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Cluster geometries from density functional calculations – prospects and limitations

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Abstract. The use of density functional methods to calculate the structures and energies of clusters of atoms is discussed. Applications to phosphorus and sulphur show that unexpected structures occur even in small clusters. Calculations of many isomers of carbon clusters from C_4 to C_{32} (n even) show striking results, with periodic patterns in several structural classes. Gradient corrections are significant, but regular within a given cluster type. Some strengths and limitations of the approach are discussed.

PACS. 36.40.-c Atomic and molecular clusters – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials

1 Introduction

The organizers have asked me to make an assessment of the status of cluster calculations using density functional techniques. I shall restrict myself to clusters of a single element, and focus on specific problems: How can one determine the stable geometries of a cluster of n atoms, how can one determine the most stable of these arrangements, and how reliable are density functional methods in determining them? After outlining the problems facing *any* method of calculating these properties, I shall indicate where the advantages (and disadvantages) of the DF approach lie. I shall show examples where DF calculations led to unexpected results, and show that results for carbon clusters ($n = 4 - 32$) underscore both the strengths and weaknesses of our approach.

2 Structure and function

The motivation behind the study of the geometrical arrangement of any molecular or condensed matter system is the relationship that exists between the *structure* and the *properties* of the material. This is obvious to many physicists and probably all chemists and molecular biologists. In focusing on the geometrical structure and related properties, we address problems that are specific to individual systems. It is not unusual, however, to find fascinating *patterns* in families of related systems. Examples in the world of atomic clusters are aggregates of different sizes of a single element, or of different elements in the same group of the periodic table. For most of these clusters it is difficult to obtain unambiguous structural information, and theory has a particularly important role to play. What problems must we address when calculating the most stable structure of a cluster of atoms?

2.1 Total energy of atomic clusters

In principle, the stable geometries of atoms in any material can be found if we can determine the total energy E of the systems of electrons and ions. We adopt a set of nuclear coordinates $\{\mathbf{R}_I\}$, determine E, and repeat the calculation for all possible configurations. The most stable structure is that with the lowest energy. There are two distinct problems associated with this procedure: the calculation of E for a given geometry, and the determination of the most stable amongst all the possible structures.

It would be natural to take advantage of the experience of molecular physicists and quantum chemists and to determine E from the exact many-electron wave function Ψ of the system. Unfortunately the numerical effort required is so great that accurate energies can be found only for systems with relatively few atoms. Nevertheless, the approach remains an essential benchmark in the assessment of approximate determinations of the energy surface $E\{\mathbf{R}_I\}$.

The second problem – the determination of the most stable of the structures corresponding to local minima in the energy surface – is probably even more challenging. The determination of the number of topologically distinct structures (isomers) consistent with a given chemical formula is one of the oldest in chemistry, and it has been known for more than 100 years that the number of isomers increases very rapidly with an increase in the number of atoms n. In the specific case of clusters interacting with pairwise potential of Lennard-Jones type, Hoare and McInnes [1] showed that the number of structures increased from 2 to 988 as n increases from 6 to 13. For clusters of identical atoms interacting with a pairwise potential, Wille and Vennik [2] showed, in fact, that the number of structures grows exponentially with increasing n.

These two problems – the calculation of E for a single geometry, and the determination of the most stable amongst the many possible – are immensely difficult and often underestimated. While a *solution* of these problems is not presently tractable, it is essential to address both. We have used in much of our work the density functional (DF) formalism [3] to evaluate E. The DF approach, with relatively simple approximations for the exchange-correlation energy, provides a tractable method for energy calculations with predictive value in a range of systems. In order to avoid unfavorable local minima in the energy surface, we (and others) have often used a "simulated annealing" technique based on the scheme of Car and Parrinello [4]. This combines molecular dynamics (MD) with energy and force calculations using DF Methods. The result is a method that is free of adjustable parameters, and the use of elevated temperatures allows an efficient sampling of the potential energy surface.

2.2 Some cluster energy surfaces

In this section I give three examples from our work that should remind us that the cluster world is full of surprises. The first two relate to small clusters of phosphorus [5], the second to clusters of sulphur [6].

I have heard on several occasions that the determination of global minima should be easier than the above arguments suggest, because the lowest energy minima are surrounded by the largest basins of attraction. This is definitely not the case in P_4, which has been known to have a tetrahedral structure for over 60 years. The basin around this minimum is, however, very narrow. If four P atoms are placed at random positions, they are more likely to lie in the basin of a much less stable "butterfly" (C_{2v}) structure.

