

Recent developments in the application of theory to structural problems in coordination chemistry

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Abstract; The development of molecular orbital techniques and their applications to structural problems in co-ordination chemistry will be reviewed. Initially semi-empirical molecular orbital methods were used to supplement symmetry based arguments in structural chemistry. This led to significant generalisations concerning the stereochemistries of co-ordination compounds and cluster compounds. Recently more sophisticated Density Functional Theory calculations have become available which enable theoretical chemists to accurately predict the structures of co-ordination and organometallic compounds . This review provides a brief background to Density Functional Theory calculations and illustrates their application to a number of topical problems .

INTRODUCTION

During the 1970's semi-empirical molecular orbital calculations (1) provided a new way of looking at geometric problems associated with co-ordination compounds by underpinning symmetry and perturbation theory ideas. This led to a flowering of new areas in a theoretical field which had become relatively dormant since the exciting developments of Crystal Field Theory in the 1950's. The applications of the latter had been essentially limited to analysing the d orbital splittings in high symmetry molecules and it had not been able to cope adequately with the increasing number of lower symmetry co-ordination and organometallic compounds which had been revealed by the more ready access to crystal structure determinations. Although the limitations of the extended Huckel methodology were well documented (2) and attempts to accurately calculate crystal field splitting energies using this one electron model were woefully inadequate it did enable chemists to trace the evolution of orbitals as the geometries of the complexes were changed. This approach was popularised by Hoffmann (3) and his co-workers (4) and widely applied to co-ordination and organometallic compounds. The approach was able to establish that the bonding capabilities of metal fragments depended on the geometries of the ligands which made up the co-ordination environment. In addition it indicated that in non-

centrosymmetric structures the metal d orbitals no longer retained their identities, but mixed extensively with the metal s and p orbitals which generated frontier orbitals which were critical for defining the bonding capabilities of the fragments. The knowledge of the bonding capabilities of these fragments when combined with simple perturbation theory ideas led to the *isolobal* analogy (5). The strength and weaknesses of the *isolobal* approach have been discussed in detail elsewhere (6). The semi-empirical molecular orbital calculations also underpinned the Polyhedral Skeletal Electron Pair Theory (7), although once again criticisms were made concerning the inability of these types of calculations to accurately define the extent of metal-metal bonding in cluster compounds.

Despite the great insights into geometric problems which the semi-empirical molecular orbital calculations provided there were limitations which hampered its application to more detailed problems. For example, the fact that the calculations did not lead to minima in the total energy, but a minimum in the sum of the one electron energies led to uncertainties in the accuracy of the predicted geometries. Similarly the extended Hückel method is notoriously bad at calculating the bond lengths in molecules. The great improvements in computing technology since the early 1970's has made it more and more practical to use more sophisticated calculations for geometric problems in co-ordination chemistry. This review summarises results using Density Functional Theory (DFT) calculations which have been obtained in my laboratories in recent years.

DENSITY FUNCTIONAL THEORY

Although the basic theorems associated with Density Functional Theory (DFT) originated in 1964 its widespread application to chemical problems is more recent (8). The more familiar *ab initio* methods solve the Schrodinger equation for a multi-electron molecule using the Hartree-Fock equations which set up effective one-electron Hamiltonians. The experimental observables of the molecule are then derived from these wave functions by operating on them with the relevant quantum mechanical operators. The problem with this methodology is that it neglects the instantaneous repulsion between electrons which are the basis of correlation effects. To improve this deficiency time consuming additional calculations have to be added to the initial Hartree-Fock calculations. In Density Functional Theory the n-electron wave function associated with the solution of the Schrodinger equation are replaced by attempts to calculate the electron density $\rho(r)$. Hohenberg and Kohn showed in 1964 (9) that the ground state energy of a many electron system is completely and uniquely determined by its electron density. The advantages of the Density Functional Approach arise because for a comparable level of accuracy the Density Functional Theory equations leading to the electron density are easier to solve than the Hartree-Fock equations.

