ijcrr
Vol 03 issue 10
Category: Review
Received on:12/07/11
Revised on:27/07/11
Accepted on:06/08/11

APPLICATION OF DENSITY FUNCTIONAL THEORY (DFT) IN ADVANCING RESEARCH IN QUEST FOR ALTERNATIVE FUELS

Rit Nanda

Pandit Deendayal Petroleum University, Gandhinagar, Gujarat

E-mail of Corresponding Author: rit.nanda@gmail.com

ABSTRACT

There is an acute shortage of energy facing the world. The existing reserves of petroleum are depleting and newer reserves are often in the deep sea or have high pressure and temperature conditions which make their exploitation unviable. The challenge facing the scientific community is to find alternative fuels to offset the demand to supply gap of conventional sources of energy like petroleum. Among various techniques used, Density Functional Theory (DFT) is a technique that is promising in the quest for alternative fuels. This paper discusses the various alternative fuels that have been studied using DFT and tries to generalise the findings of this technique over a broad spectrum of possible alternative fuels. It also suggests newer horizons that can be explored using this technique.

Keywords: DFT, Alternative Fuels, Energy Sources, Chemical Research

1. INTRODUCTION

Density Functional Theory (DFT), as the name suggests, uses functionals of electron density as a modelling method, where electron density as the basic variable. A functional is traditionally a map from a vector space to the field underlying the vector space, which is usually real or complex numbers, like functions map number to numbers. In other words, a functional takes a function as its argument or input and returns a scalar[1]. The referred source may be further accessed for detailed explanation on DFT, but this paper, in its course, will stick with only reviewing its practical applications in the field of energy.

The various applications covered in this paper are hydrogen fuel cell, newer perspectives into Fischer-Tropsch process, biofuels, photovoltaic cells used in solar energy and nuclear energy.

2. Review of DFT Applications

2.1 Hydrogen Fuel Cell

An area where DFT has been used extensively is in research of Hydrogen Fuel Cells. Hydrogen is a clean and efficient fuel, but there is a significant challenge facing its production, storage, and use. At the moment, hydride compounds cannot provide competitive storage for transportation, but research in this field is being carried out through DFT. DFT is implemented on computer clusters for calculating the electronic and crystal structures, bond strengths and heats of reaction for many compounds. This same process can and is carried out by synthesising and discovering the compounds and its properties in the laboratory, but in the same time frame, a computational tool

like DFT can generate more comprehensive information[2]. Therefore, DFT has found ready usage in hydrogen storage tools to the extent of examining the structures, hydrogen storage capacities and decomposition temperatures for 300 compounds[3]. Another aspect of DFT in hydrogen storage is the charge/release phenomena which refers to charging and discharging of hydrogen from the storage media. Nanostructures have opened up many possibilities for hydrogen storage challenge because it allows for the control of both the static and dynamic parameters of the phenomena. The reaction pathways and material science at this nanoscale can be effectively studied by DFT[2]. Another domain that has been studied with the help of DFT in this field is catalysts and catlaysis. Catalysts are needed to control the speed of the reactions occurring at the electrodes of the fuel cells. A study has already been done on Near Surface Alloys (NSAs) using DFT to check their applicability as catalysts in hydrogen rich environment like fuel cells and the results have been encouraging[4]. DFT studies have also been extended to adsorption of hydrogen for storage in fuel cells. Light metals like Magnesium and Aluminium have high storage densities and safe endothermic hydrogen release making them promising candidates for hydrogen storage devices. However, as experimental studies are not feasible on such highly reactive metals, so DFT has been used to study Al cluster properties like cluster size and hydrogen site specific effects[5].

As has been reviewed in this section, DFT has been used extensively in the research of hydrogen fuel cells as a source of alternate energy. It has been used to identify and study the compound properties for hydrogen storage. It has been used for studying the catalysts that can be used in the cells. It has been used to develop new materials for the storage of hydrogen. Thus, a review clearly shows that DFT has a huge potential to unlock the obstacles that prevent hydrogen from becoming a commercial fuel.

