Quantum chemical treatments of metal clusters

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This work focuses on finding and rationalizing the building principles of clusters with approximately 300 atoms of different types of metals: main group elements (Al, Sn), alkaline earth metals (Mg), transition metals (Pd) and clusters consisting of two different elements (Ir and Pt). Two tools are inevitable for this purpose: (i) quantum chemical methods that are able to treat a given cluster with both sufficient accuracy and efficiency and (ii) algorithms that are able to systematically scan the \((3n-6)\)-dimensional potential surface of an \(n\)-atomic cluster for promising isomers. Currently, the only quantum chemical method that can be applied to metal clusters is density functional theory (DFT). Other methods either do not account for the multi-reference character of metal clusters or are too expensive and thus can be applied only to clusters of very few atoms, which usually is not sufficient for studying the building principles. The accuracy of DFT is not known \textit{a priori}, but extrapolations to bulk values from calculated series of data show satisfying agreement with experimental data. For scans of the potential surface, simulated annealing techniques or genetic algorithms were used for the smaller clusters (approx. 20–30 atoms), and for the larger clusters considerations were restricted to selected packings and shapes. For the mixed-metallic clusters, perturbation theory turned out to be efficient and successful for finding the most promising distributions of the two atom types at the different sites.

\textbf{Keywords:} metal clusters; density functional theory; genetic algorithms; perturbation theory

1. Introduction

Metals do not form clusters or molecules that are thermodynamically stable under ambient conditions; not a single \(M_n\), \(M\) being any metal, is known that can be kept in a test tube. On the other hand, there is solid evidence that \(M_n\) clusters do exist and can be investigated for every \(M\) and virtually for every \(n\) under suitable conditions: low densities and not too high temperature. This state of affairs is a consequence of the fact that every \(M_n\), with a few possible exceptions, is energetically stable against loss of atoms or fission. Since clusters \(M_n\) may and usually do exist in various isomers, there is a huge number of metal clusters with a broad spectrum of properties. The stability of \(M_n\) towards fission

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implies the solid bulk phase (liquid for mercury) to be most stable; it is, in fact, the thermodynamically most stable phase under a wide range of conditions for all metals.

Typical non-metals show quite different behaviour: the thermodynamically most stable species under ambient conditions are molecules such as H₂, N₂, O₂, O₃, F₂, Cl₂ and so on. The preference for small aggregates is a result of features of chemical bonding and molecular electronic structure such as ‘valence saturation’, ‘directed covalent bonding’ and a relatively large highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gap. This is quite different for metals, where electrons are described by band structures with a partially filled (high-energy) conduction band of delocalized orbitals. This electronic structure leads to a strong tendency for dense packings, i.e. for maximum number of next-neighbour atoms. Metal clusters have—as much as possible—similar properties to the bulk, which always has a finite but small HOMO–LUMO gap, of course.

The small HOMO–LUMO gap of metal clusters affects their electronic structure and the computational procedures appropriate for a theoretical treatment. The electronic structure will typically be of a multiple reference (MR) type; a single Slater determinant like in Hartree–Fock (HF) theory is not a good zeroth-order approximation. Various methods are available that can cope with this situation. Some typical applications concern small clusters of groups Ia, Ib and IIa (Bonacic-Koutecky et al. 1991), a calculation of U₂, which shows an almost unbelievably complicated electronic structure (Gagliardi & Roos 2005) or the treatment of Au⁷⁻ (Johansson et al. 2008). All these treatments apply wave-function-based procedures, which become too expensive for clusters with more than 10 atoms.

Density functional theory (DFT) procedures are presently the method of choice for theoretical treatments of metal clusters with more than a few, say 5–10, atoms, where wave-function-based methods become too demanding. DFT offers an excellent price/performance ratio, is more accurate than HF, is relatively tolerant with respect to MR character of the wave function and is much more efficient than HF, as long as one does not use hybrid functionals, which are as expensive as HF. The present authors recommend non-hybrid functionals such as BP86 (Perdew 1986; Becke 1988) or TPSS (Tao et al. 2003) for the treatment of metal clusters; hybrid functionals yield poorer structure constants and energies (Furche & Perdew 2006). DFT procedures have one principal problem: they are not embedded in a hierarchy of methods with increasing accuracy (and costs) and there is no way to check the accuracy of a computed property within DFT itself. Wave-function-based methods would be at an important advantage here, if they were applicable.

