properties under lowermantle or core conditions still remains challenging. For this reason, mineral physicists have used density functional theory (DFT) methods and other simulation techniques to provide estimates of these fundamental data. Although DFT has been used in other areas of the geosciences—for example, in understanding the atomistic-scale mechanisms of pollutants in groundwater—its greatest impact has been made in studies of the deep Earth, as perhaps evidenced by the large number of publications in high-impact journals such as Nature and Science. For that reason, this review concentrates on how DFT has helped in understanding the properties of the Earth's mantle and core. Somewhat arbitrarily, we will begin at the deepest part of the Earth (the core).

According to Natural Resources Conservation Service (NRCS), soil is defined as a natural body comprised of solids (mainly minerals and organic matters), liquids, and gases that occurs at the intermediate surface of the Earth, occupies space and is

characterized by one or both of the following properties: horizons and layers, which are distinguishable from the initial materials as a result of addition, loss, transfer, and transformation of energy and matter or the ability to support rooted plants in natural circumstances. Soil constitutes the basis for life and bridges the biosphere, atmosphere, hydrosphere, and geosphere. Despite these facts, apparently less attention has been given to soil science than to other disciplines such as physics, chemistry, and biology. As said by Gardner (the past president of Soil Science Society of America) [1], "not a few people mistakenly perceive that everything worth knowing about soils has already been understood, and all we need to do is merely to apply that knowledge properly. Even knowl- edgeable scientists assume that principles and theories developed from other disciplines can be applied to the researches of soil science in a straightforward way, requiring little imagination or creativity. In their opinions, soil science is just one of expressions for the applied physics, chemistry, or biology."

The situation of soil science research is alarming. The core concepts of current soil science textbooks remain almost unchanged as compared to those of half a century ago. Obsolete or even incorrect standpoints are a commonplace [2]. Fortunately, a few researchers have recog- nized such a crisis. On the other hand, because of the complexity of systems and co-function of multiple factors, it seems challenging for experimental techniques to *in-situ* characterize "real" soil properties and processes; in addition, the experimental results from one lab may not be reproducible by others, since soil samples of different areas or even different batches may vary significantly. Computer simulations have unique advantages within this context: (1) probing the various influencing factors one by one; e.g., six factors (identity of heteroatoms, crystallo-graphically distinct T sites, structural alterations, quantity of negative charges, distance from charge centers to metal ions and source of negative charges) were identified to affect the adsorption of metal ions at clay surfaces, and their respective contributions were estimated by density functional theory (DFT) calculations. The quantity of negative charges is the foremost factor that controls the adsorption processes, while other factors in certain circumstances can also play a critical role [3]. The adsorption strengths and numbers of all metal ions increase in a direct proportion to the intensities of electric fields [4]; (2) providing useful and detailed information at the femtosecond scale such as how ions from aqueous solutions diffuse toward to clay surfaces [5]; (3) understanding the adsorption, interaction and reaction processes at the atomic level such as how metal ions interact with surface-O atoms and respond to the increase of electric fields. Based on Hirshfeld, Mulliken, and NBO charge analyses, we found that polarization rather than electrostatic interactions are more likely to result in the pronounced cation-specific effects at clay surfaces [6]; (4) unraveling the exact reaction mechanism by comparing the structural and (especially) activation barriers of competing paths. This can be considered as an extension of (3). There are a plethora of competing reactions occurring in soils; e.g., with DFT calculations, it was clarified that Mn^{4+} rather than Mn^{3+} sites are more reactive for the oxidation of As^{3+} and the oxidation processes are significantly blocked by As^{5+} complexes [7]. A more convictive example is the mechanistic study of Brönsted acid-catalyzed conversion of biomass sugars [8]. More than 120 reaction paths were explored, and the low reactivity and selectivity of glucose conversions were clearly addressed: unlike fructose that prefers to dehydrate at the anomeric O_2H group and initiates a sequence of facile reaction steps toward 5-hydroxymethyl-2-furfural (HMF), the less reactive sites in glucose (O_2H and O_3H) produces levulic acid not involving fructose and HMF intermediates, while the most reactive O_1H site leads to humin precursors or reversion products [8].

The relationship between system size and computational accuracy for representative theoretical levels is shown in Figure 1. For huge systems (100,000 or even more atoms), classical methods (Monte Carlo and Molecular Dynamics) seems to be the good choice, although the computa- tional accuracy is relatively low; In contrast, ab initio quantum mechanical methods are restricted to relatively small systems (up to several hundred atoms or even fewer atoms) while achieve high accuracy. The computational accuracy of quantum mechanics/molecular mechanics (QM/MM) [9] and semi-empirical methods fall in-between, and QM/MM methods have recently become increasingly popular due to the satisfying computational accuracy (active sites handled by QM methods) and the easy extension to large systems (all atoms except active sites disposed by classical methods). 2013 Noble Prize in Chemistry was awarded to Karplus, Levitt, and Warshel for the development of "multiscale methods for complex systems."