2.2 Fuel Generation from Synthesis Gas

Another area that has been probed extensively using DFT is the generation of fuel from Synthesis Gas. Synthesis Gas is a mixture of CO and H_2. It has been used to convert coal into liquid fuels and over the past decade is being used to convert biomass into liquid fuels[6]. DFT has been used to propose alternate reaction pathways that yield higher hydrocarbons from Synthesis Gas (CO/H_2 2:1). This was done by microkinetic simulation using DFT which showed that the main pathway of Fischer-Tropsch process on Co{0001} is not the carbide mechanism but an alternate mechanism that involves the hydrogenation of CO to oxymethylidyne species. This discovery has proposed to reduce the pressure gap in heterogeneous catalysis at realistic pressures[7]. This research was furthered on Ru catalysts as well to yield similar results and parallels could be drawn between homogenous and heterogenous catalysis[8]. Other than used for predicting reaction pathways, DFT has also been used to study the intermediates in Fischer-Tropsch process. The relative stabilities of the intermediates can be compared to give an idea of the final product and the reaction barriers may be used for determining the stepwise mechanism[9].

Thus, it may be clearly seen that DFT has contributed in a large way in the field of hydrocarbon production from Synthesis Gas. By understanding the reaction mechanism, the intermediates and the catalytic effects, one may optimize the process to viably generate different desirable products.

2.3 Biofuels

The applications of DFT in the field of biofuels are widespread. The structures and the energetics of model biofuels have been studied. Studies have been carried out, using DFT, on Isopropyl Butanoate (IPB). It is mentioned in the paper that there are seven different channels of dissociation of IPB, but the formation of Butanoic Acid and Propene via a six-member ring transition is the most favourable reaction. Formation of lower esters was found to be hindered by high energy barriers. It was also seen that IPB disassociates faster than methyl and ethyl esters[10]. Similar studies have been carried out on 2-butanol as a possible biofuel, using DFT. Studying various dissociation mechanisms, it was found that dehydration to 1- and 2- butene through four centre transition states is the most dominant channel at lower temperatures of less than 700 K. At higher temperatures of more than 800 K, however, a simple C-C bond fissure takes place[11]. However, it must be noted that there also have been claims to the contrary saying that to study the chemical kinetics of chemical combustion, DFT may be inaccurate[12]. The study on biofuels has also been extended to its synthesis. The starting materials of biofuel synthesis has been studied using DFT. By using DFT, it was possible to calculate two things. One was the ground state energy and the second was the molecular structure of the triglycerides[13]. Triglycerides are present in vegetable oils and fatty acids which are then trans-esterified with alcohol to give esters (biodiesel) and glycerol. However, vegetable oils may also be directly used as fuel oils and may be used to produce liquid hydrocarbon. A study was conducted to model the catalytic cracking of palm oil to produce hydrocarbons using MCM-41 as catalyst. The pore size distribution of the catalyst was determined using DFT[14].

Thus, it is amply clear that various uses of DFT have been employed to study biofuels. DFT has been used to study the structures of potential biofuels and their energetic on dissociation. They have also been used to model the starting triglycerides for biodiesel synthesis. Not only limited to reaction compounds, catalysts' pore size distributions have been studied using DFT, which are employed in cracking vegetable oil like palm oil.

2.4 Photovoltaic Cells

Photovoltaic cells are used widely used to harness solar energy. Semiconductor physics often operate at the micro and the nano level and it is no surprise that DFT has been used to study photovoltaic cells.

DFT has been used to study the semiconductor grain boundaries and the junctions. A combination of DFT and high-resolution electron microscope has revealed the grain physics at a variety of semiconductors like Si, CdTe, $CuInSe_2$ and $CuGaSe_2$. Of these four, it has been found that the former two semiconductors require special passivation while the other two do not[15]. Passivation significantly affects performance of photovoltaic cells and understanding this phenomena for different solar cells will help increase the efficiency[16]. DFT has also been used in thin-film photovoltaic cells to calculate the structural parameters and the formation energies. However, DFT cannot predict the band gaps and optical absorption spectra[17]. Research has also progressed to a remarkable extent on the nano scale, an example of which is the use of DFT in photovoltaic heterojunctions formed by poly-3-hexylthiophene interfaced with metallic and semiconducting carbon nano-tubes. It is found that a majority of the interfaces at these junctions are inefficient as they are in contact with the metallic carbon nano-tubes rather than the semiconducting ones[18].

