International Journal of Applied Science and Mathematics
Volume 2, Issue 4, ISSN (Online): 2394-2894

Density Function Theory: A Contemporary Perspective for the Non-Specialist

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***Abstract* – The relentless increase in the pace of technological advancement is driving the need for new materials, tailored to specific roles in previously unexplored niches. For instance, price constraints have created a need for non-platinum catalysts that are able to function in the extreme conditions of the fuel cell. Conventional chemical approaches to material development are often time consuming, highly labour intensive and thus expensive. *In silico* chemistry offers a potential route to material development and evaluation, without the need for protracted laboratory investigations. Of the *in silico* methods available, density function theory (DFT) offers the possibility of *ab initio* material development, completely free from the need of an initial laboratory study, thereby enabling new chemistries and materials to be explored at hugely reduced costs. However, there is currently only a limited conceptual understanding of DFT in the wider chemistry community, due largely to its highly computational nature being ultimately based on the Schrödinger equation, which means it is often not considered as a viable or accessible tool by many researchers, especially those for instance in the biological sciences. This brief review seeks to provide a clear introduction to DFT, along with the possibilities and limitations to using it as an investigational approach, especially for those readers who lack a specialist mathematical background. A conceptual overview is followed by a brief literature survey highlighting its current usage in a range of situations, particularly concerning surfaces and catalysts; finally some information is given, regarding its practical implementation, with the aim of bridging the conceptual divide, thus making DFT an investigative tool available to a broader range of investigators in the chemical, physical and biological sciences.**

***Keywords* – Ab Initio, Catalysis, Density Function Theory, In Silico, Slab, Cluster, Model.**

I. INTRODUCTION

In parallel with the increasing quest to find new materials with sought after physico-chemical characteristics, or those that have reaction specificities tailored to a given need or environment; our access to computational power has grown, at what would have been regarded only decades ago, as a phenomenal rate. The application of such data processing power, directed by algorithms embodying mathematics representing the processes occurring in molecular orbitals to the discovery process in materials chemistry offers a potential wealth of material design possibilities[1-4].

Computational chemistry, commonly used in reaction modelling[5-7], (bio-) process design, the the analysis of heterologous data sets and for protein modelling/design[8], is simply the use, *in silico*, of an algorithm that embodies chemical, mathematical and computing skill-sets to solve chemical problems. The computers used, which often employ parallel processors to run the algorithms, generate information related to the properties of molecules, or they use simulated experimental models to anticipate practical investigational outcomes. Not surprisingly computational chemistry has rapidly become established as a useful way to investigate novel materials and reactions that are experimentally difficult to carry out, or where the materials required are expensive, such as is the case with catalytic design where the catalyst is based upon the use of the catalytic rare earth metals, *e.g.* Pt. Readers seeking an easily accessible, non-mathematical, overview of computational catalysis, with a historical perspective, are referred to an essay by Thiel and references therein[9]. Those readers wanting a more in-depth, and mathematically rigorous, account are referred to a comprehensive review by Geerlings *et al.*[10]

Of the *in silico* approaches in use today, density function theory (DFT) is distinguished from other computational approaches, such as those based on quantum or molecular mechanics and semi-empirical approaches that are reliant on analyses based on the application of classical physics to force-fields, or on quantum physics in combination with experimentally determined parameter-approximations.[11] In contrast to the previous approaches mentioned, DFT is a rigorous quantum physics based *ab initio* method, employing starting approximations that does not require the input of any experimentally determined parameters. The trade-off for some well-known computational approaches with respect to the number of atoms able to be considered within the system being analysed and the accuracy of the resulting model is shown in Figure 1.

The freedom from the need to use classical, or quantum, physics in conjunction with empirically determined parameters affords DFT a degree of freedom in its approach and the types of problems it can address. Without the initial need for experimentally derived data DFT offers the possibility of investigating novel individual molecules, or larger macromolecular systems, for which there is no available experimental data. However, the freedom of the mathematically rigorous *ab initio* DFT method to investigate systems, without the need for experimentally determined conditions, has a price in terms of the formidable computing power needed for its implementation. It is this price that has, until recently, largely restricted the use of *ab initio* DFT to industrial applications (especially in the realm of catalysis) where

the ability to accurately model the behaviour of high value rare earth materials is essential. For reasons, related to the number of residues that need to be considered, the modelling of large macromolecules *e.g.* DNA and RNA has been largely restricted to non-DFT methods, which are usually reliant on experimentally derived data, and are outside the scope of this paper[12-16].

