Guest Articles

Engineering materials for water purification using density functional theory

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Water, a fundamental resource for life, faces increasing threats from contamination by various pollutants, such as heavy metals, dyes, fertilizers, pesticides, herbicides and other highly toxic chemicals posing significant risks to both human health and the environment. In response to this pressing global challenge, researchers are increasingly turning to computational modeling techniques to unravel the complexities of contaminant adsorption from water and develop efficient purification methods. First principles modeling techniques, grounded in density functional theory (DFT) based on the quantum theory of materials, offers a powerful approach to understanding the electronic level interactions between contaminants and adsorbent materials.

Surface adsorption plays a pivotal role in various chemical and physical processes, and it is one of the key processes utilized by materials in water purification. Density Functional Theory (DFT) calculations are widely used to predict surface properties such as surface formation energy, adsorption energy and favourable adsorption sites of the surface. DFT is derived from quantum mechanics and employs a few key approximations and numerical implementations.

In quantum mechanics, the state of a set of particles is described by a wave function, Ψ. Any observable quantity is represented by an operator acting on the wave function. To find the ground state of a set of particles, which is the state with the lowest energy, we need to solve the many-body Schrödinger equation:

$$\hat{H}\Psi = E\Psi$$

Where $\hat{H}$ is the Hamiltonian operator describing the total energy of the system, and E is the energy eigenvalue.

Introduction to Density Functional Theory

Schrödinger equation is computationally infeasible for real materials with many electrons. DFT maps this problem onto the simpler quantity of electron density n(r):

$$n(\mathrm{r}) = N\int |\Psi(\mathrm{r},\mathrm{r}_2,.....\mathrm{r}_N)|^2\ d\mathrm{r}_2....d\mathrm{r}_N$$

The two fundamental theorems of DFT state:

1. The ground state energy is a unique functional of the electron density.
2. The ground state density minimizes the energy functional.

This means the total energy can be expressed as a functional of the density (n):

$$E[n] = T[n] + V_{eN}[n] + V_{ee}[n]$$

The first two terms are known functionals of *n*, and the final exchange-correlation term $V_{ee}[n]$ must be approximated. The equations are solved self - consistently by guessing an initial *n(r)*, calculating a new *n(r)* from the Schrödinger equation, and iterating until self-consistency is reached. Common approximations for $V_{ee}[n]$ include the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA).

For crystalline solids, it is common to use a plane wave basis set to expand the Kohn-Sham orbitals in reciprocal space. Reciprocal space is a Fourier transform of real space, where periodic functions are represented by their wave vectors. The reciprocal lattice vectors G are defined by:

$$G = n_1\mathrm{b}_1 + n_2\mathrm{b}_2 + n_3\mathrm{b}_3$$

Where the *b's* are the primitive reciprocal lattice vectors and the *n's* are integers. The Brillouin zone is the primitive cell in reciprocal space. It is a periodic repetition of the reciprocal lattice, just as real space is a periodic repetition of the real-space lattice. Any wave vector *k* outside the Brillouin zone can be mapped back to a wave vector *k'* inside the zone by a translation

$$\mathrm{k'} = \mathrm{k} + \mathrm{G}$$

A cut-off energy E_{cut} is used to include only plane waves up to a certain kinetic energy in the basis set expansion:

$$\frac{1}{2}|\mathrm{k}+\mathrm{G}|^2 \le E_{cut}$$

The Brillouin zone is sampled using a grid of k-points for numerical integration over the electron wavefunctions. Pseudopotentials are used to model the effect of tightly-bound core electrons on the valence electrons.

Calculations are performed using periodic boundary conditions, where the unit cell is infinitely repeated in space. This approximation allows for efficient modeling of extended crystalline solids. Non-periodic systems like surfaces, interfaces, and defects can also be treated using supercells with sufficient vacuum spacing to minimize artificial interactions between periodic images.

The choice of energy cutoff E_{cut} is a crucial convergence parameter. A higher cutoff includes more plane waves, giving higher accuracy but increased computational cost. Convergence tests should be performed to choose the minimum E_{cut} that converge the total energy to the desired precision, typically around 1 meV/atom.