Hence, it is clear that DFT research has progressed from simple grain boundaries and passivation techniques to thin-film cells to heterojunction efficiency. This clearly illustrates the ability of DFT to keep up to date with modern advancements in the field of photovoltaics.

2.5 Nuclear Energy

This is another field of energy that can be studied using DFT. That is the field of nuclear energy. Research has been carried out already in this field. In all such research, it is vital to understand the atomic nuclei, so as to apply that knowledge to societal applications like nuclear energy generation. DFT calculations have been carried out to understand the two following parameters, namely the neutron local density in the nucleus and the ground state deformation of nuclei lying in the stable region. This helps in understanding the reactions of short-lived and stable nuclei[19]. But further study is needed for understanding those nuclei that have higher neutron number[20]. In general, DFT can be used to study the following topics related to the nuclei, namely pairing, broken symmetries, single-particle energies and improving empirical energy density functionals. Each of the topics is described further[21].

Pairing can be studied by ab initio DFT using non-local pairing fields. The details of the DFT calculations are not given here but can be looked up in the referred source[21]. Broken symmetries include the translational and rotational invariance and other phase symmetries. Broken symmetries have been well explored in for mean-field approximations but it is a relatively new concept in the context of ab initio DFT[21]. The detailed discussion of each may be again looked up in the source referred. Single-particle properties, like spectrum, may also be explored using DFT[21]. Empirical energy density functionals are generally reliable when the experimental data is available but where it is not, extrapolation becomes difficult, thus also suggesting the benefit of ab ignition DFT[21].

Further research has also been carried out using covariant DFT to analyse the nuclear structure, particularly of low-lying excited states in transitional nuclei as well as exotic nuclei, the details of which may be accessed from the referred source[22].

Thus, it has been established that DFT can be used to understand the nuclear structures and their deformation mechanism. Ab initio DFT and covariant DFT have also been used for varied applications to study different aspects of the nuclei.

3. The Global Petroleum Scenario and DFT Research Worldwide

Petroleum and other fossil fuels are the chief sources of energy to the world. The need for DFT applications, as described in the previous section, becomes paramount because of the need for alternative fuels. In the following sections, we discuss the current petroleum production scenario and the role of DFT being actively pursued to research alternative fuels.

3.1 The Global Current Petroleum Scenario

Petroleum and other fossil fuels are the primary source of energy in the world. At the moment, the production from the existing fields is declining, especially the major or the giant oil fields. It is evident that lesser numbers of giant fields are being discovered in the newer decades and it has been following a decreasing pattern since the 1960s and 70s. The average decline rate of the existing fields is an annual -6.5%[23]. It clearly illustrates the diminishing production from existing, especially large, fields.

Of the newer fields that are being discovered, many are High Pressure/High Temperature (HPHT) wells and Deep Sea wells. But these are expensive to drill and complete and are expected to increase the crude barrel price further. There

are inherent problems with HPHT wells, significant among which are pressure related problems[24]. The cost associated with deep sea drilling are also very high. On a point of comparison, a land (onshore) well of drilled depth to 20,000 feet cost around $11 million in 2003[25]. The 2010 figures quote the cost of a deep sea well to be between $100 to $200 million[26].

This clearly illustrates that with lesser large fields being discovered, existing fields declining and newer discoveries likely to increase the barrel cost of crude due to high cost of drilling and completion, the market is likely to face a supply shortage at the current cost of crude in the near future and escalating costs will make other alternative energies, that are currently uncompetitive, viable.

Of the newer fossil fuels that are being explored, the primary are tar sands, ultra heavy oil, oil shale, tight gas, and coal bed methane. However, they all have evolved on the geologic time scale and compared to our rate of energy consumption are decidedly finite. On the human time scale, alternative energies like renewable biomass can therefore compete with these newer fossil fuels, along with an added advantage of being less destructive to the environment[27].

3.2 DFT research for alternative energy

As has been described in the previous sections, DFT has wide applicability in the field of alternative energy internationally. In this section, the current research that have been completed or are in progress are discussed.