The first and foremost property of clusters to be determined is their structure. This is not a problem for small cases with approximately 10 atoms, since with some experience one can exhaust the space of isomers by guessing starting structures, which are then optimized. This is not a viable procedure for larger clusters and one needs an unbiased structure search. Several techniques have been proposed and tested for this purpose, and we just mention simulated annealing (Kirkpatrick et al. 1983), basin hopping (Wales & Doye 1997) and genetic algorithms (GAs; Hartke 1993; Deaven & Ho 1995; Sierka et al. 2007). All these procedures require a large number of single-point calculations or geometry optimizations, which limits their application to relatively small clusters with approximately 30 atoms.
2. Geometric and electronic shells

(a) Geometric shells and magic atom numbers

Atoms in metal clusters are usually densely packed, and clusters show a low surface-to-volume ratio. So, they are expected to display high symmetry and further to consist of shells of atoms specific for the respective symmetry (Martin 1996). Clusters consisting of complete shells only are said to be of ‘magic atom numbers’. As an example, clusters of the highest possible cluster symmetry $I_h$ are built as follows. The central atom is surrounded by 12 further atoms in the form of an icosahedron. The following shells consist of 42, 92, 162 atoms, etc. This leads to the magic atom numbers for icosahedral symmetry: 13, 55, 147, 309, etc. The 147-atomic icosahedral type, ico147, is shown in figure 1, together with systems of similar size but with different topologies. Icosahedral species have a fivefold axis of rotation; as a consequence, it is not possible to form periodic icosahedral systems.

The situation is different for octahedral topologies, which correspond to face-centred cubic (FCC) packing of the solid state. Closed shells of atoms can be obtained in two ways. One either starts with a central atom; the first surrounding shell is constructed by adding one atom in a (011) direction together with its 11 symmetry images in $O_h$ symmetry, which yields a cuboctahedral species, cuboct13. Next shell closings occur at 55, 147 (four atoms per edge, see figure 1) and 309 atoms (five atoms per edge). Alternatively, one starts with a central octahedron of six atoms and adds shells of 38, 102, 198, etc. atoms, leading to octahedral clusters of 6, 44, 146, 344, ... atoms; oct146 is shown in figure 1. Octahedral species can also be derived from the cuboctahedral species by adding the corner atoms, leading to oct19, oct85, oct231. On the other hand, removing the corner atoms from the octahedral systems, respectively, yields truncated octahedral species, e.g. troct116, which is derived from oct146 by removal of the six sets of five corner atoms (see figure 1), as well as troct38 and troct260.
Closely related to FCC is hexagonal close packing (HCP), which corresponds to clusters consisting of planar hexagonal sheets of $D_{3h}$ symmetry in ‘abab’ packing with the numbers of atoms in respective layers given by: ‘a’ layer, $n = 1, 7, 19, 37$; ‘b’ layer, $n = 3, 12, 27$. One typically considers truncated species (lower surface-to-volume ratio), such as hcp57 (sheets 7, 12, 19, 12, 7) or hcp153 (sheets 12, 19, 27, 19, 12) (see figure 1).

Finally, we consider decahedral species. The smallest cluster of this type is a pentagonal bipyramid, dec7. Adding further shells leads to dec23, dec54 and dec105 (see figure 1). Modifications are truncated decahedra, trdec, and ‘Marks truncated decahedra’, mtrdec (see figure 1). As for icosahedra, it is not possible to form periodic systems of a decahedral shape.

(b) Electronic shells and magic electron numbers

In contrast to atomic shells, the occurrence of electronic shells is due to the effect of quantum mechanics. Clusters often are of approximately spherical symmetry (low surface-to-volume ratio). If one assumes spherical symmetry and further replaces the positive charges of the nuclei by a uniform positively charged background (jellium model: Clemenger 1985; de Heer et al. 1987), the potential acting on a single electron is that of an isotropic harmonic oscillator. The Schrödinger equation for a single electron in this potential can be analytically solved. One obtains spherical harmonic functions (s, p, d, . . .) of the following energetic sequence of eigenfunctions (shells): (1s), (1p), (1d,2s), (1f,2p), (1g,2d,3s), . . . . Each shell is energetically separated from the next one by the same energy difference. Adding the respective occupations yields the ‘magic electron numbers’ 2, 8, 20, 40, 70, 112, 168, 240, 330, 440, . . . (figure 2, left-hand side).
Quantum chemical treatments