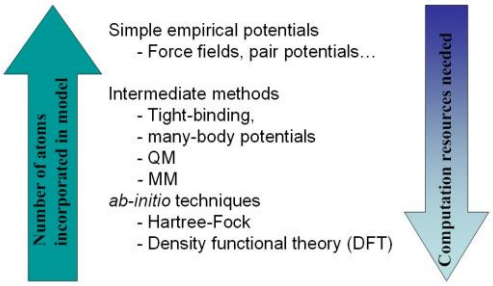

Fig.1. Computational approaches to reaction modelling (QM quantum modelling, MM molecular modelling).

Whereas approaches based on molecular mechanics do not calculate the electronic properties of the systems investigated and semi-empirical approaches are generally less rigorous and require the input of data, often from analogous experimental models, DFT is ideal for garnering morphological information and rigorously interpreting the electronic transitions of small atomic/molecular clusters and systems (typically comprising a few tens of atoms, or nanoparticles ~3-6 nm in diameter) for which there is only limited, or in many cases, no, experimental data available.

The mathematics underlying most approaches to contemporary computational chemistry is based on the Schrödinger equation, which in its form as a time dependent partial derivative, relates concepts embodied in a wave function (Ψ, the probability amplitude) for the system as a whole, to the values set for the Hamiltonian operator, *i.e.* the kinetic and potential energies of the particles that comprise the system[3]

I.I. DFT from concept to implementation.

The ability to successfully solve Schrödinger's equation would allow for the creation of a wavefunction embodying all the information that we need to fully describe a system; however, such solutions are unattainable for any system more complex than the simple hydrogen atom comprising one electron with its charge balanced by one proton, thus all computational approaches, including DFT involve compromises. Early approaches to DFT relied on the so-called Thomas-Fermi model employing only one variable, namely electron density which was represented in the model as a function of three coordinates. Such an approach, although economical in terms of the computer power needed, neglected a host of other crucial parameters and thus gave poor results.

The problems that need to be addressed mostly involve ensembles of particles, such as those within a lattice, where each particle exerts, in a time-dependent manner, an influence on the energy states (both attained and allowed) of the particles both immediately surrounding it and those distributed more widely throughout the lattice. This is the basis of the so-called N-body problem. Contemporary DFT is thus a computational method that employs various approximations to give an approximate solution to the Schrödinger equation for complex electron orbital systems.

DFT most simply stated reduces all the relevant variables, acting on a system (see below), to representations of charge density and in doing so reduces the complexity of the problem to a level such that it mirrors the single electron/proton model of the hydrogen atom. Thus, the approach of DFT is to reduce the number of degrees of freedom of the system. Central to this simplification is the Born-Oppenheimer approximation, which notes that the nucleus and electrons are attracted to each other by the same magnitude of electric charge, thus overall they exert the same force and momentum. However, the nucleus with its relatively greater mass will have, at least compared to the electron, a negligible velocity that for practical purposes can be ignored; thereby allowing the computation of the systems electron density wavefunction to be made independently from that of the nucleus.

Traditionally, the calculation of electron density approximations has made use of the Hartree–Fock method (also known as the self-consistent field method). Solutions to the Hartree–Fock equations must account for each particle behaving as if it is being subjected to a field created by all other particles in the system. Such equations, which give rise to wavefunctions embodying 3N variables - i.e. the 3 coordinates of the N atoms within the system are nearly always solved by computationally iterative algorithms[3].

In contrast to the Hartree-Fock approach to solving many body problems, DFT computes electron density as a function of only three variables, *i.e.* the three coordinate axes (x,y and z), using the Hohenburg-Kohn theorem which postulates that the ground state electron density functional (*i.e.* the ground state function written in terms of other functions, see below) determines the properties, including the electron (charge) density, of the system. This procedure allows the total energy of the system to be written, effectively as a one electron Schrödinger equation, in terms of functionals representing the coulombic potentials associated with the ion-electron potential energy, the ion-ion potential energy, the electron-electron energy, together with the kinetic energy and the exchange-correlation energy that arises from the coulombic repulsion between electrons that participate in Pauli Exchange interactions[3].

An adaptation of the DFT model, within the Hohenberg-Kohn framework that defines the ground state of a system solely as a function of electron density, is the Kohn-Sham approach, which simplifies the problem, by reducing it to a series of Schrödinger-based equations in which only one electron at a time is considered. This approach optimises the ground state, and in doing so offers a way of simplifying the many-body problem of interacting electrons to one where they are assumed not to interact, but rather to experience an 'effective potential' that accounts for the difficult to calculate Coulombic interactions, *i.e.* the exchange and correlation

interactions[17,18]. It is this approach, which despite its limitations, in large complex systems that offer competing solutions, together with the mathematical problems encountered in maintaining continuous potential energy surfaces, that is commonly used today in computational DFT. An outline of the sequence of simplifications needed to generate computable functionals (Kohl-Sham equations) is shown schematically in Figure 2.