DFT has left solid foundations for research in alternative energy in the future. The majority of the research that is ongoing in the field of alternative energy are happening in the countries of USA, Germany, China, Japan, Great Britain with USA topping the list[28].

In 2007 in the USA, it was decided that computational needs in alternative and renewable energy were paramount. It urged academia and industry to work in tandem with the governmental Department of Energy to meet these ends. The key priority research directions were designated as hydrogen fuels, bioenergy conversion, photovoltaic solar energy conversion, wind energy, and grid futures and reliability[29]. It was a great step towards prominent role of computational methods in the energy sector within the chemical engineering domain; the stated goals of computational chemistry being to reduce the costs of development, improve energy efficiency and environmental performance, and increase productivity and profitability[30].

In 2010, research was carried out in European Synchrotron Radiation Facility, Grenoble, France (ESRF), to develop new energy sources and improve the efficiency of existing sources by X-Ray beams of Synchrotron Radiation Source, which help in understanding the structure and behaviour at the fundamental microscopic level. The results were compared with DFT calculations and they were found to be similar[31].

In India, research groups at the National Chemical Laboratory, Pune are involved in the study of organic molecules using ab initio DFT modelling.

4. CONCLUSION

The review of the various DFT applications in the field of alternative energy clearly suggest its immense potential. It has been used to study a variety of alternative fuels, ranging from nuclear energy to biofuels. It clearly has an advantage over time consuming physical experimentation by using faster computational methods. The final word comes from the pioneer of DFT, Dr. Walter Kohn, who received the 1998 Nobel Prize in Chemistry for his role in the development of density functional theory. He talks about the decline in crude oil production

and the increase in greenhouse gas production and he envisages 'a world powered predominantly by solar and wind energy'[32].

With increasingly better computational methods and with the interest shown in DFT research by various international agencies, coupled with the growing need for viable alternative energy, DFT presents an exciting prospect for further research.

REFERENCES

1. Finocchi F. Density Functional Theory for Beginners. In: Basic DFT Theory. Institut des NanoSciences de Paris (INSP), CNRS and University Pierre et Marie Curie; 2009. p 6-12.
2. Crabtree G.W., Dresselhaus M.S. The Hydrogen Fuel Alternative. MRS Bulletin 2008. 421-8.
3. Alapati S.V., Johnson J.K., Sholl D.S. Using first principles calculations to identify new destabilized metal hydride reactions for reversible hydrogen storage. Physical Chemistry Chemical Physics 2007. 1438-52.
4. Greeley J, Mavrikakis M. Alloy Catalysts Designed from First Principles. Nature Materials 2004. 810-15.
5. Accelrys Software Inc. Hydrogen Storage For Fuel Cells - A Density Functional Theory Study of Hydrogen Adsorption on Aluminium Clusters. 2008.
6. Schulz H. Short History and Present Trends of Fischer-Tropsch Synthesis. Applied Catalysis A: General 1999. 3-12.
7. Inderwildi O.R., Jenkins S.J., King D.A. Fisher-Tropsch Mechanism Revisited: Alternative Pathways for the Production of Higher Hydrocarbons from Synthesis Gas. The Journal of Physical Chemistry C 2008. 1305-7
8. Inderwildi O.R., King D.A., Jenkins S.J. Fischer-Tropsch Synthesis of Liquid Fuels: Learning Lessons from Homogeneous Catalysis. Physical Chemistry Chemical Physics 2009. 11110-12.
9. Liu Z.P., Hu P. A New Insight into Fischer-Tropsch Synthesis. Journal of the American Chemical Society 2002. 11568-9.
10. El-Nahas A.M., Heikal A.L., Mangood A.H., El-Shereefy E.E., Structures and Energetics of Unimolecular Thermal Degradation of Isopropyl Butanoate as a Model Biofuel: Density Functional Theory and Ab Initio Studies. The Journal of Physical Chemistry A 2010. 7996-8002.
11. El-Nahas A.M., Mangood A.H., Takeuchi H., Taketsugu T. Thermal Decomposition of 2-Butanol as a Potential Nonfossil Fuel: A Computational Study. The Journal of Physical Chemistry A 2011. 2837-46.
12. Sarathy S.M. Chemical Kinetic Modeling of Biofuel Combustion. [Thesis]. Toronto: University of Toronto; 2010.
13. Marton G., Pleşu V., Marton A., Bercaru M.T. A Quantum Mechanics Approach to Biofuel Synthesis. Chemical Engineering Transactions 2010. 1351-6.
14. Yared I., Kurniawan H., Wibisono M., Sudaryanto Y., Hindarso H., Ismadji S. Modeling Of Liquid Hydrocarbon Fuel Production From Palm Oil Via Catalytic Cracking Using Mcm-41 As Catalyst. ARPN Journal of Engineering and Applied Sciences 2008. 55-61.
15. Yan Y., Jiang C.S., Wu X.Z., Noufi R., Wei S.H., Al-Jassim M.M. In: 33rd IEEE Photovoltaic Specialists Conference; 2008 May 11-16; San Diego, California, USA.
16. Aberle A.G. Surface Passivation of Crystalline Silicon Solar Cells: A Review. Progress in Photovoltaics 2000. 473-87.
17. Botti S. CIGS Photovoltaic Technology: The Alternative to Silicon Solar Cells. Coimbra, Portugal 2010.

