

# Density functional calculations for polymers and clusters – progress and limitations

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## Abstract

The applicability of density functional (DF) methods has progressed greatly since the first workshop of this series ten years ago. Applications that show both the successes and the limitations can be found in the fields of: (a) the structures of the isomers of atomic clusters, and (b) the structure of organic molecules and polymers, and their reactions with additional molecules. We shall review some of the results and the lessons to be learned from them. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The last decade has seen many changes in the world of density functional (DF) theory and its applications. It is not surprising that the method has held its place as the basis of most calculations in condensed matter science that are free of adjustable parameters. However, its acceptance by large elements of the chemical community in the early 1990s followed many years where DF theory and its results had been treated with scepticism and worse. There have been improvements in approximations still needed for the exchange-correlation energy, and the overall reliability and predictive power of DF calculations have followed.

In this contribution, we examine some specific cases that exemplify these changes. We have chosen calculations in two main areas: Firstly, it is possible to study many isomers of atomic clusters, to examine their relative energies and their vibration frequencies, and to make comparisons with experimental data where available. Secondly, we show that we can study the structure, energetics, and reactions of organic molecules. It has proved to be possible to perform calculations on systems with more than 100 atoms and to map out reaction paths that have convinced experts of their relevance. Even this brief survey shows, however, that the developments of the past decade point to serious problems as well as interesting results. They indicate the limits on the applicability of the DF method, and that some problems require extensions of the method or other approaches entirely.

The calculations described here use methods that have become widespread during the past ten years. The structures and relative energies presented below were determined using all-electron

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DF calculations with an extended Gaussian basis set [1]. The local spin density (LSD) approximation to the exchange-correlation energy was used [1], together with the functional form associated with the names of Becke and Perdew [2,3]. The remaining calculations were performed using the combined molecular dynamics/DF developed by Car and Parrinello [4,5]. The use of “simulated annealing” allows us to avoid unfavorable local minima in the energy surface.

## 2. Cluster calculations

### 2.1. Carbon clusters

Carbon clusters have been the subjects of intense study since 1984, when they were first generated as cations with up to 190 atoms [6], and particularly after the identification of the football-like structure of  $C_{60}$  [7]. An extensive study of isomers of  $C_n$  with even values of  $n$  up to 32 has led to some interesting results [8]. In Fig. 1 we give results for  $n = 22$  as an example.

There are isomers with stable structures corresponding to several *types* of structures, including rings, cages, and planar (graphitic) structures. It has often been noted that it is not possible to construct a cage-like structure of pentagons and hexagons with 22 vertices, but this does not prevent cages with faces with four and six vertices from being among the most stable. The calculations for the local density (LD) and Becke–Perdew (BP) functionals show marked differences. Within a given structural *type* (e.g., cages or graphitic structures) the relative energies of different isomers are almost the same. This is shown, for example, by the parallel lines connecting the energies of the different cage structures. However, the LD approximation favors cage structures over the monotonic ring by approximately 4 eV, which is a dramatic effect. The effects of gradient corrections increase as the average coordination number decreases, and they change the predictions of the most stable isomers in several cases.

The unambiguous experimental determination of the structure of the most stable isomer of a given cluster would provide a direct test of the rel-

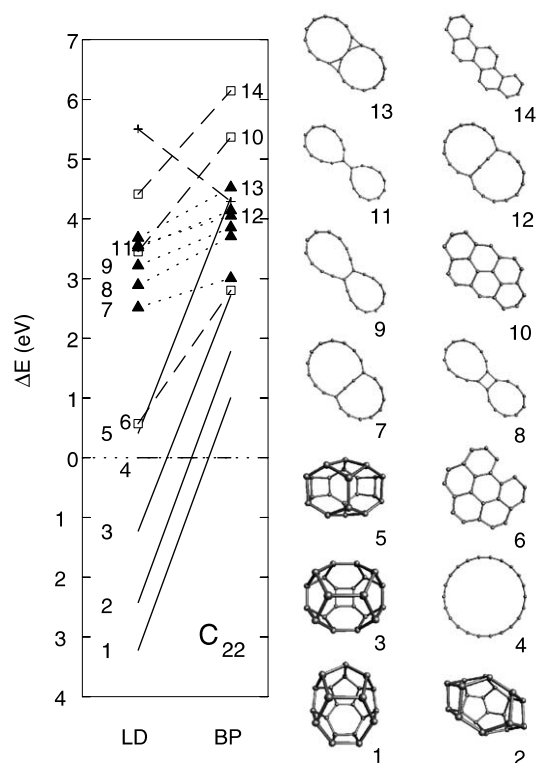


Fig. 1. Structures and cohesive energies – relative to the monocyclic ring – of isomers of  $C_{22}$ . LSD and BP values are connected by lines representing the structural type: full, cages; dotted, double rings; crosses, chains; squares, graphitic; dash-dotted, monocyclic rings. The structures are ordered from below according to the LSD energies.

ative merits of different approximations to the exchange-correlation energy. However, this is an immensely difficult task. Clusters often have very short lifetimes, so that vibrational spectroscopy is usually difficult. The measurement of the ionization energies of the anions (also called the vertical detachment energy, VDE), where the kinetic energy of the emitted photoelectron is determined, is a promising technique.