The k-point grid spacing is another important convergence parameter, particularly for metals where accurate integration of the Fermi surface is required. Denser k-point grids improve accuracy but increase computational cost. Convergence of total energies with respect to k-point spacing should be tested for each new system.

In general, higher energy cutoffs and denser k-point grids are required for systems with rapidly varying electron densities, strong electron correlations, or properties sensitive to subtle energy differences. The required accuracy settings depend on the property being calculated. For example, very high precision may be needed to predict reaction energies within chemical accuracy of ~1 kcal/mol. With the above understanding we are ready to delve into the intricacies of utilizing DFT for surface adsorption calculations.

Modelling surface adsorption using DFT

Surface adsorption depends on the interaction between atoms or molecules and the surface of a material. This interaction is governed by various factors, including the chemical nature of the adsorbate, the structure and composition of the surface, and the energetics of the adsorption process. Understanding these interactions is crucial for elucidating the mechanisms of surface reactions and designing materials with tailored surface properties.

The first step in conducting surface adsorption calculations is to construct a model of the surface of interest. This involves defining the surface geometry, including the arrangement of surface atoms and the presence of any defects or adsorption sites. The choice of surface model depends on factors such as the crystal structure of the material and the specific adsorption sites under investigation. Amorphous material should be constructed such that the simulation cell is greater than 12 $°A$ in the x and y directions to minimize the effect of periodic images in DFT. A surface simulation cell can be constructed once the bulk simulation cell is designed. To create the surface model the bulk simulation cell should be modified by slicing perpendicular to normal vector to the surface and then adding a vacuum space of 12 $°A$ or above to minimize the interactions between the surface images.

Adsorbates, or molecules of interest, are then introduced onto the surface model. These adsorbates can interact with the surface through various mechanisms, including physisorption (weak, van der Waals interactions) or chemisorption (strong, covalent bonding). The energetics of these interactions are quantified by calculating the adsorption energy, which represents the change in total energy upon adsorption of the molecule onto the surface.

To obtain accurate adsorption energies, it is essential to perform relaxation calculations, where both the positions of the surface atoms and the adsorbate are allowed to adjust to minimize the system's total energy. This relaxation process ensures that the surface and adsorbate reach their most stable configurations, reflecting the true energetics of the adsorption process. By comparing the total energies of the relaxed surface with and without adsorbates, researchers can determine the adsorption energy and assess the stability of adsorption configurations.

Case studies of contaminant adsorbing materials using DFT.

Heavy metal adsorption

DFT studies have provided valuable atomistic

insights into the adsorption mechanisms of heavy metal ions on various adsorbent materials like graphene and its derivatives. Elgengehi *et al*. employed DFT calculations to investigate the adsorption of cadmium (Cd) and lead (Pb) heavy metal ions onto graphene and graphene oxide surfaces.[1] Their findings revealed that graphene oxide exhibits higher adsorption capacities for both Cd and Pb compared to pristine graphene due to the presence of oxygen-containing functional groups that facilitate strong binding interactions. The study elucidated the role of these functional groups in mediating the adsorption process and identified the most favorable adsorption sites on the surfaces.

In another study, Garg and Goel used DFT to examine the adsorption of heavy metal ions (Pb^{2+}, Cd^{2+}, Zn^{2+}) on a cellulose/ZnO composite material [2]. Their calculations showed that the composite effectively adsorbs these metal ions, with the adsorption strength following the order $Pb^{2+} > Cd^{2+} > Zn^{2+}$. The authors attributed this trend to the varying ionic radii and electronegativity values of the metal ions, which influence their binding interactions with the adsorbent surface. The study provided insights into the encapsulation mechanism and highlighted the potential of cellulose/ZnO composites for heavy metal removal from wastewater.

Adsorption of air and water pollutants

DFT has also been employed to study the adsorption of various air and water pollutants on two-dimensional (2D) materials like MXenes. Zhang *et al*. conducted a comprehensive DFT investigation of the adsorption of pollutants such as heavy metals (Pb, Cd, Hg), organic dyes (methylene blue, rhodamine B), and gases (CO_2, NO_2, SO_2) on different MXene surfaces.[3] Their results showed that MXenes exhibit excellent adsorption capacities for these pollutants, with the adsorption strength and mechanisms varying depending on the specific MXene composition and surface terminations. The study highlighted the potential of MXenes as promising adsorbents for environmental remediation applications and provided valuable insights into the design of MXene-based adsorbents with tailored properties.