These numbers usually cannot be associated with clusters of particular stability for two reasons. Firstly, for many-electron systems, one has to consider additionally the (average) potential arising from the presence of other electrons leading to energetic splitting of the degenerate shells, and so no longer showing constant energy differences. This results in subshell closings and modified magic electron numbers. For higher shells, energetic differences of shells with radial quantum number \( n \) but with different angular quantum numbers become so large that the energetic sequence is affected, e.g. the 1g shell is lower in energy than the 2p shell (figure 2, middle), which leads to the vanishing of the ‘magic’ electron number corresponding to the (1g,2d,3s) shell closing, 70, as well as most of the other of the above-mentioned numbers. Secondly, energetic degeneracy within a set of spherical harmonics can only be expected if the cluster displays (approximately) spherical symmetry; in other words, typically, only the low-lying cluster orbitals, which are mainly localized in the cluster centre, can be labelled as s, p, d, \ldots{} (sub-)shells; energetically high-lying cluster orbitals can be grouped into energetically similar (sub-)shells of the same angular momentum only for icosahedral clusters (\( I_h \) is close to spherical symmetry). Even for topologies with a slightly larger deviation from spherical symmetry, like \( O_h \) (see figure 2, right-hand side), splitting of previously degenerate shells to irreducible representations (irreps) of \( O_h \) and mixing within the same irreps destroys the electronic shell structure.

3. Clusters of magnesium

Mg clusters might serve as an example for the relevance of the electronic shell model. Experimental findings indicate that they are of an icosahedral shape up to large sizes (Martin et al. 1991). As mentioned earlier, this is an important precondition for the occurrence of electronic (s, p, d, \ldots{}) shells. Mg\(_n\) clusters were calculated (Köhn et al. 2001) with DFT (BP86) methods using comparatively small basis sets (split valence plus polarization, SVP; Schäfer et al. 1992), with an additional d function. This choice of parameters was justified by comparison with CCSD(T) (Bauschlicher & Partridge 1999) results for tetrahedral Mg\(_4\). Both the bond distance (309.4 versus 310.3 pm) and the dissociation energy (1.22 versus 1.14 eV) show very reasonable agreement.

We start our considerations by inspecting the electronic structure of Mg\(_{55}\) (see figure 3). At the right-hand side, plots of the simulated density of states (DOS) are shown: for ico55, left scale; and for cuboct55, right scale. The simulated DOSs were obtained by broadening the discrete energy levels with Gaussians (width 0.1 eV), mainly to help the eye in finding energy gaps. For ico55, one observes significant energy gaps that correspond to shell closings after 2, 8, 20, 40, 58 and 92 electrons. By contrast, for cuboct55, only the first three shell closings (1s,2p and 2s,1d) can be observed. For higher orbital energies, they occur at different numbers, which is the above-mentioned consequence of larger deviations from spherical symmetry leading to splitting of formerly degenerate shells. For ico55, which is very close to spherical symmetry, contour plots of the corresponding eigenfunctions are shown on the left; for degenerate states, only one representative is shown. It is evident that the angular parts of the orbitals of the icosahedral Mg\(_{55}\) cluster are spherical harmonics.
Next, we discuss the relative stability of different Mg clusters and try to identify particularly stable cluster sizes and types of packing. The basic quantity for discussing the stability of clusters is the cohesive energy $\varepsilon_{\text{coh}}$ defined as

$$\varepsilon_{\text{coh}} = E(\text{Mg}) - \frac{E(\text{Mg}_n)}{n}. \quad (3.1)$$

For space-filling systems, one expects an increase of the cohesive energy finally reaching the bulk value $\varepsilon_{\text{coh,bulk}}$ as

$$\varepsilon_{\text{coh}}(\text{Mg}_n) = \varepsilon_{\text{coh,bulk}} - a_{\text{surface}} n^{-1/3} - a_{\text{edge}} n^{-2/3} - a_{\text{corner}} n^{-1}. \quad (3.2)$$

So, by plotting $\varepsilon_{\text{coh}}$ versus $n^{-1/3}$, particular stable cluster topologies and cluster sizes can be identified. Further, in this way extrapolation to the bulk value is possible, which may be used for the estimation of the accuracy of the method of calculation, DFT(BP86).