### 2.2. Sulphur clusters

Photoelectron spectroscopy of beams of sulphur anions  $S_n^-$  has been carried out [9], and we shall mention one particular aspect of the results here. DF calculations of the vertical detachment energies showed pronounced differences for “ring”

and “chain” structures. The former show almost constant VDE with increasing cluster size, while the values for the chains increase initially and then saturate. The VDE for the ring structures are typically 1 eV less than those of the chains.

Measurements of the VDE [9] were in remarkably good agreement with calculated values, but there was one feature of particular interest. Depending on the experimental conditions used to generate the beam, two quite different time-of-flight spectra were obtained for  $S_6^-$  and  $S_7^-$ . A comparison with the calculations showed that different cooling rates in the beam led to the generation of different isomers. Rapid cooling favors chain production, slower cooling the formation of rings. This is a direct demonstration of the fact that a low total energy is not the only criterion for the observation of a particular isomer. The ring structures are more stable than the chains, but there are many more possible structures of the latter type. Rapid cooling of the beam of cluster anions will result in chains, even if they are energetically unfavorable

### 3. Organic molecules and polymers

Organic chemistry has inexhaustible scope, and the move from the familiar world of homonuclear clusters of main group elements is not easy. Approximations for the exchange-correlation energy functional must be tested in new environments, such as the weak bonds between organic groups or the ubiquitous hydrogen bonds.

In our group we have performed calculations on numerous small organic molecules [10], and we have found that many aspects of the results match our experience in other systems. Geometric structures and vibration frequencies are usually described satisfactorily, as are the relative energies of different conformers and the singlet–triplet splittings where experimental or theoretical results are available for comparison. On the other hand, the choice of functional led to dramatic changes in the description of weak intermolecular bonds.

A clear test case is offered by polyethylene, which crystallizes in an orthorhombic structure (Fig. 2) and has been studied by both X-ray and

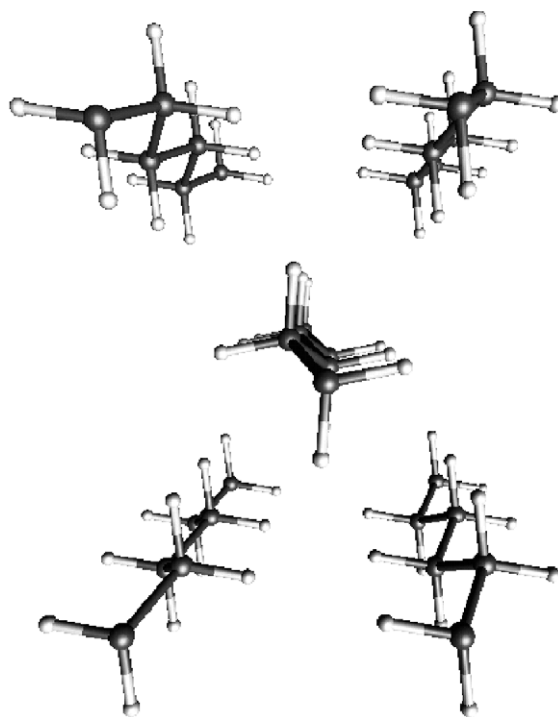


Fig. 2. Orthorhombic crystalline polyethylene viewed along the axis parallel to the chains. Carbon atoms are grey, hydrogen atoms white.

neutron diffraction. The structures of the individual chains are reproduced well by the LD and BP functionals, and also by the more recent form developed by Perdew, Burke, and Ernzerhof (PBE) [11]. Like the BP functional, this form has a correction to the LSD approximation that depends on the gradient of the local density. However, it incorporates an accurate description of the linear response of the uniform electron gas, and it has a smoother potential and the correct behavior under uniform scaling.

The calculated separation between the chains is less than the experimental value if the LD approximation is used, but there is no binding at all with the BP approximation. A similar result was found in calculations of the interactions between two benzene rings [12]. If we use the PBE approximation, there is a weak minimum in the total energy at an interchain separation about 12% larger than the measured value. The incorporation of dispersion forces, absent in all three

approximations, would improve the result. This test of the PBE approximation for organic molecules was sufficiently encouraging that we adopted it in the calculations described below.