I have also been told on numerous occasions that the determination of low-lying minima is aided by "intuition", which can apparently tell us that some structures will not be favoured. A counter-example is provided by the P_8 cluster, which was assumed for decades to be perfectly cubic. This structure has the three-fold coordination favoured by this element, and a low strain should result because the p_x, p_y, and p_z orbitals are mutually orthogonal. The "simulated annealing" strategy resulted, however, in two much more stable structures [5]. The most stable – a C_{2v} structure obtained by rotating one edge of the cube through 90° – is 1.7 eV more stable and is, in fact, a structural unit of the violet allotrope of phosphorus.

The final example provides a demonstration of the fact that the most stable isomer is not necessarily the one that is seen in a measurement. In the case of sulphur anions up to S_9^-, we showed that there were stable anions with 'chain-like' structures as well as the ring structures familiar from studies of the neutral clusters [6]. The structures are shown in Fig. 1, where we also show the corresponding ionization energies, also known as the vertical detachment energies (VDE). The VDE of the rings and chains are strikingly different. The broken rings show almost constant VDE with increasing cluster size, while the values for the chains increase initially and saturate near S_6^-. The comparison with photoelectron detachment spectroscopy measurements [6] proved to be particularly interesting, as two different adjustments of the beam source gave quite different spectra for S_6^- and S_7^-. The remarkably good agreement with the calculated values (see Fig. 1) for both rings and chains indicated that different beam conditions gave rise to different isomers, i.e., it is possible to generate chain-like isomers, even though they are not favoured energetically. The reason is simple: The number of possible open structures is much greater, since the beginnings and ends of the chains are not constrained to coincide, and chain formation will be favoured if the time available for cluster formation is too short to allow annealing.

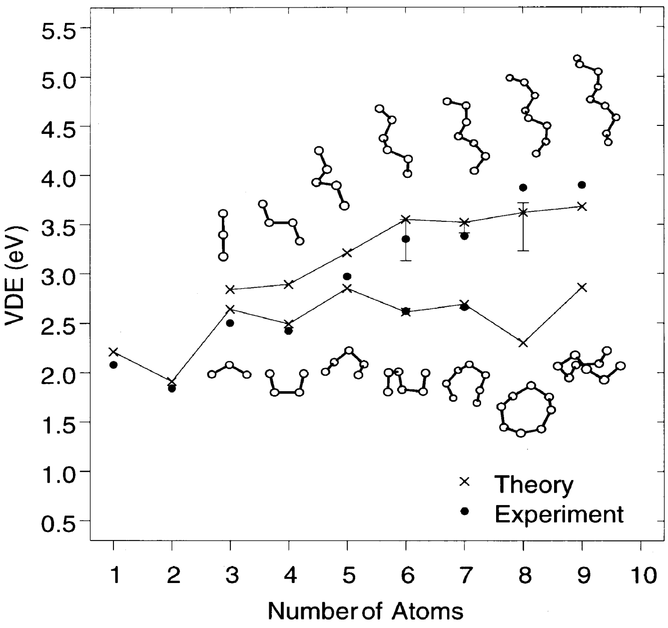

Fig. 1. Vertical detachment energies of sulphur anions S_n^-, $n = 1-9$. Circles: experiment, crosses: calculations, including values for helical chains. The bars cover the values for other chain structures.

3 Carbon clusters, C_n, $n = 4-32$

We now turn to the results of recent calculations on carbon clusters. The identification of carbon cluster cations C_n^+ up to $n = 190$ [7] and the postulation of the "fullerene" structure for C_{60} [8] caused an explosion of interest in carbon clusters. The possible mechanisms for formation of larger carbon clusters – often cagelike structures comprising hexagons and pentagons [9] – has focused attention in turn on smaller clusters and the relative stability of their isomers. The mass spectra for carbon clusters are distinctly bimodal [7], with clusters for $n \geq 32$ occurring mainly for even values of n, while smaller clusters occur for all n. It is often assumed that this break arises from a transition to structures that are formed by pentagons and hexagons [10].

