Density Functional Theory Calculations for Sustainable Chemicals and Fuels Production

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Abstract:

The fossil fuels produced and consumed today are products from a very complex mix of processes. These processes of nature have been and still are of great inspiration to those who are developing biomass conversion processes today. 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. In the present work, DFT calculations for sustainable chemicals and fuels production are reviewed and discussed. It is concluded that DFT calculations provide insight into chemicals and fuels production and may lead to new catalyst design and development.

1 Introduction

Sustainable chemistry is a scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services. [1, 2] Sustainable chemistry encompasses the design, manufacture and use of efficient, effective, safe and more environmentally benign chemical products and processes. [3] Sustainable chemistry is also a process that stimulates innovation across all sectors to design and discover new chemicals, production processes, and product stewardship practices that will provide increased performance and increased value while meeting the goals of protecting and enhancing human health and the environment. [4, 5]

Energy efficiency and renewable energy are said to be the twin pillars of sustainable energy. [6, 7] In the broader context of sustainable development, there are three pillars, ecology, economy and society. [8] Some ways in which sustainable energy has been defined are: Effectively, the provision of energy such that it meets the needs of the present without compromising the ability of future generations to meet their own needs. [9, 10] Sustainable Energy has two key components: renewable energy and energy efficiency. [11] Renewable Energy and Efficiency Partnership (British); Dynamic harmony between equitable availability of energy-intensive goods and services to all people and the preservation of the earth for future generations. [12] The solution will lie in

finding sustainable energy sources and more efficient means of converting and utilizing energy. [13] Any energy generation, efficiency and conservation source where: Resources are available to enable massive scaling to become a significant portion of energy generation, long term, preferably 100 years. [14] Invest, a green technology non-profit organization. Energy which is replenishable within a human lifetime and causes no long-term damage to the environment. [15, 16]

DFT has been very popular for calculations in solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. Computational costs are relatively low when compared to traditional methods, such as exchange only Hartree-Fock theory and its descendants that include electron correlation. [17]

Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions (of critical importance to understanding chemical reactions), [18, 19, 20] especially van der Waals forces (dispersion); charge transfer excitations; transition states, global potential energy surfaces, dopant interactions and some other strongly correlated systems; and in calculations of the band gap and ferromagnetism in semiconductors. [21, 22, 23] Its incomplete treatment of dispersion can adversely affect the accuracy of DFT (at least when used alone and uncorrected) in the treatment of systems which are dominated by dispersion (e.g. interacting noble gas atoms) or where dispersion competes significantly with other effects (e.g. in biomolecules). [24] The development of new DFT methods designed to overcome this problem, by alterations to the functional or by the inclusion of additive terms is a current research topic.

2 Sustainable Chemicals and Fuels Production

Neither today nor in the future, may sustainable chemicals have unacceptable (eco-) toxic impacts on man and the environment. They may not or only insignificantly contribute to the depletion of natural resources. Furthermore, they may not cause or enhance socially precarious situations or unhealthy workplaces, however they are beneficial to the entire economy and to enterprises. The sustainable use of (sustainable) chemicals aims at providing socially necessary products while minimising resource consumption, reducing substance losses and controlling exposures by corporate, design oriented, organizational and technical means and at the same time enhancing healthy workplaces and fair social conditions. [25, 26]

The selection of sustainable chemicals can have advantages for the protection of workers, consumers and the environment. In the long run, sustainability leads to more innovative uses of chemicals and is therefore also economically attractive. Hence, a sustainable product is a product that is successful on the market, for which less dangerous substances are used and which have less adverse impacts on the environment and to the society than a comparable product.

[27, 28, 29]

Sustainable energy is energy that is consumed at insignificant rates compared to its supply and with manageable collateral effects, especially environmental effects. [18, 30] Another common definition of sustainable energy is an energy system that serves the needs of the present without compromising the ability of future generations to meet their needs. [31, 32, 33] The organizing principle for sustainability is sustainable development, which includes the four interconnected domains: ecology, economics, politics and culture. [34, 35] Sustainability science is the study of sustainable development and environmental science. [36] Technologies promote sustainable energy including renewable energy sources, such as hydroelectricity, solar energy, wind energy, wave power, geothermal energy, bioenergy, tidal power and also technologies designed to improve energy efficiency. [37, 38] Costs have decreased immensely throughout the years, and continue to fall. [39, 40] Increasingly, effective government policies support investor confidence and these markets are expanding. [41] Considerable progress is being made in the energy transition from fossil fuels to ecologically sustainable systems, to the point where many studies support 100% renewable energy.