A severe test of any method of calculating molecular structures is provided by carbonic acid ( $\text{H}_2\text{CO}_3$ ) and its clusters. The interaction of carbon dioxide with water plays a central role in many biological, ecological, extra-terrestrial (particularly cometary), and industrial processes. Carbonic acid ( $\text{H}_2\text{CO}_3$ , denoted CA), formed by the hydration of  $\text{CO}_2$ , dissociates rapidly in water, so that the evidence for its existence is often indirect. The gas phase reaction:



has an activation energy of over 50 kcal/mol, although it is catalyzed by the presence of water. For a survey of the literature, see [13].

We have carried out an extensive series of DF calculations on clusters of carbonic acid  $\text{H}_2\text{CO}_3$  with up to five structural units. The hydrogen-bonded, planar chains shown in Fig. 3 follow the pattern found in the dimer (Fig. 3(a)), a hydrogen-bonded pair of the *trans-trans* isomer of the monomer. We know of no experimental evidence for the existence of such long chains in carbonic acid, but the chain structure is stable against

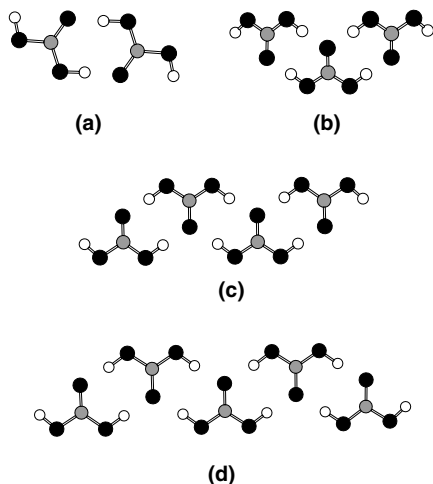


Fig. 3. Structures of planar clusters of carbonic acid: (a) dimer, (b) trimer, (c) tetramer, (d) pentamer. Carbon atoms are grey, oxygen atoms black, hydrogen atoms white.

bending (a structure with  $\sim 20$   $\text{H}_2\text{CO}_3$  units is needed before a ring becomes more stable than a chain), and it has a substantial tensile strength. The structures of the carbonic acid polymorphs, particularly possible three-dimensional forms, remains a challenge to theory *and* experiment.

#### 4. Reaction of polymer segments

The final area we shall examine involves model polymer systems and their reactions with nucleophilic molecules, and we adopt bisphenol-A polycarbonate (BPA-PC) as our prototype. This polymer has many favorable properties, including high stability against mechanical shock, a high melting temperature, and good optical properties. Furthermore, many cyclic oligomers can be prepared, and the cyclic dimer, trimer, and tetramer have been isolated and analyzed spectroscopically [14,15], and the crystal structures of the dimer and tetramer have been determined by X-ray diffraction [15].

The tetramer (Fig. 4) is an ideal model for theoretical studies of the microscopic properties of polycarbonate. It has a very large, open cyclic structure, with a cavity of 14–16 Å and outside diameter of 20.7 Å [15], and the size of the ring (132 atoms) means that there is no hindrance to ring-flipping or *cis-trans-trans-trans* isomerization about the carbonyl group. We have used it in an extensive study of the nucleophilic attack of lithium and sodium phenoxides, as well as phenol, on the carbonate group [16]. The calculations cover the attack of each molecule from inside and outside the ring. They are performed by adopting a single reaction coordinate (e.g., the distance  $R_C$  between the C atom of a carbonate group of the ring and the O atom on phenol or phenoxide).  $R_C$  is reduced from values  $>5$  Å, where the interaction is very weak, in progressively shorter steps until a structural transformation or a large energy increase occurs. For each value of  $R_C$ , we relax *all* other degrees of freedom of the structure until the energy gradients along the unconstrained directions are less than  $10^{-5}$  a.u.