II. ACID RAIN

In 1852, Smith demonstrated the relationship between acid rain and atmospheric pollution in Manchester, and after 20 years (i.e., 1872), he coined the term "acid rain." Now acid rain has become a popular term and one of the world's biggest environmental concerns, especially in North America, Europe, and China [28]. Acid rain refers to any form of precipitations with acidic components that fall to the ground from the atmosphere, including rain, snow, flog, hail, or even dust that is acidic. It results mainly from SO_2 and NO_X emissions to the atmosphere and the further transport by wind and air currents, during when SO_2 and NO_X react with water, oxygen, and other substances leading to the formation of sulfuric (H_2SO_4) and nitric (HNO_3) acids. The pH of acid rain is approximately 5.6 and since 1940s, researchers began to recognize its strong impacts on the ecosystem and human health so that soils, freshwaters, forests, and buildings will be damaged. With regard to soils, acid rain inhibits the decomposition of organic matter [29], fixation of nitrogen [30], elution of calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), and other nutrients [31]. As a result, soil fertility and microbial activity show an obvious reduction [32]. Geochemical modeling indicated that Ca^{2+} leaching in marble due to acid rain neutralization

approximates 0.158 mmol/L, in contrast to 10.5 mmol/L by dry deposition, and the corres- ponding Cu^{2+} losses in bronze are ca. 0.21 and 47.3 mmol/L, respectively [33].

As aforementioned, SO_2 emissions are one of the principal causes of acid rain and also represent a primary source of atmospheric aerosols, which can lead to respiratory diseases, premature deaths, and even climate changes by affecting the properties of clouds and the balance of solar radiation. Therefore, it is of great significance to convert SO_2 to other less contaminated compounds, and a number of measures to control SO_2 emissions have been proposed. During 1982–1999, SO_2 emissions have reduced by approximately 65% in Europe and 40% in the United States, and SO_2 emissions in China decline in the late 1990s while again increase after then. DFT calculations provide useful information about the adsorption of SO_2 onto mineral surfaces as well as reaction mechanisms that seem difficult to capture by current experimental techniques [34–45], which are, however, critical to understand the formation of acid rain at the molecular level and to remediate the ecosystem. Clay minerals, such as alumina (Al_2O_3), iron oxides (Fe_xO_y), are good candidates for the adsorption of acid compo- nents from acid rain and then convert them into less hazardous compounds. Lo et al. [35] studied the adsorption of SO_2 on clean (100), dehydrated (110), and hydrated (110) surfaces of γ-Al_2O_3, finding that significant adsorption differences exist for the various surfaces and the calculated adsorption energies (-13 to –85 kcal/mol) are consistent with experimental results.

The γ-Al_2O_3(100) surface is composed by bridging-O and five-coordinated Al atoms, and a total of five stable configurations are produced for SO_2 adsorption (Figure 4). The feeble interaction between S and surface-O atoms results in the physisorption configuration (CM3) with the S-O distance of 2.915 Å, and the corresponding binding energy is very small (-2.0 kcal/mol). The interaction between O@SO_2 and Al atoms leads to a chemisorption state named CM4, and the O-Al bond distance and adsorption energy are 2.123 Å and -23.9 kcal/mol, respectively. The other three configurations are also ascribed to chemisorption. In CM5, one O@SO_2 atom is coordinated to two Al atoms in the vicinity of an octahedral vacancy, and

