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Review

The role of density functional theory methods in the prediction of nanostructured gas-adsorbent materials

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ABSTRACT

With the advent of new synthesis and large-scale production technologies, nanostructured gas-adsorbent materials (GAM) such as carbon nanocomposites and metal-organic frameworks are becoming increasingly more influential in our everyday lives. First-principles methods based on density functional theory (DFT) have been pivotal in establishing the rational design of GAM, a factor which has tremendously boosted their development. However, DFT methods are not perfect and due to the stringent accuracy thresholds demanded in modeling of GAM (e.g., exact binding energies to within ~0.01 eV) these techniques may provide erroneous conclusions in some challenging situations. Examples of problematic circumstances include gas-adsorption processes in which both electronic long-range exchange and non-local correlations are important, and systems where many-body energy and Coulomb screening effects cannot be disregarded. In this critical review, we analyze recent efforts done in the assessment of the performance of DFT methods in the prediction and understanding of GAM. Our inquiry is constrained to the areas of hydrogen storage and carbon capture and sequestration, for which we expose a number of unresolved modeling controversies and define a set of best practice principles. Also, we identify the subtle problems found in the generalization of DFT benchmark conclusions obtained in model cluster systems to real extended materials, and discuss effective approaches to circumvent them. The increasing awareness of the strengths and imperfections of DFT methods in the simulation of gas-adsorption phenomena should lead in the medium term to more precise, and hence even more fruitful, *ab initio* engineering of GAM.

1. Introduction

1.1. Rational design of gas-adsorbent materials

Nanostructured gas-adsorbent materials (GAM) are the cornerstones of potentially revolutionary advancements in critical and fast growing technological fields such as molecular sensing, energy storage and harvesting, and environmental and sustainability engineering. Their exceptional high surface to volume ratio, regular atomic composition, tunable reactivity, transport properties, and assembling affinity to form supramolecular systems, have permitted the realization of timely and cost-effective applications such as the detection and removal of toxic substances from water and air, dense storage of hydrogen and natural gas in solid state matrices, sequestration of carbon dioxide from flue gases generated in electricity production plants, design of high-performance photovoltaic cells, and enhanced long-lasting operation of batteries, to cite just a few examples [1–5].

Popular families of nanostructured GAM include zeolites, metal oxides nanocrystals (e.g., CaO and Al_2O_3), carbon-based nanomaterials (CN, e.g., nanotubes, sheets, met-cars, graphite intercalation compounds, and frameworks of organic pillared graphene), metal hydrides nanoparticles (e.g., MgH_2 and $LiBH_4$), and covalent- and metal-organic frameworks (COF and MOF). Of all these species CN and MOF (see Fig. 1) stand out as some of the most promising GAM for energy and environmental applications, particularly to what concerns the capture and storage of hydrogen (H_2), carbon dioxide (CO_2), and methane gases [6–15].

Currently reported GAM gas-selectivity and storage capacities, however, still remain below the stringent commercial targets set by specialized government bodies and agencies. For instance, hydrogen storage systems need to achieve an overall capacity of 5.5 wt.% hydrogen with a volumetric ratio of 40 g/L for competitive vehicle applications [16], and capture of the 90% of the carbon dioxide produced in the generation of electricity must be reached within less than a 35% of increase in the final costs [17,18]. The search for optimal gas-adsorption processes and GAM, therefore, remains an area of very active scientific and technological research.

A key aspect for potential GAM to be successful is to find the optimal chemical compositions and pore topologies to work under specific thermodynamic conditions. The number of possible stoichiometric and structural GAM configurations is tremendously large, hence in practice systematic experimental searches based on trial-error strategies turn out to be cumbersome and very inefficient. Rational engineering of gas-adsorbent interactions at the atomic scale, represents a key notion to achieve success on such a design grand challenge in the short and middle term. In this context, computational simulation methods emerge as invaluable theoretical tools for the screening and rational engineering of auspicious GAM.

1.2. Computational simulation techniques for modeling of GAM

Common simulation techniques in the study of GAM can be classified into two major categories: “semi-empirical” and “first-principles”. In semi-empirical approaches, the interactions between atoms are modeled with analytical functions, known as force fields or classical potentials, which are devised to reproduce a certain amount of experimental data or the results of high-accuracy calculations. The inherent simplicity of classical potentials makes it possible to address the study of GAM and gas-adsorption processes considering realistic thermodynamic conditions and length/time scales, with well-established simulation techniques such as molecular dynamics and grand canonical Monte Carlo [19]. With the current computational power and algorithm development, key features in GAM which are directly comparable to observations (e.g., adsorption isotherms, elastic properties and diffusion coefficients [20–24]) can be computed routinely on a standard office computer. Also, the relevance of quantum nuclear effects in gas-adsorption phenomena can be estimated accurately with semi-empirical approaches [25–28]. Nevertheless, in spite of the great versatility of semi-empirical methods, classical potentials may present impeding transferability issues in certain situations. This type of drawbacks is related to the impossibility of mimicking the features of the targeted material at conditions different from those in which the setup of the corresponding force field was performed [29,30].

In this context, the output of first-principles calculations turn out to be crucial. As the name indicates, empirical information is not contained on first-principles methods, also known as *ab initio*. The interactions between atoms are directly obtained from applying the principles of quantum mechanics to the electrons and nuclei. Transferability issues, therefore, are totally missing in *ab initio* approaches. Examples of first-principles techniques include, density functional theory and quantum Monte Carlo, to cite just a few.