3 Density Functional Theory Calculations

In the context of computational materials science, ab initio (from first principles) 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 system electrons. This DFT potential is constructed as the sum of external potentials, which is determined solely by the structure and the elemental composition of the system, and an effective potential, which represents inter-electronic interactions. Thus, a problem for a representative super-cell of a material with n electrons can be studied as a set of n one-electron Schrodinger like equations, which are also known as KohnSham equations. [42]

Although density functional theory has its roots in the Thomas-Fermi model for the electronic structure of materials, DFT was first put on a firm theoretical footing by Walter Kohn and Pierre Hohenberg in the framework of the two Hohenberg-Kohn theorems (H-K). The original H-K theorems held only for non-degenerate ground states in the absence of a magnetic field, although they have since been generalized to encompass these. The first H-K theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates. It set down the groundwork for reducing the many-body problem of N electrons with 3N spatial coordinates to 3 spatial coordinates, through the use of functionals of the electron density. This theorem has since been extended to the time-dependent domain to develop time-dependent density functional theory (TDDFT), which can be used to describe excited states. [43]

In work that later won them the Nobel prize in chemistry, The H-K theorem was further developed by Walter Kohn and Lu Jeu Sham to produce Kohn-Sham DFT (KS DFT). Within this framework, the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the exchange and correlation interactions. Modeling the latter two interactions becomes the difficulty within KS DFT. The simplest approximation is the local-density approximation (LDA), which is based upon exact exchange energy for a uniform electron gas, which can be obtained from the Thomas-Fermi model, and from fits to the correlation energy for a uniform electron gas. Non-interacting systems are relatively easy to solve as the wavefunction can be represented as a Slater determinant of orbitals. Further, the kinetic energy functional of such a system is known exactly. The exchange-correlation part of the total-energy functional remains unknown and must be approximated. [44]

The DFT formalism described above breaks down, to various degrees, in the presence of a vector potential, i.e. a magnetic field. In such a situation, the one-to-one mapping between the ground-state electron density and wavefunction is lost. Generalizations to include the effects of magnetic fields have led to two different theories: current density functional theory (CDFT) and magnetic field density functional theory (BDFT). In both these theories, the functional used for the exchange and correlation must be generalized to include more than just the electron density. In current density functional theory, developed by Vignale and Rasolt, the functionals become dependent on both the electron density and the paramagnetic current density. In magnetic field density functional theory, developed by Salsbury, Grayce and Harris, the functionals depend on the electron density and the magnetic field, and the functional form can depend on the form of the magnetic field. In both of these theories it has been difficult to develop functionals beyond their equivalent to LDA, which are also readily implementable computationally. Recently an extension by Pan and Sahni extended the Hohenberg-Kohn theorem for non constant magnetic fields using the density and the current density as fundamental variables. [45, 46]

4 Concluding Remarks

In the present work, DFT calculations for sustainable chemicals and fuels production are reviewed and discussed. It is concluded that DFT calculations provide insight into chemicals and fuels production and may lead to new catalyst design and development.

5 Acknowledgments

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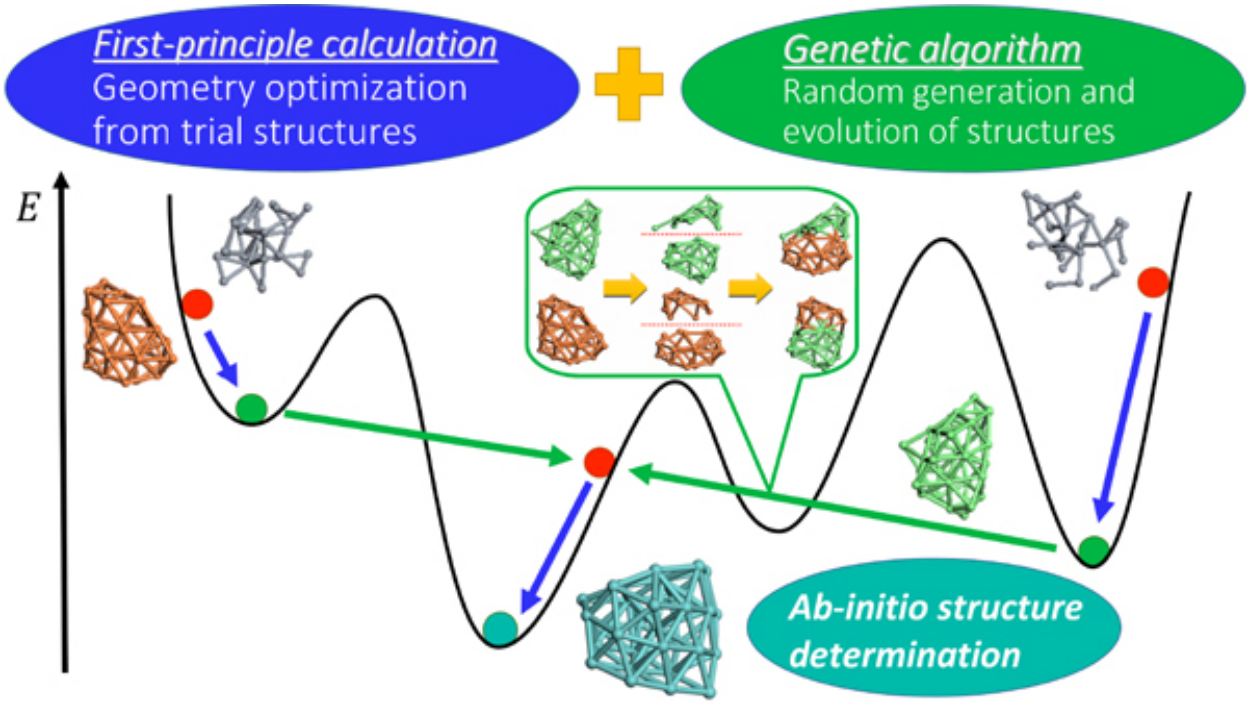

Figure 1: Density Functional Theory Calculations for Sustainable Chemicals and Fuels Production

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Catalog: ***Catalytic Performance***