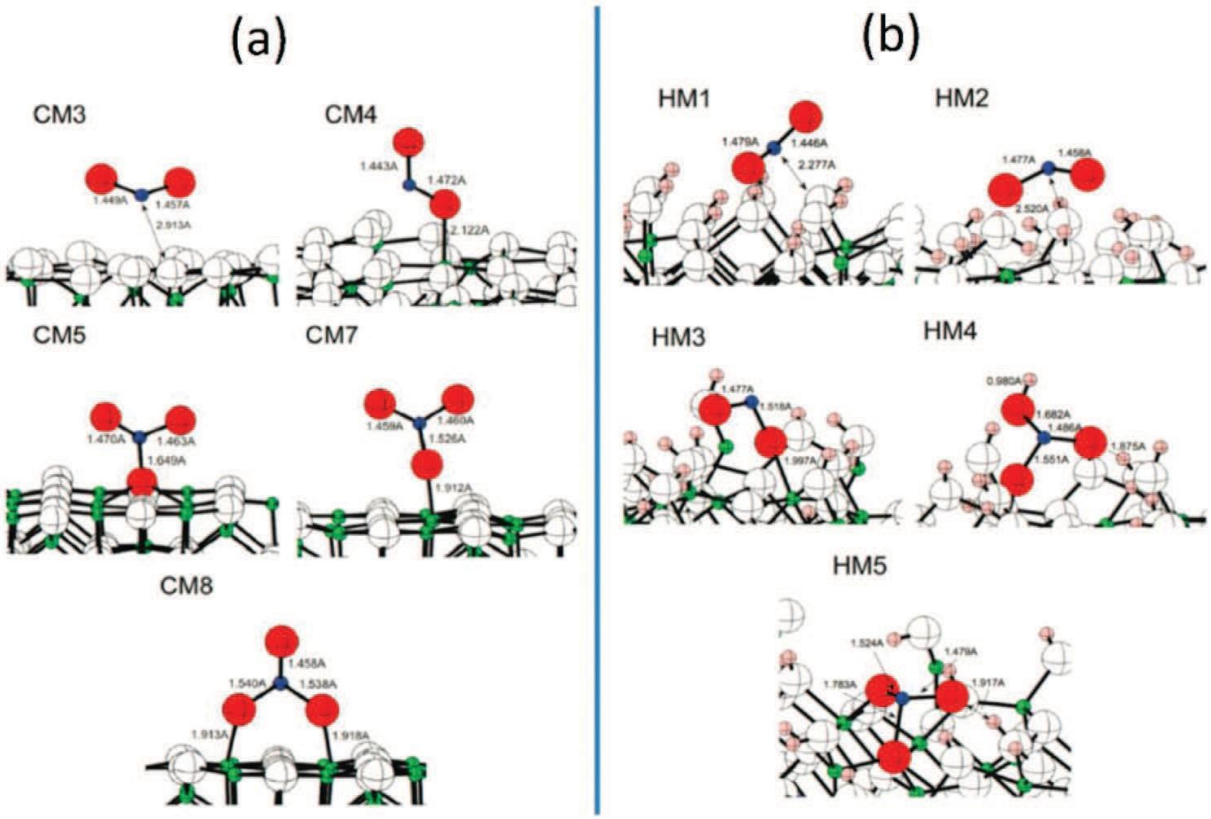

Figure 1. Optimized configurations of SO_2 adsorption on (a) dehydrated (100) and (b) hydrated (110) surfaces of γ-Al_2O_3, where Al, H, O, S, and O attached to S are presented in green, pink, white, blue, and red balls, respectively.

CM7 and CM8 can be considered to generate from CM5 conversion and recombination. As compared to CM5 and CM7, the adsorption configuration CM8 possesses a superior symme- try, and both O@SO_2 atoms participate in the formation of direct bonds with the Al atoms. The adsorption energies of SO_2 are calculated to be -39.2, -15.1, and -45.2 kcal/mol, respectively, for CM5, CM7, and CM8. In consequence, three types of sulfite (SO_3^{2-}) are produced during the adsorption of

SO_2 onto γ-Al_2O_3(100) surface. For all adsorption configurations including three with positive adsorption energies (CM1: 1.0 kcal/mol, CM2: 2.7 kcal/mol, and CM6:21.4 kcal/mol), no direct coupling is detected between S@SO_2 and Al atoms. When γ- Al_2O_3(110) surface is hydrated, five stable adsorption configurations arise that are distinct from dehydrated condition: two physisorption modes (HM1 and HM2) and three chemisorp- tion modes (HM3, HM4, and HM5), see Figure 4. HM1 and HM2 are structurally similar in that their S atoms are coordinated to a surface hydroxyl, while the coordination numbers of their Al atoms are different from each other. HM3 is produced by interaction of O@SO_2 atom with five-fold Al sites. HM4 and HM5 contain the sulfite species where the S atom is coordi- nated with surface-O atoms. The adsorption energies are calculated to be -20.4, -25.3, -31.1,-17.5, and -35.0 kcal/mol, respectively, for HM1, HM2, HM3, HM4, and HM5. In conse- quence, HM5 with formation of the sulfite species represents the lowest-energy adsorption configuration, which is the same as in dehydrated condition (CM8). Two IR peaks at 1214 and 1349 cm^{-1} are assigned to the sulfate species, which can be been finely interpreted by DFT calculated results.Goethite (α-FeO(OH)), which can be found in soils and other low-temperature environments, is an iron-bearing hydroxide. Because of the considerable adsorption capacity for organic acids and anions, goethite has also been widely used in environmental remediation and protection [35]. Zubieta et al. [37] investigated the adsorption of SO_2 on partially and fully hydrated (110) surfaces of goethite and obtained eight stable products: six sulfite, one bisulfate, and one sulfate (Figure 5). The six adsorption structures containing sulfite species, created only on two types of partially dehydrated goethite surfaces, are further divided into two monodentric mononuclear (MdMn) and four bidentate (Bd) configurations. In the MdMn configurations (I and II), the S-O_{Fe} distances are elongated as compared to the other S-O distances, and they display two symmetrical stretching modes (OSO and OSO_{Fe}) centered at ca. 1126 and 976 cm^{-1}. In BdBn configurations (I and II), the two S-O_{Fe} distances are approximately 1.62 Å,and although with similar geometries and stretching modes, the vibrational frequencies devi- ate significantly from those of MdMn configurations and fall at around 672 and 661 cm^{-1}. In BdPn configurations (I and II), one S-O_{Fe} distance is optimized at 1.75 Å and lengthened as compared to those of BdPn configurations, while the other S-O_{Fe} distance equals 1.55 Å and is obviously contracted. The Bader analyses indicate that all sulfite species carry approximately.