Contemporary approaches to DFT yield data that can be used to interpret, predict and explain *e.g.* electronic structures; energetic reaction barriers; rate constants; charge distributions; spectroscopic characteristics; molecular geometries, including optimizations and transitional structures; protein conformations and interactions; potential energy surfaces (PES); and thermodynamic data calculations, such as heats of reactions and activation energies.

I.II. Density functional theory calculations.

As introduced in the previous section there are two fundamentally different approaches to the calculation of the electronic structures and total energies of molecules and solids: the wave function-based methods and the DFT methods. The wave function-based methods can be very accurate if sufficient interactions are included; however current software is restricted to considering systems having 10–100 electrons. If we consider transition metal surfaces, this limits the number of atoms that can be treated to about 10, since each transition metal has on the order of 10 valence electrons. This generally makes these methods unattractive for the routine treatment of the complex systems that are needed to model catalysts. However, elegant ways have been developed to embed a very accurately described region into a less accurately described surrounding region, which can increase the system size and make wave function-based methods more accessible[19,20].

In contrast to the wave function-based methods, DFT based approaches attempt to compute the ground state electron density and the total system energy by solving a set of one-electron Schrödinger equations (the Kohn–Sham equations) instead of the original and far more complicated many-electron Schrödinger equation. This approach results in an enormous computational simplification and in doing so allows systems with more than 1000 electrons to be modelled.

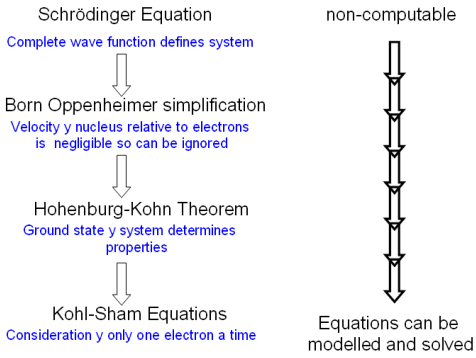

Fig.2. Sequential simplification starting from the non-computable Schrödinger wave equation to systems able to be modelled using the Kohl-Sham equations.

I.III. DFT implementation: concepts, computation and software.

Within the DFT computational environment there are several different approaches that can be used to solve the Kohn–Sham equations. The approaches are in general characterized by the surface model used, the parameters embodied in the basis set (starting conditions), and by the approximations employed in the treatment of the computationally demanding exchange-correlation term[3,17]. Using DFT we can approach the modelling of a molecular system on a catalyst's surface in a systematic way by first addressing the problem of its geometric and electronic structures and the relationship between them[21]. At this point the lattice constant, also known as the lattice parameter, becomes an important term to be specified. It is this term which refers to the physical dimensions of a unit cell within a crystal lattice and thereby determines the lattice's minimum repetition distance. This in turn allows us to describe the periodic arrangement of atoms in three dimensions.

Input charge density and wavefunctions are independent input quantities, the initial values of which need to set at start-up. Within each iterative computational loop the charge density is used to set up the total (*i.e.* a summation of the kinetic and potential) energy of the system. The wavefunctions are then optimized iteratively so that they closer approximate the exact wavefunctions. From the new 'optimized' wavefunction a new charge density is calculated, which is then used for the next computational cycle.

Also needing to be specified is the degree of relaxation that should be applied to the model. Relaxation results from small, yet energetically significant, adjustments in the layer spacing perpendicular to the surface, which does not involve changes either to the periodicity parallel to the surface, or to the symmetry.

While the Hohenburg-Kohn theorem highlights the importance of the ground state energy to the crystals resulting overall properties the determination of this energy requires the forces on the atoms, created within the *in silico* model, to be 'relaxed'. The rate of relaxation (step length) should be set such that the system does not to get trapped in a local-energy-minimum and yet still converges at an acceptable rate.

After the 'structures' have been modelled *in silico*, we can investigate the system's dynamic properties, *i.e.* how it behaves when it is put in a given environment possessing certain properties, such as temperature and magnetic field, to which numerical values can be ascribed. Finally and most importantly, we wish to be able to represent the topology of the potential energy surface and how it behaves, especially when a chemical reaction, involving the making and breaking of bonds, takes place[7].

As has already been noted it is not possible to use the wave equation to describe anything other than the simplest of systems. However, initially creating, and subsequently analysing the overall composite probability electron density function that DFT relies upon is intimately associated with the computational algorithms employed. At the level of the computational code employed the

embedded mathematics seeks to determine the ground state of the system by minimising the electron density functionals to generate a so-called pseudopotential, or composite electron density field through which any given electron can be visualised as passing and in doing so removes the need to consider each electron separately and the likelihood of finding it at any particular location[3].

