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The role of density functional theory in chemistry: Some historical landmarks and applications to zeolites

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Dedicated to Dr Annick Goursot in honor of her 60th birthday.

Abstract

Density functional theory (DFT) has progressively emerged in the last 40 years as a leading methodology for the modelling and simulation of chemical systems. In this paper, some historical landmarks in the development of this method are outlined, emphasizing on its main characteristic being an electron density-based theory. This is in contrast with wavefunction-based methodologies which were exclusively employed previously. Interestingly, DFT has been first applied to solids, with a rather late recognition by chemists and molecular scientists. After this historical survey, several applications of DFT to the structure and properties of zeolites are reviewed as a tribute to Dr Annick Goursot.

Keywords: Density functional theory; Historical landmarks; Zeolites; Magnetic properties; A. Goursot contributions

1. Introduction

It is an indisputable fact that computational chemistry (CC) has become nowadays a well-accepted partner of experimental chemistry. CC is a very broad topic, which has been the subject of recent textbooks [1–4]. We shall limit ourselves in this article to the part devoted to the development of modelling and simulation of molecules and materials using quantum methods. More specifically, we wish here to retrace the main steps of the development of a quantum mechanical method, which is universally used today, namely density functional theory (DFT) [3,5]. The history of this methodology has followed an exciting path, being the subject of multiple debates and controversies among theoreticians. However today, everybody agrees that it is an indispensable tool for most applications in chemistry and physics. First, the characteristics of DFT, as compared with more traditional quantum chemical methods, will be briefly reviewed. Then some of its most prominent applications to zeolites will be outlined.

Before focusing on DFT, it is worthwhile to recall the basic features of ab initio methods traditionally used in quantum chemistry. The common goal of conventional ab initio methods consists in solving the Schrödinger equation, within the Born–Oppenheimer approximation:

$$\hat{H}\Psi = E\Psi \quad (1)$$

$\hat{H}$ is the Hamiltonian of the system

$$\hat{H} = \hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{nn}} \quad (2)$$

where $\hat{T}_{\mathrm{e}}$, $\hat{V}_{\mathrm{ee}}$, $\hat{V}_{\mathrm{ne}}$, and $\hat{V}_{\mathrm{nn}}$ are the kinetic energy, electron–electron repulsion, electron–nucleus attraction, and nucleus–nucleus repulsion operators, respectively. E is the total energy, and Ψ is the N-particle wavefunction. The term ab initio means that no empirical parameters are introduced to solve Eq. (1). Practically, the fundamental principles of most ab initio methods are based on the Hartree–Fock (HF) approximation, which is central to chemistry. Within this approximation, the wavefunction Ψ is represented using a Slater determinant of one-electron wavefunctions ψ_i, leading to the HF equations

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{eff},i}^{\mathrm{HF}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \quad (3)$$

where ∇^2 is the laplacian operator and $v_{\mathrm{eff},i}^{\mathrm{HF}}$ is the effective HF operator:

$$v_{\mathrm{eff},i}^{\mathrm{HF}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{x},i}^{\mathrm{HF}}(\mathbf{r}) \quad (4)$$

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In Eq. (4), v_{ext}, v_{H}, and $v_{\mathrm{x},i}^{\mathrm{HF}}$ are the external, Hartree, and non-local exchange potentials, respectively. ε_i is the eigenvalue of electron i in spin–orbital ψ_i.

The problem is that HF does not account for electron correlation due to the rigid form of the single determinant wavefunction. Indeed, to solve the HF equations, the assumption has to be made that each electron interacts with the average potential generated by the other ones, neglecting thus the instantaneous repulsion (i.e. the Coulomb correlation). To take correlation into account, it is necessary to go beyond the HF approximation and to make use of the so-called post-HF methods, such as configuration interaction, coupled-cluster or Møller–Plesset perturbation theory [1]. In post-HF methods, the wavefunction is generally represented by a linear combination of determinants accounting for correlation. Moreover, whereas the post-HF methods offer a systematic way to improve the accuracy of the results, they scale as fifth or even higher power with the size of the system, implying then a considerable computational effort.