18. Kanai Y., Grossman J.C. Role of Semiconducting and Metallic Tubes in P3HT/Carbon-Nanotube Photovoltaic Heterojunctions: Density Functional Theory Calculations. Nano Letters 2008. 908-12.
19. Stoitsov M., More J., Nazarewicz W., Pei J.C., Sarich J., Schunck N. et al. Towards the Universal Nuclear Energy Density Functional. Journal of Physics: Conference Series 180 2009. 1-5.
20. Papenbrock T. Nuclear Structure from Light to Heavy Nuclei. In: Lecture 3: Self-Consistent Mean-Field And Single-Particle Methods. TRIUMF Summer Institute 2008.
21. Drut J.E., Furnstahl R.J., Platter L. Toward Ab Initio Density Functional Theory For Nuclei. Columbus, Ohio: Department of Physics, Ohio State University; 2009.
22. Meng J., Li Z.P., Liang H.Z., Niu Z.M., Peng J., Qi B. et al. Covariant Density Functional Theory for Nuclear Structure and Application in Astrophysics. Nuclear Physics A 2010. 436c-9c.
23. Höök M., Hirsch R., Aleklett K. Giant Oil Field Decline Rates And Their Influence On World Oil Production. Energy Policy 2009. 2262-72.
24. Ward C.D., Coghill K., Broussard M.D. The Application of Petrophysical Data to Improve Pore and Fracture Pressure Determination in North Sea Central Graben HPHT Wells. Society of Petroleum Engineers 28297 1994. 53-61.
25. Augustine C., Tester J.W., Anderson B., Petty S., Livesay B. A Comparison Of Geothermal With Oil And Gas Well Drilling Costs. In: Proceedings, Thirty-First Workshop on Geothermal Reservoir Engineering; 2006 Jan 30 – Feb 1; Stanford, California, USA.
26. ASME Strategic Issues Committee. Future of Deep Water Drilling. Washington DC: ASME; 2010.
27. Patzek T.W. The Earth, Energy and Agriculture. In: Proceedings of the 27th Annual Summer Conference – Climate Change and Future of the American West; 2006 June 7-9; Boulder, Colorado, USA.
28. Chopra N., editor. Editorial, Nanomaterials and Energy. London: ICE Publishing; 11 March 2011.
29. Computational Research Needs in Alternative and Renewable Energy. In: US Department of Energy Workshop; 2007 Sep 19-20; Rockville, MD, USA.
30. Issued by Council for Chemical Research (CCR): Thompson T.B., editor. Chemical Industry of the Future: Technology Roadmap for Computational Chemistry. Final Roadmap for Computational Chemistry. Council for Chemical Research (CCR); 1999 Sep.
31. Admans G., Fitch A. Energy Research at the ESRF. Synchrotron Radiation News 2010. 22-9.
32. Kohn W. A World Powered Predominantly By Solar And Wind Energy. In: Richard E. Prange Prize and Lectureship in Condensed Matter Theory and Related Areas; 2010 Oct 19; University of Maryland, Maryland, USA.