A multitude of DFT software packages, both open source and commercial, are currently available. Currently, most of the underlying code, the details of which are outside the scope of this review, is written in either C++, or Fortran (or, in a combination of these two languages). Quite commonly the packages on offer employ techniques derived from several approaches *e.g.* DFT in combination with molecular mechanics and semi-empirical methods, with each approach being coded as a separate program in the underlying software[11].

As previously mentioned the main computational barrier encountered with DFT is the determination of the exchange-correlation energy functional term. There are two generally accepted (simple) approaches to computing this approximation. Local density approximations (LDAs) that depend only on the electron density (regarded as homogeneous) at each point in space and generalized gradient approximations (GGAs) that offer improved accuracy, in terms of the final model, which go beyond the LDA model by including electron density gradients[22]. A generalised hierarchy of the conceptual models employed is given in Fig 3.

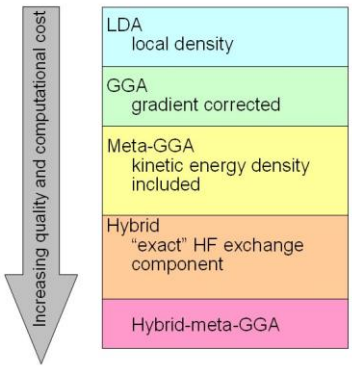

Fig.3. Density Function concepts used compared to increasing cost and quality of computational outcome (HF = Hartree-Fock).

I.IV. Applications of DFT

The outcome of a DFT investigation generates numerical data that can be used to aid our understanding of, or to represent, the structural, magnetic and electronic properties of molecules and materials - and in doing so hopefully offers a route to avoiding long, expensive laboratory investigations that may ultimately prove fruitless[4]. The insights gleaned may be applied to a variety of problems, including those related to the biological/biochemical sciences[23,24]. Such approaches therefore potentially offer a route to bridging the traditional divide between the metallic surface based catalysts studied in physical chemistry and the non-metallic proteinacious catalysis central to biochemistry. However, computational chemistry, especially when combined with quantum physics (and its attendant mathematics), is usually only introduced late (if ever) in the undergraduate career of chemistry and physics students and rarely, if at all, into the curriculum of students pursuing studies in the biological sciences.

Thus, although DFT is a tool that has the potential to aid in the investigation of a wide spectrum of materials, its use, possibly due to its reliance on mathematically advanced computational algorithms, has meant its use has been largely directed away from the biological sciences towards the physical sciences, particularly towards the materials sciences involving physical chemistry, and especially towards subjects such as catalysts and membranes.

In this review, we will discuss how the calculation methods, used in close conjunction with experiments, can be used to develop some useful concepts to describe and understand adsorption phenomena and reactions on various surfaces. We will concentrate mainly on metal surfaces (contrasting this occasionally with biological applications) because, as already mentioned, this is the area in which both the experiments and the calculations are most advanced. We show how we are now beginning to understand which surface properties govern the variations in reactivity from one surface to another and how the DFT modelling of adsorbate–adsorbate interactions, is starting to reveal key reactivity determinants such as surface structure, strain, alloying, defects, and how impurities may affect reactivity and other crucial parameters.

I.V. Metallic catalysis: a surface dependent phenomenon.

When a solid catalyst is used to speed up a chemical process, the overall reaction can usually be describe in terms of a number of elementary steps[7,25]. These include adsorption of the reactants on a solid's surface (Figure 4a), followed by surface diffusion (aggregation, dissociation, or nucleation), the breaking of some reactant bonds, and the creation of new bonds to form the product molecules, which eventually desorb from the surface (Figure 4b)[26]. The complexity of these processes and of the catalysts makes it a demanding task to establish a molecular-level understanding of heterogeneous catalysis[4,27-30].

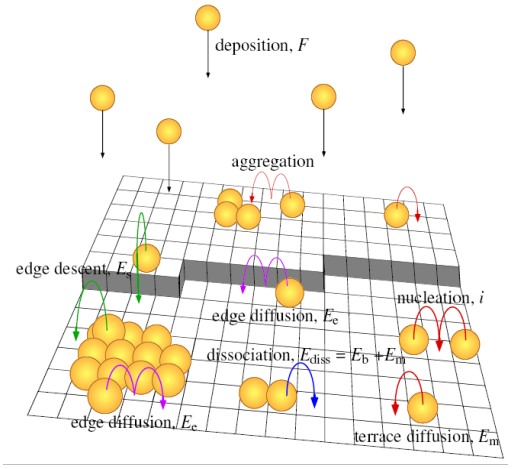

Fig.4a. Schematic of the various reaction possibilities after adsorption.