For these reasons, density functional theory is nowadays a valuable alternative for including correlations effects, without using intricate wavefunctions methods. Indeed, the basic idea of DFT is to replace the complicated N-electron wavefunction by the electron density ρ as a basic local variable. As demonstrated by the theorems of Hohenberg and Kohn [6], this fundamental change of variable can be done without loss of rigor. These authors proved, indeed, that the electron density ρ can determine, in a unique way, all the properties of the system. They also demonstrated that the total energy of the system is stationary with respect to the density ρ (i.e. the minimum of the total energy functional $E[\rho]$ is obtained when evaluated using the exact density of the ground state). Unfortunately, the Hohenberg–Kohn theorems do not provide the exact form of the total energy functional $E[\rho]$. Among the different components of the total energy, the exact density functional forms of both kinetic and exchange-correlation terms remain unknown. To circumvent the problem of the kinetic part (much larger than the exchange-correlation one), Kohn and Sham (KS) [7] proposed to introduce a set of fictitious one-electron wavefunctions ψ_i to build a Slater determinant. This leads to the KS equations

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}^{\mathrm{KS}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \tag{5}$$

which are HF-like equations (Eq. (3)), $v_{\mathrm{eff}}^{\mathrm{KS}}$ being the effective KS operator

$$v_{\mathrm{eff}}^{\mathrm{KS}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{xc}}^{\mathrm{KS}}(\mathbf{r}) \tag{6}$$

where v_{ext}, v_{H}, and $v_{\mathrm{xc}}^{\mathrm{KS}}$ are the external, Hartree, and exchange-correlation potentials, respectively. The electron density ρ is then obtained as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \tag{7}$$

The only unknown part in the KS scheme of DFT is thus the exchange-correlation part, for which many approximations have been proposed [3,5].

The appearance of the KS version of DFT resulted in a clash, which immediately divided the community of quantum chemists into two opposite groups: the one using the traditional ab initio methods and the other using the KS equations. During the 1970s and 1980s there were strong oppositions between the two communities. As it has been mentioned above, the wavefunction-based methods allow in principle to gradually and systematically improve the level of calculations by using linear combination of Slater determinants. The problem is that satisfactory improvements are generally intractable for systems larger than, say, 10–15 atoms. On the other hand, DFT-based methods are readily applicable to much larger systems with an accuracy comparable to second-order Møller–Plesset perturbation theory, though it is difficult to carry out a gradual and systematic improvement of exchange-correlation potentials. It is interesting to quote here long and vivid discussions between the late Demuynck and one of us (J.W.) about "the cleaner way to improve results in ab initio, but the unreasonable computational effort so involved, as compared to the approximate level of the KS Hamiltonian allowing to rather easily carry out calculations for large compounds, without knowing really how to improve them if needed" [8]. To make a long story short, these arguments between the two communities, have now significantly decreased, becoming irrelevant, and DFT has finally obtained recognition and acceptance as illustrated by the 1998 Nobel Prize attributed to both Kohn and Pople [9,10].

2. Some historical landmarks

It is generally accepted that electronic structure calculations trace back to the early 1930s when Dirac [11] and Wigner and Seitz [12,13] suggested approximations for the self-consistent field in which each individual electron of a molecule or a solid is moving. These authors addressed the problem of the exchange energy of the Thomas–Fermi atom, leading to a local expression in 4/3 power of the electron density. Then, in the late 1930s, Slater proposed a scheme of spherically symmetric atomic potentials embedded in a region of constant potential expanded in plane waves [14]. This method, later used to calculate energy bands of crystals, was called the augmented plane wave method, using the muffin-tin or atomic sphere approximation.