Nanomaterial-based adsorbents

DFT simulations have also been instrumental in studying the adsorption properties of various nanomaterials and their composites for pollutant removal. For example, the studies mentioned above by Elgengehi *et al*. and Garg and Goel also explored the adsorption behavior of graphene-based and cellulose/ZnO composite nanomaterials, respectively, highlighting their potential as effective adsorbents for heavy metal ions.

A myriad of studies have utilized DFT to investigate the adsorption of pollutants on nanomaterials such as metal oxide surfaces, carbon nanotubes, metal-organic frameworks (MOFs), and other porous materials. These simulations provide crucial insights into the adsorption mechanisms, binding energies, and the influence of structural and chemical modifications on the adsorption performance of these nanomaterials, thereby guiding the rational design of advanced adsorbents for various environmental remediation applications.

First principles modeling, grounded in density functional theory (DFT), offers a powerful approach to understanding the intricate interactions between contaminants and adsorbent materials in water. By simulating the electronic structure and energies of atoms and molecules, DFT provides valuable insights into adsorption mechanisms, aiding in the design of effective purification strategies. However, Traditional DFT methods have discrepancies between theoretical predictions and experimental observations. One of the reasons is that traditional DFT methods often fail to accurately capture the electronic correlations in transition metal systems. To address this challenge, researchers have incorporated the Hubbard *U* parameter into DFT calculations, which accounts for the onsite Coulomb repulsion between localized electrons. By properly tuning the Hubbard *U* parameter, researchers can achieve better agreement with experimental data and improved predictive capabilities.

Integration with experimental studies is essential for validating computational predictions and advancing the development of practical water purification technologies. Collaborative efforts between computational researchers and experimentalists have led to the discovery of novel adsorbent materials and purification methods with improved efficiency and

sustainability.

Looking ahead, first principles modeling of contaminant adsorption in water, holds great promise for addressing global water challenges. By leveraging the predictive power of DFT simulations and interdisciplinary collaboration, researchers are developing next-generation water purification technologies.

References

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Electrospun nanocomposite fibers for the adsorption removal of antibiotics from water bodies

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1. Introduction

In the recent past, the overuse of antibiotics in various disciplines such as medicine (cancer treatment, heart surgery, and organ transplant), agriculture, and animal husbandry has led to the excess discharge of antibiotics from their working environments to the various water bodies, posing a major threat to both public health and the ecosystem.[1] However, the ability of antibiotics to act effectively against a wide array of microbial strains has made them the best choice to mitigate the problem of microbes in many fields.[2]

Antibiotics are typically abundant in sewage and then enter to the wastewater treatment plants. Even though the wastewater plants could remove nitrogen (N), phosphorus (P), and chemical oxygen demand (COD), they have been incapable of removing the antibiotics present, therefore they are found to be present in 10-3000 ng/L range in the secondary effluents.[1] Furthermore, they are also found to be abundant in surface water, groundwater, seawater, drinking water, and sediments.[3] However, their distribution is typically high in hospital sewage accounting for values in the range of mg/L.[4] Albeit these amounts have appeared to be very low, the impact it could create is significant and considerable. As they have very complex structures, high stability, and lower degradability they have become persistent as micropollutants in wastewater.[5] It is a well-identified fact that antibiotics could also reach the water bodies *via* the feces and urine of humans and animals, direct contamination from pharmaceutical discharge from production plants, and discharge from aquaculture plants.[6]

According to recent reports, about 21 antibiotics with concentrations ranging from 5800 ng/g are found to be present in different wastewater treatment plants4 where the commonly identified antibiotics from water bodies include quinolones, sulfonamides, tetracyclines, beta-lactams, trimethoprim, and macrolides, which are frequently used in medical treatments.[1] The abundance of antibiotics in water bodies has been identified in various parts of the world including Vietnam, United States, South Korea, Canada, China, Hong Kong,