An example of the results is shown in Fig. 4, where LiOPh approaches the cyclic tetramer from

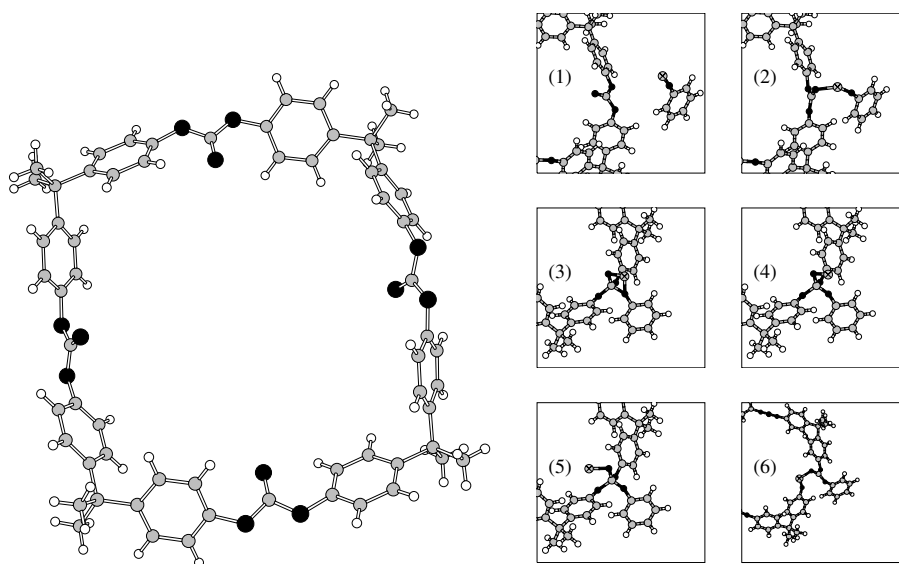


Fig. 4. (Left) Cyclic tetramer of BPA-PC: C atoms, grey; O, black; H, white. (Right) Reaction of LiOPh with cyclic tetramer of BPA-PC. Only part of the ring is shown.

outside the ring. The first stage of the reaction is the formation of a bridge between Li and the O of the carbonyl group, and a small reduction in  $E_{\text{tot}}$  favors a further approach of the molecule to the ring. There follow significant changes in the geometry (particularly in the torsion and bending angles) that allow the reaction to proceed. The change from  $sp^2$  to  $sp^3$  of the electronic configuration of the carbonate C atom is crucial, as the compact surroundings of negatively charged O atoms facilitate the passage of the Li ion around the reaction center. The final state is an open structure with a weak bond between the Li and the new carbonyl group. Thermal effects and the interaction with other carbonate molecules would break this bond readily above room temperature.

This picture is consistent with known information about the reaction. The measured and calculated heats of reaction are very small, and the system is a beautiful example of a “living polymer”. We note that the final product of this reaction is again a system (a longer chain) with a Li ion at the end. This ion can, of course, react with another carbonate group in just the same way, and such a chain reaction can continue. A similar picture is found in the case of phenoxide approach from inside the ring, and in the case of NaOPh. In

the case of phenol, however, the energy cost in bringing the molecule towards the carbonate group is very high, and a reaction cannot proceed. This, too, is consistent with the known properties of BPA-PC, during the production of which phenol is produced and removed.

## 5. Conclusions

The decade since 1990 has seen many developments in DF theory and its applications. Some of these were perhaps foreseeable, others less so. The calculations on carbon clusters with up to 30 atoms do not come as a surprise, although the sensitivity of the energy ordering to the choice of functional was larger than anticipated. On the other hand, the results for sulphur cluster, where experimental parameters can be chosen that favor the production of cluster anions that are not those with the lowest energy, warn against the common assumption that the energetically most stable system will inevitably be favored. One of the difficulties facing cluster science at the moment come from the problems associated with measuring the structures of the isomers and their relative stability.

The sensitivity of results to the choice of functional is also evident in the calculations of intermolecular interactions, as we have seen for some organic molecules. The PBE functional (developed in 1996) appears to describe these interactions adequately, and earlier approximations (LSD and BP) are much less satisfactory. Much effort is currently being expended on developing new functionals, particularly ones that can describe dispersion (Van der Waals) forces. It remains a challenge to find accurate functionals that can be used with systems of many atoms.

It was by no means obvious ten years ago that DF methods would be able to describe reactions of the complexity of that described above, the nucleophilic attack of a group of a polymer segment. Before cheering too loudly, however, we should note the limitations of such calculations. Firstly, their immense demands on computer resources mean that they cannot be used at present for the routine study of complex reactions. Secondly, it is impossible to ensure that the reaction path is close to the optimal. There are numerous minima in the energy surface and the most stable minimum for a given choice of reaction coordinate will be found in few cases. Finally, the reaction of a single molecule with a single chain ignores many effects that may be crucial in studying such reactions in the real world. These reactions typically proceed at elevated temperatures, with the reactants surrounded by other molecules such as solvents. The simulation of such systems, particularly over the longer time scales that are relevant in practice, will require in the foreseeable future the further development of other methods. These include simulations using classical force fields, and we are confident that the energy surfaces calculated using DF methods will play an important role in developing and refining such fields. A first attempt in this direction is described in [17].

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