However, it is only later, in 1951, that Slater proposed the so-called Hartree–Fock–Slater [15] approximation as a simplification of the Hartree–Fock method. The idea was to approach the complicated non-local Fock exchange operator $v_{\mathrm{x},i}^{\mathrm{HF}}$ of the one-electron HF Hamiltonian by an average local $v_{\mathrm{x}}^{\mathrm{S}}$ potential. This derivation represents actually a generalization and extension of Wigner and Seitz concepts. In 1952, the first applications to solids using the $v_{\mathrm{x}}^{\mathrm{S}}$ potential appeared (see Refs. [16,17] for examples and Ref. [18] for a review). In 1954, Gáspár [19] questioned the magnitude of the Slater exchange term in the Hamiltonian and obtained $(2/3)v_{\mathrm{x}}^{\mathrm{S}}$ by varying the spin–orbitals to minimize the total energy. The situation remained as such until, between 1965 and 1968, several theoreticians performed calculations by multiplying the exchange potential by different values called α. Several factors other than Slater's ($\alpha = 1$) and Gáspár's ($\alpha = 2/3$) have been considered, in order to improve the results of model calculations, leading to the Xα equations, and Ref. [20] reports such results. In the meantime, the original muffin-tin approximation of Slater [14] was generalized for molecular clusters by Johnson [21]. The multiple scattering-Xα (MS-Xα) method, resulting from this development, is thus based on the local Hartree–Fock–Slater approximation, whose eigensolutions are found by using the multiple-scattering approximation. This important step represented historically the first adaptation of a solid-state physical method to molecular systems. The α exchange parameter was later optimized for free atoms, leading to better results for atomic and molecular properties [22]. In 1992, Chermette published a detailed review of the methodology and major applications of the MS-Xα method [23].

On the other hand, density functional theory started from the famous 1964 paper by Hohenberg and Kohn [6] and its chief method of implementation as derived in the 1965 paper by Kohn and Sham [7]. In this work, it is shown that a convenient DFT approach amounts to solving Schrödinger-like one-electron equations incorporating an exchange-correlation potential in the Hamiltonian. In a similar way as Gáspár [19], Kohn and Sham [7] obtained $(2/3)v_x^S$ for the exchange potential. In addition, they formally considered the introduction of a correlation potential. It should be noted however that, as early as 1961, self-consistent-field calculations including an approximate correlation potential in addition to the exchange one had already been performed [24].

With the derivation of Kohn and Sham, it was also realized that the Xα equations are equivalent to the well-known local density approximation (LDA) if correlation is ignored. Even though both Hohenberg–Kohn and Kohn–Sham papers have been subsequently shown to have an enormous importance for chemistry, they were only lately recognized by the community of theoretical chemists. Meanwhile, the MS-Xα method received much more attention: for example, in 1970, Johnson and Smith addressed for the first time polyatomic molecules such as perchlorate and sulphate ions [25]. A landmark application of MS-Xα was the investigation for the first time by Johnson and Smith of the electronic structure of a coordination compound, namely the permanganate ion [26]. Since then, the interest in the MS-Xα method for calculating the electronic structure of transition metal complexes increased rapidly and realistic results were soon obtained [27,28].

This was the starting point for a broad range of MS-Xα applications, including valence band and ESCA photoemission spectra [29,30], chemisorption and catalysis [31], geometrical and electronic structures of metal clusters [32] or metal dimers [33] as well as inclusion of relativistic corrections [34]. Further ambitious investigations were devoted to the study of biosystems such as the ferrodoxin active site [35] or porphine systems [36]. Finally, in the late 1970s Case and Karplus developed a general formalism and performed the first one-electron properties calculations using the MS-Xα method [37]. Besides, their contributions constituted a basis for numerous further publications of molecular properties such as hyperfine tensors [38–40] or electrostatic potentials [41,42].