III. CONCLUSION

Conclusions Although we have concentrated here on applications of density functional theory to the deep Earth (core and mantle), there are many other areas of the geosciences where ab initio calculations have an important role. For instance, the combination of spectroscopic techniques with DFT makes a particularly powerful tool for understanding the coordination environment of ions in aqueous solutions.65 Similarly, combining DFT calculations with techniques such as extended x-ray absorption fine structure is a powerful way to probe the mechanism of absorption of ions and molecules onto surfaces (e.g., References 66 and 67). Both of these have a direct environmental benefit. The illite–smectite clay minerals have also been studied with DFT with a view to understanding the diagenetic process (the process of turning sediment into rock),68 something that has implications for the maturation, migration, and development of hydrocarbons; and ab initio MD simulations have recently been applied to silicate melts. But we would argue that nowhere has the application been so successful as in predicting the properties of minerals under the high temperatures and pressures of the Earth's mantle and core.

In contrast to the rapid development of chemistry, physics, and biology and other disciplines, soil science remains almost stagnant in the past few decades, and to best of our knowledge, no breakthroughs have been reported for rather a long time. Despite that, no one can deny the vital significance of soil to our life, and soil science has been widely acknowledged as the final frontier.

The slow progresses for soil science, we think, should be attributed to two reasons: (1) wrong and outdated perceptions. A majority of soil researchers mistakenly believe that all knowledge worth knowing about soils has already been understood and no revolutionary progresses would take place; (2) complex systems. Soils are very structurally complicated and there are multiple factors to co-function, which makes it very difficult to characterize by experimental techniques. Computer simulations have unique advantages to handle complex systems, while currently its role in soil science is far from being recognized. In this chapter, two examples are elaborately discussed with regard to application of DFT calculations in soil science: one focuses on the adsorption of uranyl onto mineral surfaces, and the other involves the adsorption of SO_2 onto mineral surfaces and reaction mechanisms to form acid rain. It can be seen from these discussions that DFT calculations are able to provide useful and detailed information about the adsorption, interaction and reactions at the atomic level that greatly promote our understand- ing about soil science.

With advent of high-performance computing platforms, the same DFT calculation tasks of 10 years ago can now finish within a remarkably shorter time, even if you increase model size (periodic model is also an option), consider solvent effects by adding explicit solvent molecules or/and choose more accurate methods. The methodological developments regarding to DFT calculations have also made remarkable progresses over the recent three decades, and as a result, thermodynamics and reaction barriers can now be predicted with nearly chemical accuracy (≤1 kJ/mol). In consequence, computer simulations including DFT are the right key to unravel the complicated phenomena and processes occurring within soils; e.g., with DFT calculations, the aggregation mechanisms of "real" soils and the driving force therein were unveiled at an atomic level [6].

In addition to DFT methods, there are a number of other computational methods, such as QM/ MM and Molecular Dynamics (MD). The choice of suitable computational methods is strongly recommended. We are pleased to see the birth of the ClayFF force-field [66] that was devel- oped specially for clay minerals and the capability of the ReaxFF force-field [67] to handle reaction mechanisms. The 2013 Noble Prize in Chemistry was awarded to the development of "multiscale methods for complex systems," and now it is time to apply these methods to tackle complex soil systems.

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