The practical application of DFT is associated with a set of one electron equations derived by Kohn and Sham (KS) (10) from which one could in principle derive the electron density distribution in the molecule. These serve as the starting point for approximate methods such as multiple scattering techniques (MS) which derive the electron density by partitioning the volume into (spherical) atomic,

interatomic and (spherical) extramolecular regions. The KS potential was initially derived using the X_α formalism and has led to good predictions of certain electronic properties of transition metals, but cannot be used reliably for geometry minimizations.

The discrete variational method uses a Slater type orbital expansion basis set to derive the electron density based on one centre auxiliary functions (11). This leads to a N^3 scaling of the computational effort compared to N^4 for Hartree-Fock *ab initio* calculations. This has allowed the study of the electronic properties of transition metal compounds with a sufficient number of atoms (50) to be chemically interesting. DFT calculations have now been reported for a wide range of transition metal systems and have successfully been applied for describing: ground state geometries, activation energies, dissociation energies, vibrational frequencies, dipole moments, polarizabilities, ionization energies, excitation energies, proton affinities, electrostatic potentials and chemisorption energies.

RECENT APPLICATIONS OF DENSITY FUNCTIONAL THEORY

During the last few years density functional based methods have been applied to a wide range of chemical problems. This section provides a brief survey of the various applications which have been reported by other groups. The optimization of molecular structures by non-local density functional theory has been reviewed and examples of applications to main group molecules, organic molecules and transition metal complexes (12) have been discussed. The application of non-local DFT to atoms, molecules, solids and surfaces has also been reported demonstrating the potential usefulness of density functional methods for almost every field of modern chemistry (13).

Organometallic molecules

The most successful chemical applications of density functional theory have probably been in the field of organometallic chemistry and in particular there have been detailed analyses of the hydroformylation reaction (14) and related processes of industrial importance. For example, Chauvin's mechanism for the olefin metathesis reaction catalyzed by tungsten and molybdenum carbenes (15), and the acetylene metathesis reaction catalyzed by high oxidation state molybdenum and tungsten carbyne complexes (16). The insertion of Ni into the C-H bond of CH_4 , an important step in the steam reforming process of natural gas, has also been studied in some detail (17).

The electron rich early transition metals are known to stimulate breaking and generation of H-H and C-H bonds by oxidative addition and subsequent reductive elimination reactions. One study dealt with the activation of H-H and C-H bonds by $\text{Cp}_2\text{Sc-H}$ and $\text{Cp}_2\text{Sc-CH}_3$ in order to investigate a proposed σ -bond metathesis-like pathway for the electron poor early transition metals, where the formal oxidation state and electron count on the metal remain unchanged (18).

The strengths of the metal-metal bonds in $\text{Co}_2(\text{CO})_8$ and $\text{Mn}_2(\text{CO})_{10}$ and of the M-H and M-C bonds in $\text{R-Mn}(\text{CO})_5$ and $\text{R-Co}(\text{CO})_4$ have also been investigated recently using high level Density

Functional Theory calculations (19). In a further study on the octahedral complexes $(OC)_5Cr-L$ with $L = CO, NR_3, PR_3, AsR_3, SR_2, SeR_2, OR_2$ a method was developed to break down the Cr-L bond energy into contributions originating from σ -donation and π -backbonding components(20).

A helpful investigation of the structures and vibrational frequencies of a wide range of molecular transition metal compounds and a comparison with the corresponding Hartree-Fock results (21) has also been reported

Polymeric molecules

Density Functional Theory has been applied to molecules with high molecular weights which are not amenable to *ab initio* Hartree-Fock methods. The molecules of interest are often so complex that the much simpler semiempirical or molecular-mechanics methods are the only viable alternative methods. A density functional theory for polymer liquids has been derived and applied to model compounds (22). Another study developed a general microscopic approach for the crystallization of flexible polymer melts on the basis of density functional theory and applied it to polyethylene (23). A rare example for the application of DFT on biomolecules is given in a review on enzyme catalyzed reaction mechanisms [24]. Density functional methods have also been applied successfully to the calculation of bond lengths, binding energies and HOMO-LUMO gaps of a range of carbon fullerenes C_n (25).