Despite its success in describing one-electron properties of molecules and solids, the MS-Xα method was unreliable in the description of geometries, mainly due to the muffin-tin approximation. An improvement was suggested by Slater so as to use overlapping atomic spheres [43]. However, a much more significant progress consisted in the introduction of the LCAO (linear combination of atomic orbitals) scheme, based on the use of either Gaussian [44,45] or Slater [46] orbitals. Important methodological developments have then been possible, allowing the computation of properties for large systems employing both Xα and, later, DFT-based methods. On the other hand, the fitting of electron density introduced first by Baerends et al. [46] in the discrete variational method [47], allows to reduce the scaling of the computational effort from N^4 (N being the number of electrons) into an N^3 one, without a loss of accuracy. Sambe and Felton [48] proposed to fit also the exchange potential using an entire set of auxiliary functions, in addition to the electron density fitting. The contribution made by Dunlap et al. [49] in improving the fitting procedure allowed for more accurate total energies (see also the contribution by Ipatov et al. [50] in this issue).

It is interesting to note that, during many years, Xα was presented as an independent self-contained method, and it is only in 1977 that the review of Connolly [51] revealed that it was actually an approximation to an 'exact' density functional theory.

On the other hand, physicists paid an early attention to DFT. The first Kohn–Sham LDA calculations on atoms were carried out by Tong and Sham in 1966 [52]. In 1967, papers reporting calculations on solids using the Gáspár–Kohn–Sham potential for the exchange (with or without a correlation potential) appeared, and the work of Kohn and Sham [7] started to be frequently cited (see, e.g. Ref. [53]). However, it is only in the 1970s that theoreticians started to systematically develop local correlation functionals for calculations on solids in the framework of Kohn–Sham equations [54,55].

From a chemical point of view, the pioneers in the application of the density functional concept, Xα practitioners excepted, were Nikulin and collaborators [56,57] and Gordon and Kim [58]. In a series of papers starting in 1970, these authors considered rare gas and ion–ion interactions, taking into account three-body effects. Introduction of gradient corrections to the exchange-correlation functional has then been considered [59], which led to several difficulties. Therefore, by the middle of the 1970s, both the successes and the limitations of the KS-LDA method started to be realized.

Initiated by a calculation on H_2 in 1976 [60], there has been a series of impressive Kohn–Sham-type DFT calculations on molecules performed by Gunnarsson et al. [61]. These results show that the KS-LDA method is able to describe molecular bonding reasonably well, which is in contrast with the well-known non-bonding effects in the Thomas–Fermi theory. By the early 1980s the first reviews on DFT appeared (see, e.g. Ref. [62]), alerting the chemical community to "the promise and the charm of density functional theory of electronic structure of atoms and molecules" [62]. It is interesting to also note in this respect the comments made by Parr in 1983 [62]: "There seems to be no reason such methods should not be regarded as becoming competitive with traditional wavefunction methods for determining ground-state molecular properties".

The 1980s have witnessed continuous developments of DFT, in particular of new exchange and correlation functionals, trying to incorporate the non-local effects of the correlation. Indeed, quite soon, it was recognized that the local exchange energy term was introducing a substantial error in the total energy. The so-called generalized gradient approximation model of Perdew and Wang [63] initiated then a long series of gradient corrected functionals, which led to much more accurate energetic properties. Another class of functionals, referred to as hybrid functionals [64], incorporates a mixing of both DFT and HF exchange. This includes the B3LYP functional [45], which remains one of the mostly used in chemistry. This development is certainly at the origin of the growing popularity of DFT calculations for organic and inorganic molecules. Another important development was performed in 1985 by Car and Parrinello in the form of an elegant molecular dynamics scheme based on DFT [65]. More recently, in the early 1990s, the first DFT codes became broadly available. In particular, the first DFT option in the widely used Gaussian program [45] and ADF code [46,66] became available in 1992. Here again this step contributed considerably to the wide use of DFT in modelling and simulation applications. It is impossible to review here all significant applications and performances of DFT in the 1990s and 2000s as they are much too numerous. The interested reader is referred to, e.g. the excellent textbook of Koch and Holthausen [3] and review articles [67–70]