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Quantum chemical treatments

Figure 4. Cohesive energy, $\varepsilon_{\text{coh}}$, for (a) Mg clusters and (b) Al clusters. Upper panels: $\varepsilon_{\text{coh}}$ versus $n$ for $n < 23$; lower panels: $\varepsilon_{\text{coh}}$ versus $n^{-1/3}$ for $n \geq 23$ (square, dec; circle, hcp, triangle, oct; cross, ico).

For the clarification of the building principles, a systematic search across all the potential surfaces would, of course, be desirable. Currently, this is feasible only for comparatively small systems. We thus followed two different routes for smaller and larger systems. For clusters up to 22 atoms, the potential surface was systematically scanned by simulated annealing techniques, and for the larger systems (up to 309 atoms), only the highly symmetric prototypes presented in the previous section were treated. In figure 4a (upper panel), $\varepsilon_{\text{coh}}$ is plotted for the most stable Mg$_n$ systems found for $n = 2$–22. Particularly stable are clusters with $n = 4$ (tetrahedron), 10 (tetracapped trigonal prism) and 20 (tetrahedron), which all correspond to magic electron numbers. Generally, most stable isomers up to $n = 8$ can be derived from tetrahedra; a capped trigonal prism is the dominant motif for clusters up to Mg$_{16}$. Mg$_{17}$ to Mg$_{22}$ usually consist of distorted fragments of decahedral or icosahedral structures. For larger systems, we focus on the comparison of the stability of the icosahedral topology compared with the HCP structure, as the latter is the packing of the bulk, whereas the former might be favourable for clusters because of the comparatively large number of next-neighbour atoms. In figure 4a (lower panel), the cohesive energy is plotted versus $n^{-1/3}$. The energies for different types of packing are not too different, but it is evident that, all over the investigated range, the HCP type is less stable than the other types. Icosahedral packing is slightly favoured towards decahedral or octahedral. The preference for icosahedral structures for larger Mg clusters is in line with mass spectroscopic investigations for Mg$_n$ (147 < $n$ < 2869; Martin et al. 1991). For the sake of completeness, we point out that tetrahedra beyond

Phil. Trans. R. Soc. A (2010)
Mg\textsubscript{20}, which all lead to the magic numbers of the harmonic shell model, are of low stability. For tet\textsubscript{56}, we obtain $\varepsilon_{\text{coh}} = 0.77$ eV, markedly below that for ico\textsubscript{55} or hcp\textsubscript{57}. Extrapolation for the cohesive energy of the bulk from the data shown in figure 4a (lower panel) leads to a value of 1.38 eV, which is reasonably close to experimental data (1.51 eV; Wagman \textit{et al.} 1982) and to DFT calculations for the bulk (1.43 eV).

4. Clusters of aluminium

The synthesis of [Al\textsubscript{57}\{AlN(SiH\textsubscript{3})\textsubscript{2}\}\textsubscript{20}]\textsuperscript{2−} by Köhnlein \textit{et al.} (2001) was a breakthrough in the chemistry of ligand-stabilized metal clusters, in general, and of aluminium, in particular. A consideration of the structural features of the aluminium core and the relevant literature revealed that there was no systematic study of Al\textsubscript{n} clusters in the range up to 60 atoms, which motivated the first systematic theoretical study of clusters of Al in the range up to 150 atoms (Ahlrichs & Elliott 1999). It was the main goal of that investigation to determine the preferred packing and shape of Al\textsubscript{n} as a function of size. For this purpose, a quite systematic structure search was carried out for the small clusters up to Al\textsubscript{15} and Al\textsubscript{19}, which was partly based on previous work (Jones 1993). We have checked these results by a GA search, which resulted in slightly more stable ground-state structures for Al\textsubscript{9} to Al\textsubscript{11} (Drebov & Ahlrichs in preparation). Beyond Al\textsubscript{19}, only selected clusters were treated, mainly those corresponding to the geometrically closed shells of the most probable packings: icosahedral, decahedral, FCC, HCP and body-centred cubic (BCC). These packings were combined with the shapes discussed earlier. The calculations were of the DFT type employing the BP86 functional together with an SVP basis set, and this computational procedure was validated by comparison to wave-function-based results for the smaller clusters as much as available (Pettersson \textit{et al.} 1987; Meier \textit{et al.} 1990). We will now sketch some pertinent results from Ahlrichs & Elliott (1999) in comparison with more recent investigations.