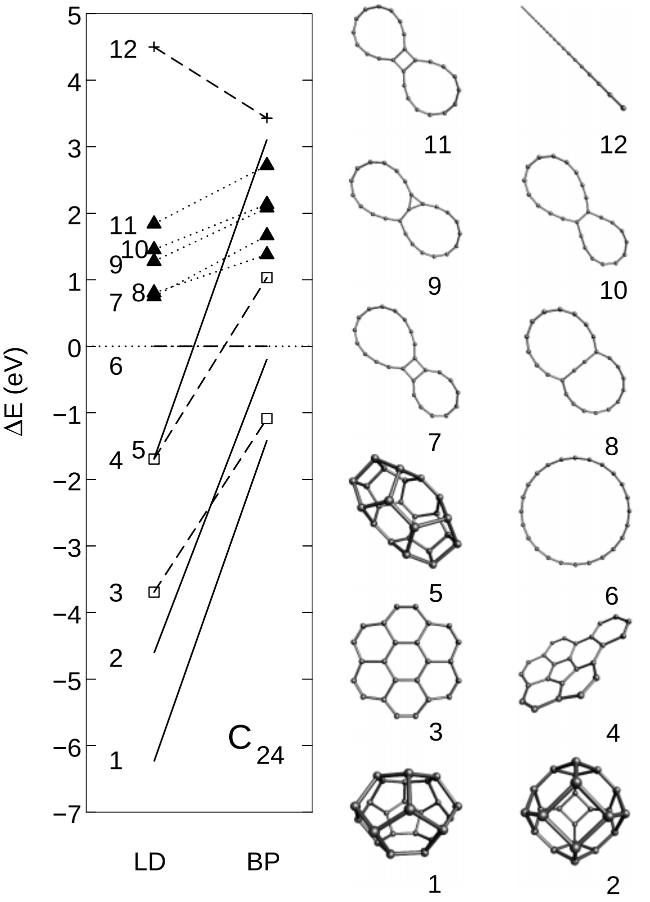

Fig. 2. Structures and energies – relative to the monocyclic ring – of isomers of C_{24}. LSD and BP values are connected by lines representing the structural type: full, cages; dotted, double rings; crosses, chains; squares, graphitic; dash-dotted, monocyclic rings. The structures are ordered from below according to the LSD energies.

A study of many isomers of C_n clusters ($n = 4-32$) has been carried out using DF methods with both LSD and gradient-corrected approximations (BP, [11]) for the exchange-correlation energy. The clusters of between four and ten atoms allow comparison with earlier work, but the existence of stable cage structures for C_8 and C_{10} were unexpected results. The number of possible isomers increases very rapidly with increasing cluster size, and it is not possible to study all in clusters with up to 32 atoms. Nevertheless, the extent of the present survey enables us to identify unambiguously several bonding trends.

The structures and relative energies presented below were determined using all-electron DF calculations with an extended Gaussian basis set [12]. Full details of all clusters will be given elsewhere [13], and we show the results for the representative case of C_{24} in Fig. 2. Energies of different isomers are shown relative to that of the monocyclic ring structures, and the lines joining the LSD and BP values represent the structural *type*: Full lines indicate cages, dotted lines with solid triangles represent double rings, and "graphitic" structures (squares) include both planar ("plate") and bent ("bowl") forms. The isomers of a given cluster are labeled according to the relative energies of the LSD calculations.

The fullerene structure 24(1) is more stable than the other cages 24(2) and 24(5), both of which contain four-membered rings. The graphitic structures 24(3) [D_{6h}] and 24(4) [C_s, the C_{20} bowl with four atoms added to form a "ladle"] are amongst the most stable. The structural difference between 24(3) and 24(4) may be viewed as the transfer of a four-membered unit from the planar structure to form an external ring. The plate structure now has a central pentagon and forms a bowl to lower the strain. The energy difference between these structures is 2.0 eV (LSD).

Graphitic structures and bicyclic rings are found for all clusters, and there are *non-planar* (buckled) forms of each for C_{16} and C_{20}. The monocyclic rings are more stable than the bicyclic forms in all clusters. The bicyclic rings in C_{24} are planar, and all show show low-frequency vibration modes ($\leq 30\,\mathrm{cm}^{-1}$) corresponding to out-of-plane bending. This suggests that they will convert readily to more stable, three-dimensional structures.

The calculated cohesive energies (binding energies per atom) of the most stable isomer of each type are shown in Fig. 3 for all clusters. LSD calculations predict that cages are the most stable isomers for $n \geq 18$, and there are stable cage structures for all $n \geq 8$. C_{24} is the first cluster for which cage structures are unambiguously the most stable in both LSD and gradient-corrected calculations. Figure 3 shows that gradient corrections lower the LSD values of the cohesive energy by ~ 1 eV, a change similar to that found in clusters of other main group elements [14]. However, the effects of gradient corrections on the total energy are quite different for different structural types (see also Fig. 2). They are smallest in cages, followed by the graphitic (plate) and double ring structures, i.e., the effects increase as the average coordination number decreases. There are fewer bonds in the (metastable) linear chains than in the monocyclic rings, and the gradient corrections *reduce* the energy difference between them.