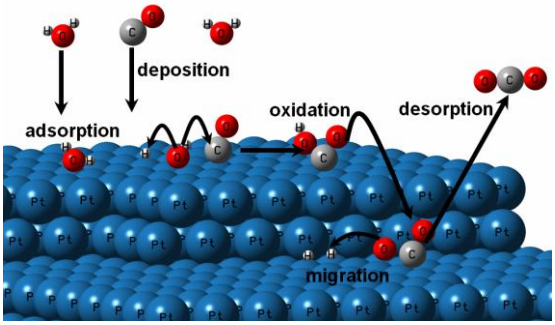

Fig.4b. Schematic diagram of some reaction possibilities that lead to product desorption from the surface.

The approach taken in surface science has been to study elementary reactions on well-defined single-crystal surfaces in order to build an understanding of some of the basic processes involved in catalysis. However, single-crystal surfaces are only crude models of the high-surface-area catalysts used industrially. Catalysts need to have a high surface area, and they often consist of mixtures of phases, some of which have a catalytically active surface, whereas others support the small particles that form the active phases. Recently, as a consequence of the development of improved surface science methods, it has become possible to produce models of supported catalysts and use them to investigate *in silico* their catalytic behaviour under computationally realistic conditions of high-pressure and high-temperature. This is rapidly closing the gap between surface science studies and studies of real catalysts[31]. In parallel with *in silico* advances, the methods used to physically and chemically characterize high-surface-area catalysts have also been refined, meaning that it has become possible to characterize both the structure and properties of catalysts *in situ.*

I.VI. Models used to describe the surfaces.

A successful DFT algorithm must embody within its code a rigorous theoretical description of the adsorbate–surface interactions crucial to the catalytic process. Such descriptions can be divided into:

1. Those that are accurate, but computationally demanding, often requiring extensive basis sets to enable the generation of an electron density contour profile along with calculations of adsorption properties; and
2. Those that are less accurate but computationally simple.

The resulting calculations, which describe these two situations, can be viewed as computer experiments. They complement real experiments in several ways. It is useful to be able to check experimentally derived data to have a basis for comparison. There are also cases in which the calculation is simpler (and possibly safer) than the experiment. For example, consider an important fundamental property of a surface, such as its surface energy, which is very difficult to measure. Currently, the best current source of surface energy data is derived from calculations, which have now been performed for all the metals in the periodic table.

Finally, the calculations can sometimes be performed for situations that are not easily realizable experimentally. For instance, it is very simple to change the lattice constant of a metal in a calculation to show the effect of strain on reactivity without any concerns related to the problems associated with straining a crystal in real life. The ability to use computer experiments to test models and theories of catalysis has recently breathed new life into the development of such models and our understanding of catalysis. The models are needed to bring into focus the concepts around which our descriptions and understanding of catalysis revolve.

As explained already, the calculations cannot describe all the atoms in a solid or a catalytic particle, thus a strategy must be chosen to limit the number of atoms considered. Two basic approaches exist:

i) *Cluster methods*, which describe only a limited cluster of the surface atoms, in the hope that the surface atoms furthest away from the adsorbates of interest are not important, and

ii) *Slab methods*, in which the surface is described as a slab with a periodic structure. The size of the surface unit cell determines the computational effort required, and in principle the unit cell should be chosen to be large enough so that the adsorbates in neighboring unit cells do not interact. The two types of models are illustrated in Fig. 5. The slab should be thick enough that the middle layers obtain bulk properties and that the two surfaces do not interact with each other through the slab. In addition the vacuum region should be thick enough that the two surfaces do not interact with each other through the vacuum region. However, in both methods, due to limitations imposed by computer processing capacity, only a finite number of atomic layers can be included, thereby always imposing an approximation[32,33].

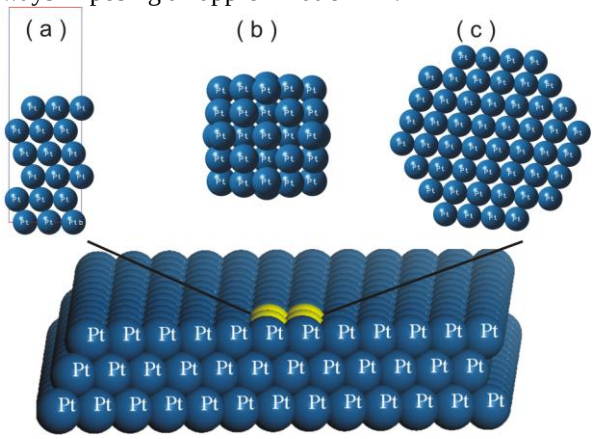

Fig.5. (a) Left-top: a well-defined, finite vacuum space is used to model the surface (in the slab approach) (b) middle: a finite cluster (Pt_{55} atom) is used to model the surface (in the cluster approach) (c) Right-top: a finite cluster (Pt_{236} atom) is used to model the surface (in the cluster approach).