3. Applications to zeolites: a tribute to Dr Annick Goursot

In the 1990s, DFT methods have become de facto the standard techniques for routine modelling structures and properties of coordination compounds, organic, organometallic and inorganic systems, clusters, catalysts, new materials, surfaces, etc. An impressive number of papers have been recently published showing, for example, that DFT methods lead to quantitatively accurate results for the structures [67], bond energies [71], vibrational frequencies [72], NMR chemical shifts and ESR tensors [73], reaction mechanisms implying homogenous catalysis [74,75], Ziegler–Natta catalysis [76], surfaces [77], zeolites [78], or biochemical systems [79], just to quote a few successful applications of DFT.

We would like to concentrate here on zeolites and on the prominent role Dr Annick Goursot has played in DFT investigations on these systems. Zeolites are crystalline microporous aluminosilicates [80] which are used in a wide variety of industrial applications, and the prediction of their structures and properties is essential in many respects. DFT has proved to be an efficient methodology for theoretical studies on these systems, as exemplified, e.g. by the recent publications of Mora-Fonz et al. [81] on the formation of their cyclic structures, of Datka et al. [82] reporting the activation of C=C bonds by Cu^+ ions in zeolites, and of Barbosa and van Santen [83] emphasizing the influence of the zeolite framework geometry on the activation of C–H and H–H chemical bonds by the $[ZnOZn]^+$ oxycation. It is also important to quote here the studies of Davidova et al. [84] on the nature of the Cu^+–NO bond at different types of Cu^+ sites in zeolite catalysts, the investigations of Lesthaeghe et al. [85] describing the bifunctional acid–base properties of amine-substituted zeolites and the calculations of Baute et al. [86] on carboxylate binding in copper–histidine complexes in zeolite Y. Let us note that the publications reported here are only part of the numerous DFT studies reported on the catalytic properties of zeolites.

The early publications of Dr Annick Goursot on zeolites trace back to the 1980s with some attempts to correlate the acid strengths in offretite with the main features of their molecular electrostatic potentials calculated with extended Hückel wavefunctions [87,88]. Then, she turned in the 1990s to numerous DFT investigations of the structure, stability and adsorption properties (see Fig. 1) of a number of zeolites (see, e.g. Refs. [89–94]). In the mid-1990s, she investigated the structural parameters and the energetic of offretite [89–91] using the local density approximation within the framework of Car–Parrinello method [65]. In the meantime, the substitution of silicon by aluminum at different tetrahedral sites of zeolite-β and the influence of the counter ion were performed for the first time at a correlated level of theory [92]. These preliminary DFT studies of zeolites were followed by analysis of the adsorption properties of small probe molecules onto various zeolite types [93,94]. Using an embedded cluster approach, these studies revealed an appealing correlation between the

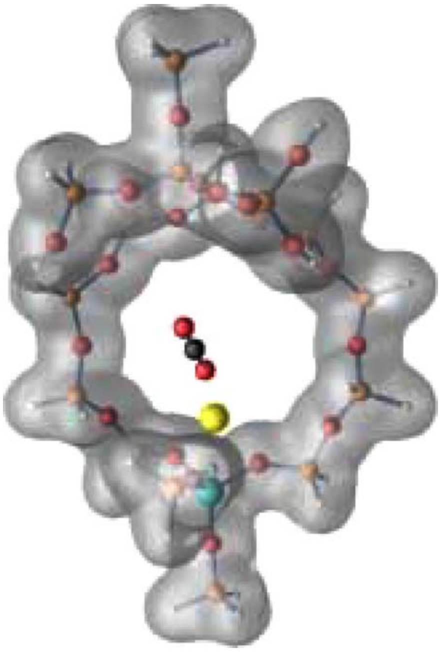

Fig. 1. Structure and isoelectronic density surface (in grey) of a cluster model of ZSM-5 zeolite with CO_2 adsorbed on a lithium cation.

structure of the zeolite and its corresponding adsorption properties.