Infinite Solids

The theoretical study of infinite solids is one of the oldest applications of Density Functional Theory. A recent study reported the optimizations of the crystal structures and energies of a number of oxides including SiO_2 (quartz, cristobalite and stishovite), TiO_2 (rutile), $MgSiO_3$ (perovskite) and Mg_2SiO_4 (spinel) and analysed the distortions associated with the anions (26). The bonding properties of 3d transition metals (cohesive energies, equilibrium lattice parameters, bulk moduli) have been reported and non-local extensions to the local density approximation were included (27). The extension of Density Functional Theory to excited states has made it possible to calculate band gaps in insulators and semiconductors (28).

DFT methods have also been successfully applied to the investigation of superconductivity. In 1988 Hartree-Fock-Slater calculations on the high- T_C superconductors La_2CuO_4 and $YBa_2Cu_3O_{7-x}$ were performed and the calculated critical temperatures, isotope effects, coherence lengths and critical fields were in good agreement with experiment (29). A more recent study investigated the ground state density, energy and band gap of a model semiconductor at a higher level of density functional theory (30). The influence of oxygen content and magnetic ordering on the electronic structure of $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ has also been studied by means of density functional methods (31).

Surfaces and interfaces

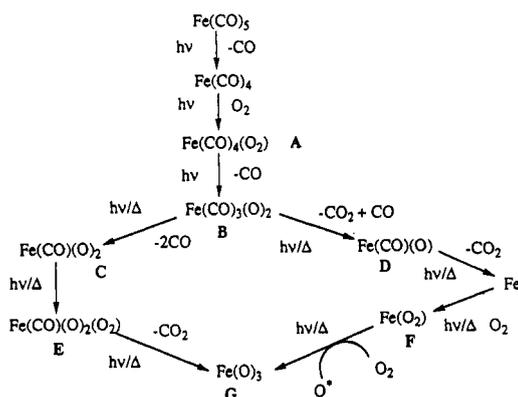
A combination of DFT techniques with the van der Waals' approximation and the hard sphere fluid model system has been used to develop a microscopic theory of planar crystal surface melting (32). Another study has provided a density functional theory of the water liquid-vapor interface (33). In a more chemical example DFT methods were used to investigate the co-adsorption of CO and alkali atoms at transition metal surfaces (34).

The following sections describe the applications of the Density Functional Theory methods to problems of interest to my own research group.

Characterisation of Matrix isolated Molecules

Matrix isolation techniques have been widely used to study reactive molecules in organometallic chemistry. Metal carbonyls have been particularly widely studied because the CO stretching modes may be used to determine the geometry of the fragments by means of group theoretical analyses and isotopic substitution techniques. However, these techniques are less definitive when other molecules are introduced into the metal co-ordination sphere. For example, in the complexes $M(O)_x(CO)_y$ the spectroscopic techniques can establish the local symmetry associated with the metal carbonyl containing fragment and whether the oxygen atoms are co-ordinated as oxo- or dioxygen ligands, but the total geometry of the complex is more difficult to establish by these techniques. We have utilised Density Functional Theory calculations to provide additional supporting evidence for characterising these intermediates in the matrix.

The reactions of metal carbonyls with dioxygen in an argon matrix have been studied by Downs *et al* at Oxford University (35). For example, the study of the reactions of dioxygen with $Fe(CO)_5$ under photolytic conditions in a matrix has established that although the final product is $Fe(O)_3$ a range of carbonyl oxo and dioxygen complexes are formed as intermediates. The proposed reaction intermediates are illustrated in the Scheme.