One such model used to describe the terrain of the catalytic surface is the so-called terrace, kink and step (TSK) model (also sometimes referred to as the Terrace Ledge Kink (TLK) model), originally proposed by Kossel and Stranski, early in the twentieth century[34] - see figure 6. This is a simple model based on the thermodynamic

stability of crystalline step edges, adjacent to terraces, which can be used to describe the thermodynamics of crystal surface formation, transformation and growth, as well as the energetics of surface defect formation, surface diffusion and vaporisation. The TSK model, which regards atoms that have traversed the various steps and terraces as having crossed one or more energy barriers, focuses on the two points below:

1. The energy of an atom's position on a crystal surface is determined by its bonding to its neighbouring atoms, and
2. Phase growth or transition - simply involves changes in the numbers of broken and formed bonds.

This model and the *in silico* DFT algorithms that are based on it can be applied to surface science topics such as crystal growth [including epitaxial and non-epitaxial (ordered and disordered) growth], surface diffusion, and vaporization.

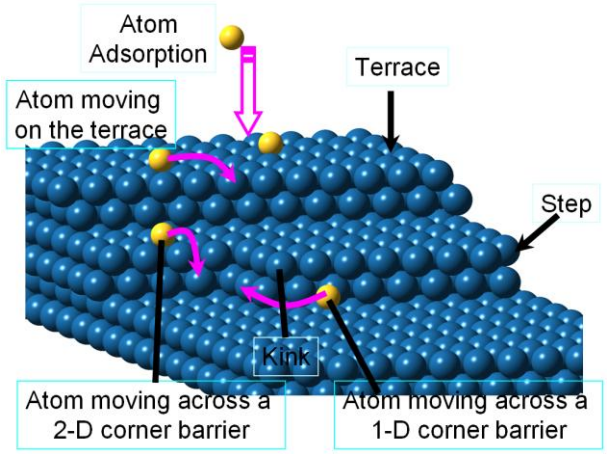

Fig.6. Terrace, Step, Kink (TSK) model of crystalline surface.

II. Discussion

Fuel cells are devices that convert chemical energy, which needs to be continuously supplied in the form of a fuel *e.g.* methanol, into electricity, normally by using a catalysed oxidation reaction involving air or molecular oxygen. Currently fuel cells are used to power various appliances ranging from handheld devices to submarines.

Although there are many types of fuel cells, they all possess an anode, a cathode and an electrolyte. In a typical fuel cell it is at the anode that a catalyst promotes the splitting of hydrogen into protons and electrons which are then able to be drawn through the external circuit as direct current[35].

The catalysts employed typically use platinum, which due to its limited supply is highly expensive. Therefore strategies that aim to optimise, reduce, or replace, Pt usage are the subject of much investigation. Recently studies have highlighted the importance of the Pt environment[36,37], especially studies of the micro-environment where catalytic properties become manifest will hopefully lead to strategies that reduce Pt usage. For example the behaviour of Pt prepared as a nano-particulate catalyst will diverge from its bulk-counterparts properties in terms of surface coverage, surface energy electrochemical response and reaction kinetics. A descriptive, in-depth and insightful, comparative study of cluster and slab models was used to show the differences in the energy barriers on edge sites (Pt_{55} cluster) in comparison with a slab Pt(111) model's facet sites by Lin *et al.*[36] Central to the paper was the role played by DFT in the discovery that different catalytic mechanisms, *i.e.* diffusion controlled and kinetic controlled, operate on bulk and nanosized Pt catalysts respectively.

Complimentary to the catalytic metal is its support. No longer recognised as a benign 'carrier' for the catalyst, the role of the support is now an area of active investigation: for example DFT based structural assignment studies of the binary metal oxide support $Ti_{0.7}Ru_{0.3}O_2$ have been used, in conjunction with XRD patterns, to give mechanistic insights into the co-catalysts synthesis and activity[38].

Taufany *et al*., in a recent paper related the composition, especially with respect to the alloying extent, of platinum, and ruthenium particles supported on carbon, to their electrochemical activity for methanol oxidation.[39] Within their approach which comprised the use of several spectroscopic techniques in conjunction with cyclic voltammetry they used DFT computations employing a PtRu(111) slab model to estimate the extent of charge transfer in the PtRu nanoparticles (NPs) they synthesised. The resulting electron density contour map, which was significantly different to either pure Pt(111) or Ru(001), showed unique overlap of the Pt and Ru orbitals to form a linked structure, able to facilitate charge transfer to from Ru to Pt within the alloy