The small clusters are planar up to Al\textsubscript{5}: the trimer has $D_{3h}$ symmetry, the tetramer is a rhombus ($D_{2h}$) and the pentamer is W-shaped ($C_{2v}$). The hexamer is the smallest three-dimensional cluster with a distorted octahedron ($D_{3d}$). For Al\textsubscript{7} to Al\textsubscript{12}, one finds mainly structures of relatively low symmetry, which can be derived from smaller clusters, particularly Al\textsubscript{6}, by capping triangular faces. There are usually various structures close in energy, with a preference for low-spin states. The pronounced shoulder seen in figure 4b (upper panel) for the cohesive energy of Al\textsubscript{7} could be associated with the shell closing for 20 electrons, i.e. a stable Al\textsuperscript{7+}. The electronic shell closing for 40 electrons is realized for Al\textsuperscript{−13} with icosahedral structure, which is slightly Jahn–Teller-distorted for the neutral species. DFT studies of medium-sized neutral and ionic clusters, Al\textsubscript{n}, $n = 13–70$, have very recently been reported by Sun \textit{et al.} (2008), Aguado & Lopez (2009) and Starace \textit{et al.} (2009). These are so far the most advanced treatments in the given size range, as shown by the fact that better global minima have been determined than reported previously for various $n$. Since the search procedure employed did not include an unbiased method, future work will show to what extent global minima have really been located.

\textit{Phil. Trans. R. Soc. A} (2010)
We now consider the preferred packing as a function of size (figure 4b, lower panel) and try to link these data to experiments. Relative stabilities are best discussed for cluster sizes $n = 13, 55$ and $147$, since these are geometrically closed for types cuboct, trdec and ico, and allow for comparison. The following results have been obtained in Ahlrichs & Elliott (1999), where the values in parentheses are relative energies in eV normalized to the sizes 55 and 147 (i.e. for Al$_{54}$, we scale the total energy by 55/54):

$$
\text{ico}_{13}(0.0) < \text{trdec}_{13}(0.19) \approx \text{hcp}_{13}(0.46) < \text{cuboct}_{13}(0.87),
$$

$$
\text{dec}_{54}(-0.87) < \text{trdec}_{55}(0.0) \approx \text{hcp}_{57}(0.0) < \text{cuboct}_{55}(1.74) < \text{ico}_{55}(2.24)
$$

and

$$
\text{troct}_{146}(-0.67) \approx \text{oct}_{140}(-0.65) < \text{cuboct}_{147}(0.0) < \text{ntrdec}_{146}(0.61)
$$

$$
< \text{trdec}_{147}(1.33) < \text{hcp}_{153}(2.50) < \text{ico}_{147}(2.72).
$$

Icosahedra are most stable only for $n = 13$ and probably for clusters derived from it by adding a few atoms, but they are quite unstable for the larger clusters with 55 and 147 atoms. Decahedral packing is relatively stable for Al$_{13}$ and is favoured at around 55 atoms. Octahedra and cuboctahedra are high in energy for $n = 13$, but they are clearly most stable for 140 atoms or more. HCP could be competitive with the others around 55 atoms, whereas BCC is always computed high in energy. Preferred shapes appear to be those with (111) faces: oct$_{146}$ and troct$_{140}$ (just oct$_{146}$ with corner atoms removed) are more stable than cuboct$_{147}$, and dec$_{54}$ is larger in cohesive energy than trdec$_{55}$, to mention two out of many cases. Clusters with truncated shape have a smaller surface-to-volume ratio, but they always have (100) faces that appear to be high in energy.