In the last few years, Dr Annick Goursot started extensive investigations of the magnetic properties of zeolites. Over the last 10 years, theoretical prediction of magnetic properties has become indeed an essential tool for the chemical community. Although, no reasonable (or efficient) exchange-correlation current density functional has yet been proposed, the application of uncoupled DFT for the computation of NMR chemical shifts has been rather successful [95]. The calculation of NMR properties of zeolites may not only be used as a tool to characterize these systems, but it is also essential for the understanding of their catalytic behavior. In this context, solid-state NMR techniques such as magic angle spinning (MAS) has been of great importance. In particular, ^{29}Si NMR spectra, carries the richest information due to its sensitivity to local geometries, which produce a wide range of ^{29}Si chemical shifts [96–98]. In the mid-1990s Sauer and his collaborators initiated the calculation of ^{29}Si, ^{1}H and ^{17}O NMR chemical shifts for zeolites [99,100] and zeolites precursors [101] at the coupled Hartree–Fock-GIAO level. They demonstrated the crucial importance of both the size of the model cluster and the accuracy of the structural parameters to obtain converged NMR ^{29}Si chemical shifts. Predictably, it was Goursot and collaborators who performed the first DFT-based ^{29}Si and ^{27}Al chemical shifts calculations on the distinct crystallographic nuclei sites of a zeolites-β [102] and on the simpler zeolite mazzite [103,104]. As a result, they opened a new route to the determination of zeolite structures and brought new insight into their catalytic reactions within the DFT framework.

To overcome the finite-size cluster limitation, Mauri and collaborators [105,106] recently developed a novel promising methodology to calculate NMR shielding within periodic boundary conditions using pseudo-wavefunction. Based on DFT, this gauge-including projector augmented wave (GIPAW) method has already considerably improved the theoretical ^{17}O NMR spectra of the zeolites faujasite and ferrierite as compared to chemical shielding calculated on single cluster zeolite models [107].

Although the static theoretical investigation of chemical shielding on nuclei site of zeolites provide various informations which nicely complement experimental spectra, the modelling of the dynamical aspect of the interaction between the guest molecule and the zeolite and/or the solvent represents a logical route for improvement. Using a DFT-based Born–Oppenheimer dynamics approach, Goursot and collaborators [108] evaluated the evolution of the ^{29}Si NMR chemical shifts of the solvated smallest zeolite precursors, $Si(OH)_4$. This preliminary study concluded that the explicit inclusion of water–$Si(OH)_4$ and water–water interaction is needed to obtain ^{29}Si NMR in close agreement with experiment. In addition, the solvent was shown to significantly influence the structural ⟨SiOH⟩ angles and electronic (polarization) parameters of the monomer, through a competition between internal and external hydrogen bonds. In the particular context of catalytic properties of zeolites, there is no doubt that DFT-based ab initio molecular dynamics will provide the most appealing results in the near future.

4. Conclusions

In this paper we first aimed to address the early ideas and theoretical developments that led to the present recognition of DFT as an indispensable tool in computational quantum chemistry. Several controversies and difficulties directly related to the emergence of DFT methods have been outlined and discussed. It is remarkable that important methodological developments in DFT took place in the last 40 years, to such an extent that it has become today, in addition to practically all fields of chemistry, a very promising technique in drug design, combinatorial chemistry, materials science, etc. Such a rapid emergence of a new modelling and simulation procedure is to our knowledge unprecedented in the whole history of quantum chemistry. Finally, DFT applications to zeolites have been presented so as to substantiate these optimistic statements. Emphasis has been placed on the achievements of Dr Annick Goursot as a tribute to her long-standing involvement in this field. In our opinion, there is no doubt that due to progresses in both methodology and computer technology, DFT modelling and simulations will be intimately connected with the future developments of molecular sciences, in particular of materials such as zeolites.

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