An alternative and promising approach in the quest for a cost effective means of bulk fabricating bimetallic nanostructures is the fabrication of core-shell structures in which a dimensionally stable core, typically formed of a less expensive metal, is used as a support for the active catalytic metal shell, which is often Pt. The mass of material needed for the supported metal can be effectively reduced by fabricating it as an ultra-thin layered shell. In a recently reported approach directed at addressing the problems associated with the bulk production of core-shell nanoparticles a DFT modelling study was used to help devise a non-electrochemical means to deposit an ultra-thin Cu layer on Pd/C core which could later be sacrificially oxidised by Pt redox transmetallation to produce the sought after ultra-thin catalytic Pt layer[40]. This study was the first reported to use first principles DFT calculations to replace a conventional thermodynamically controlled electrochemical method (*e.g.* under potential deposition) with a kinetically controlled synthesis that overcomes the limited production capacity of the former approach.

PtRu bimetallic nanoparticles, synthesised as a Ru(0001) core supporting a Pt(111) shell, have been used as anode materials in methanol fuel cells. The synthesised nanoparticles were shown to have a remarkably enhanced catalytic activity for methanol oxidation and resistance to methanol poisoning, compared to other Pt based nanoparticles[41]. The mechanistic basis of the activity was investigated and found to originate in a bifunctional mechanism in which Ru provides an absorbed hydroxyl to

Pt for oxidation as well as an electron to transfer to Pt accompanied by a decrease in the d-band vacancy leading to reduced carbon monoxide adsorption.

The growth of Pt on Ru has been shown to proceed by heterogeneous nucleation and island growth. Such a mixed growth mechanism is highly unusual and was investigated and resolved by DFT[41]. Pt on Ru nanoparticle interactions were modelled by a two-layer slab of an Ru hexagonal close packed (hcp) lattice. Within the simulation a three-layer slab of Pt(111) face centred cubic (fcc) lattice was 'placed' above the Ru(0001) slab and the adsorbed Pt atoms, together with the Ru atoms in the top Ru layer were subject to a given level of perturbation. The system was gradually relaxed to achieve a balanced state of equilibrium at its lowest energy. The DFT simulation was able to explain the experimental findings in which the formation of conformal epitaxial growth of Pt on a Ru substrate can be attributed to the lateral displacement of adsorbate and core layers together with a large energy relaxation.

The same group also published a paper examining the structural relationship of bimetallic alloyed NPs, formulated as Pt_3Cr_1/C, to their electrocatalytic activity, stability and selectivity in the oxygen reduction reaction (ORR).[42] The authors were able to show, by using a combination of techniques *i.e.* x-ray absorption spectroscopy, transmission electron microscopy and DFT slab modelling calculations, in combination with electrochemical methods, the importance of the alloying extent in determining the Pt d-band vacancy. It was additionally found that the alloying extent was a major determinant of selectivity and stability in the ORR. As in the previous paper the Pt orbital was found to overlap with that of the second metal (Cr) to form a linked structure allowing charge transfer, from Cr to Pt, within the alloy. Also apparent from the DFT study was the fact that the extent of electron donation is a crucial determinant of the binding energy of surface adsorbed gaseous molecules *e.g.* O_2, which as has been noted before is a determinant of catalytic utility. Using DFT in a similar approach for the study of the architecture of Pt_xCo_{1-x} ORR electrocatalysts Lai *et al*., were able to show the critical importance of the orbital overlap between Pt and Co in increasing the charge on Pt, thereby influencing the Pt-Co bond distance as well as the binding energy of the adsorbed gas molecule O_2 or CO[43].

DFT was used to offer a far more mechanistic insight in a paper by Wang *et al*.,[44] in their study focused on the preparation of catalytic ternary $Fe_{1-x}PtRu_x$ nanocrystals for methanol oxidation. In their work DFT occupied a central role in determining the mechanistic basis of the ternary catalysts superior resistance to CO poisoning, by computing the gases adsorption energy on the nano-crystalline surface. Their results showed that the introduction of the third metal, into Pt/Ru or Pt/Fe, weakened Pt-CO bonding. This finding together with the discovery that the overall extent of charge transfer from Fe/Ru to Pt was heavily dependent on the alloying extent of the ternary system, was claimed, by the authors, to show the way to the discovery of new (low Pt usage) metal alloyed catalysts with superior resistance to CO poisoning with potential applications in fuel cells.

Considerably more developed is the application of DFT to the modelling of catalytic solid surface phenomena in comparison to the modelling of macromolecular (proteinacious) biological catalysts[8]. In biological systems the enzyme that controls the alternative lower energy of activation reaction pathway often possess an easily deformed complex 3-dimensional structure, in addition to which the environment in which the reaction takes place (biological matrix) is of more significance than is the solid metal surface model.