Density Functional Theory studies have been used to define the probable geometries of these intermediates. In each case the optimised geometry was calculated and the energetics of the individual steps were estimated. In general the calculations have confirmed the structures proposed on the basis of spectroscopic data (36). Unfortunately the calculated vibrational frequencies for the carbonyl, oxo- and dioxygen ligands were not accurately calculated by the DFT calculations and therefore could not be used to identify the intermediates with complete certainty. Advances in the methodology in future years should remove this deficiency. The combination of the detailed spectroscopic data with a computational method which predicts accurately the infrared spectral band positions and their intensities would have a major impact on matrix isolation techniques.

Molecular geometries derived from electron diffraction data

Terminal alkylimido- ligands in transition metal complexes may be either *linear* or *bent* at nitrogen. In the *linear* examples the metal-nitrogen bond is regarded formally as being a triple bond and the nitrogen as a four electron donor, whereas in the *bent* complexes the ligand is viewed as a two electron donor and the metal nitrogen bond is written as a double bond. The choice of the appropriate formulation in a specific complex is frequently guided by the 18 electron rule. For example, in $\text{Os}(\text{N}^t\text{Bu})_2\text{O}_2$ one ligand is *bent* at nitrogen with $\text{Os-N-C} = 155^\circ$ and the second is *linear*. The oxygen atoms of the oxo- ligands and the *bent* imido- ligand are two electron donors and the *linear* imido- ligand as a four electron ligand leading to a total valence electron count of 18. However, in many other examples the formulation is less clear cut and angles between $150\text{-}180^\circ$ have been noted. Recently the electron diffraction study of $\text{Os}(\text{N}^t\text{Bu})_4$ has been completed and the symmetry of the molecule is effectively S_4 and the Os-N-C bond angles are 156° . Therefore, the molecule does not attempt to conform to the 18 electron rule by bending three of the ligands and retaining one as linear, but instead adopts a geometry with all the ligands partially bent.

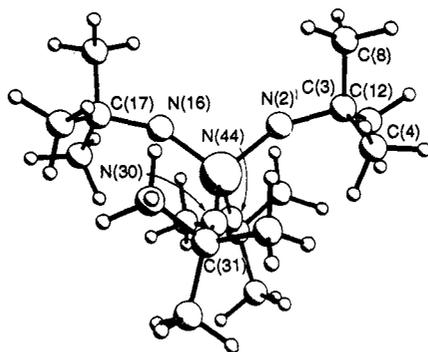


Fig. 1 Structure of $\text{Os}(\text{N}^t\text{Bu})_4$ derived by electron diffraction.

These geometries have been reproduced in Density Functional Theory calculations on $\text{Os}(\text{NMe})_4$ and interpreted in terms of the effect of lowering the symmetry on the interactions between the filled π -orbitals on the ligands and the metal d orbitals. Related calculations on the $\text{Os}(\text{NH})_4$ complex have indicated that the angle at nitrogen is probably very sensitive to the substituents (37)

Trans- Influence in metal nitrido- complexes

The *trans* - influence of metal nitrido- and oxo- ligands in complexes of the early transition metals is well documented and has been the subject of some debate. Electronic arguments based on orbital sharing involving the p-orbitals on the ligands and the metal d orbitals have been developed by Burdett and Shustorovich (38, 39) using perturbation theory ideas. However, steric arguments based on the repulsions introduced by the very short metal-nitrido (or oxo-) multiple bond and the *cis*- ligands have also been proposed (40). This problem has been reinvestigated using Density Functional Theory calculations (41). These calculations have reproduced the observed structures very well and have quantitatively established the relative importance of the steric and electronic effects. The effects of changing the ligands in the *cis*-positions have also been investigated.

Summary and conclusions

Density functional theory presents a comparatively new method for the theoretical description of atoms, molecules, solids and surfaces. Its main advantage over the conventional *ab initio* methods arises because it is computationally more efficient whilst yielding results of comparable accuracy to Hartree-Fock calculations. During the last few years the quite crude local density approximations (HFS or $X\alpha$ and LDA methods) have been further developed and non-local extensions have been included. Furthermore, DFT has been extended to excited states, thus removing its disadvantage of being basically a ground state method.

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