It is clear from Fig. 3 that gradient corrections have a large effect on the relative energies of C_n isomers and change the predictions for the most stable isomers in several cases. The unambiguous experimental determination of cluster structures would then provide a direct test of the relative merits of different approximations to the exchange-correlation energy. Nevertheless, the relative energies of the isomers are remarkably similar *within* a given structural family (the lines connecting LSD and BP results are nearly parallel in all cases), i.e. the bonding errors are similar in similar bonding situations.

This fact has been used by Raghavachari [15] in an interesting study of the low-lying isomers of C_{20}. If we consider "isodesmic" reactions, in which the number of bonds of each formal type is conserved, then errors in energy differences may be minimized. Raghavachari was able to relate the formation energy of the ring isomer of C_{20} to the heats of formation of acetylene and diacetylene, and that of the bowl isomer to those of ethylene and benzyne. The final result was that the bowl and cage isomers are comparable in energy and significantly (~ 1.4 eV) more stable than

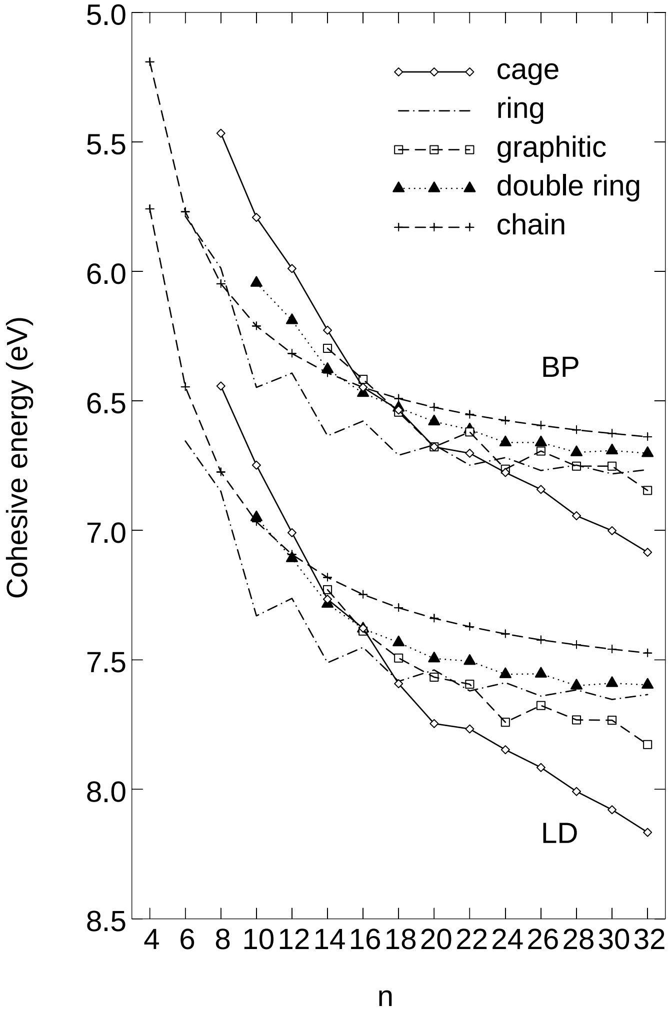

Fig. 3. Cohesive energies of the most stable of different types of C_n isomers. See caption of Fig. 2.

the ring. A suitable choice of reaction paths could provide reliable information in other clusters as well.

There are other trends apparent in Fig. 3. The first is the fourfold ("$n = 4N + 2$", N integer) periodicity evident in the binding energies of the monocyclic rings. This is related to the Hückel rules for the stability of aromatic molecules and was observed long ago in semi-empirical calculations of C_n rings [16]. In the present calculations these rings are "cumulenic" (with identical bond lengths) in C_{14}, C_{18}, C_{22}, ... , but "polyacetylenic" (with alternating bond lengths) otherwise. A similar periodicity is evident in the planar structures with triangular units, such as 24(9). These triangles occur singly in the family $n = 4N$, but in pairs in the clusters with $n = 4N + 2$. Other planar structures show a similar, although weaker, periodicity.

4 Concluding remarks

Cluster science covers an area of immense variety, and I have been able to cover exciting applications of density functional methods to clusters. I have focused here on the structural properties and their determination by total energy calculations. I am convinced that geometric structures are of central importance in this field, and I hope that I have convinced you that we have been surprised many times in the past and can expect the same in the future. In this field, as in most areas, progress will depend on the close cooperation between theory and experiment.

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