Of the studies that have been carried out using biological molecules, a paper by Liu and Gao[45] used ibuprofen as a model for the optimisation of various DFT parameters to predict the molecule's molecular geometry and vibrational structure using various DFT methods and basis sets. In a study of 22 amino acids Yu *et al*.,[46] applied various DFT methods to the determination of molecular parameters such as conformational energy, proton/deprotonation energy, to reveal which DFT approach was best suited for the study of small peptides and other bio-molecular systems with intramolecular hydrogen bonds.

In contrast to both of the above studies; both of which, although focused on a biological moiety, nevertheless reported DFT relevant data for algorithm optimisation rather than using DFT as a tool to develop or investigate a biological system, a paper by Xu *et al*.,[47] investigated the anomalous ligand binding behaviour shown by H-NOX (Heme-Nitric Oxide) and Fe-CO and CO (heme adducts) and in doing so showed DFT's potential as an investigative tool. The authors noted that the stretching frequencies, found using Raman spectroscopy, for Fe-CO and CO (heme adducts) when used as probes to investigate the electrostatic and mechanical forces operating in the heme binding pocket showed unexpected behaviour, due to localised electrostatic effects related to bound CO affecting the back donation of electron density from Fe(II) $d\pi$ to the empty CO π^* orbitals, that strengthened the Fe-C bond while weakening C-O bonds. The authors used DFT to generate a more realistic model of the interplay of the substituents that modulate electron donating behaviour and concluded that DFT modelling could be used to discriminate various possible effects, thereby leading to fresh mechanistic insights.

A critical overview of the use of DFT in modelling processes, structures and properties relevant to photosynthesis has been given by Orio *et al.*[48]. The authors commented that DFT appears to be generally reliable for determining geometries, vibrational frequencies and total energies. They also commented that DFT appears to be quite successful for the prediction of molecular properties as well, since a number of spectroscopic properties of interest to the bioinorganic community can be predicted with good accuracy. Interestingly, and absent from most other studies, the authors go on to make a suggestion that applies equally to all the areas to which DFT is applied, that being: "in order to enhance their credibility, DFT applications must include

some form of validation or estimation of the error range on the basis of careful comparison between calculated and measured observables".

III. Conclusions and Future Perspectives

It is well known that subtle changes to the values of the initial starting conditions of a physical system in terms of material composition, temperature etc., can radically affect the outcome in terms of the nature and yield of a product. While we would like to be able to understand directly, and therefore be able to predict with confidence, how such changes lead to alterations in reactivity, the reality of the situation is such that it is not possible to perform a complete calculation, and even less an experiment, for each variation of a given system. DFT in its evolved-form, draws upon ideas from a multitude of disciplines: from physics *e.g.* Schrödinger's equation, potential energy surfaces; chemistry, *e.g.* molecular orbitals and geometry, electron density; mathematics, *e.g.* statistics, numerical linear algebra, numerical optimization, functional generation; and from computing. Currently DFT has evolved to the point where it is able to provide a reasonably accurate model of electron density contours and by extension to give a semi-quantitative description of adsorption and reaction processes, although accurately predicting the rate of a chemical reaction remains problematic. The method has shown great utility as a screening tool for comparing different systems, *e.g.* in the search for catalysts with a desired activity or selectivity for a given chemical reaction prior to practical investigation.

Although the progress in DFT modelling has been genuinely impressive the derivation of functionals for certain problems and the data supplied to the *ab initio* basis sets remains problematic. Currently DFT problems associated with surfaces are associated with the treatment of solvation and dispersion effects. However, with regard to bio-catalysis - the number of atoms involved and the complexity of many systems currently means they remain more suited to simulation by the faster quantum based models. The creation of a 'complete' basis set would theoretically be able to overcome all the problems associated with the treatment of intermolecular interactions, *e.g.* London dispersion forces, van der Waals forces[49]; charge transfer; transition states, global potential energy surfaces, dopant interactions and in doing so would describe all aspects of a molecular orbital (by solving the one-electron Kohn-Sham equations). However, there are still problems that need to be addressed; for instance how to create the functionals required and also provision of the enormous computing power needed to solve them.

The current relative lack of publications related to the use of DFT in the biological sciences may be reflective of several problems. As already alluded to; biologists, if they follow a traditional undergraduate curriculum, tend to eschew mathematics; thus the idea of employing DFT (or any other computational approach) is unlikely to be considered as a practical approach. Additionally, in any biological system nothing is static; proteins, ligands and cells all exist in a complex dynamic matrix and constantly interacting with each other in complex patterns. However, despite the problems that are innately associated with biological systems the recent advances in DFT methods combined with constantly increasing computing power should soon bring us to the point where DFT predicted properties can complement and in some cases, *e.g.* live animal testing, even replace experimental investigations with the intriguing possibility of allowing us to venture into regions that are experimentally, or ethically problematic.

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