It remains to link the computed data to experiments. The preference for octahedral clusters with FCC packing, which calculations indicate as occurring somewhere between 55 and 140 atoms, is solidly documented in mass spectrometric investigations for the range $n = 250$–10000 (Martin et al. 1992), providing at least some confirmation for the theory. From the computed energies, one can extrapolate the cohesive energy of the bulk (see equation (3.2)). One finds that $\varepsilon_{\text{coh, bulk}} = 3.35 \text{eV}$ is in close agreement with the experimental value of 3.36 eV (Wagman et al. 1982). The theoretical $\varepsilon_{\text{coh, bulk}}$ does not include the zero-point vibrational energy (ZPVE) of about 0.03 eV per atom. Dissociation energies ($\text{Al}_n \rightarrow \text{Al}_{n-1} + \text{Al}$) are also in reasonable agreement with those of experiments; deviations amount to a few 0.1 eV for $n = 5$, 6 and 8, but are otherwise within experimental errors. The situation is similar for the adiabatic ionization potentials (IPs) of anions, where theory and experiment agree within 0.1 eV. Clusters of aluminium appear to be a benign case for DFT treatments with the functional BP86, and there are no serious discrepancies with experiments.

5. Clusters of palladium

Mednikov & Dahl (2010) have prepared and structurally characterized an entire family of ligand-stabilized clusters of palladium, a work reviewed in this Theme Issue. The ligands, CO and/or PR$_3$, neither oxidize nor reduce the Pd cluster core and should have a limited influence on its electronic structure. The Pd core
of these clusters often shows fused icosahedra, which are found as global minima of Lennard-Jones clusters. These unusual structural features could result from energetic preferences or from growth patterns involving icosahedral fragments as the start. Mednikov’s and Dahl’s clusters provide experimental information useful for checking DFT methods and also pose problems that can be investigated by DFT.

This was done in two papers (Nava et al. 2003, 2004), which addressed the following questions: What is the preferred packing and shape of Pd$_n$? How does the total spin change with cluster size? To what extent are the properties of Pd$_n$ affected by the ligand coverage? Is it possible to predict preferred patterns of the ligand coverage? This treatment goes beyond previous ones (Krüger et al. 2001) in the number of clusters considered and in the full optimization of structure parameters.

We have termed the problems encountered in the calculation of aluminium ‘benign’; this is certainly not the case for palladium. The atom has a closed-shell 4d$^{10}$ electronic configuration leading to a weakly bound dimer Pd$_2$ with dissociation energy $D_e$ of 1 eV only in a $^3\Sigma^+_u$ ground state. The small $D_e$ of the dimer and also the relatively small (for a group 10 element) cohesive energy of bulk Pd result from a balance of promotion from 4d$^{10}$ to 4d$^9$5s$^1$ and bonding effects, which have to be described correctly.

Another problem has to do with spin: Pd clusters prefer high-spin states, which necessitates an optimization of spin populations in the minimization of ground-state energy. We have followed Warren & Dunlap (1996) and applied fractional occupation numbers

$$n_i = \frac{1}{2} \text{erfc} \left(\frac{\varepsilon_i - \varepsilon_F}{fT}\right),$$

where $i$ labels spin orbitals, $\varepsilon_i$ their orbital energy, $\varepsilon_F$ the Fermi energy and $f = 4k/\sqrt{\pi}$. With an initial ‘temperature’ of $T = 300$ K, which is gradually reduced during self-consistent field (SCF) iterations, one usually converges to integer occupations, i.e. a state-specific solution of the Kohn–Sham equations. Convergence is very often quite difficult to achieve, and for this reason we have neglected spin polarization for cases beyond 100 atoms, which resulted in non-integer occupations with a high density of orbitals (about 100 MOs within 0.1 eV for Pd$_{309}$).

The following general picture emerges from the DFT/BP86 treatment. Pd prefers dense packing, and the clusters are three-dimensional from Pd$_4$ onwards. Symmetries are relatively high with bipyramids for $n = 5$ ($D_{3h}$) and $n = 7$ ($D_{5h}$) and a distorted icosahedron ($D_{3d}$) for Pd$_{13}$. The clusters up to $n = 15$ are relatively floppy and there is no guarantee that the lowest-energy isomer has been located (even within DFT/BP86). Low-energy states tend to have high spin, e.g. $S = 4$ for several states of Pd$_{13}$. The largest spins have been found for bcc65 ($O_h$) with $S = 17$ and mtrdec75 ($D_{5h}$) with $S = 16$. Icosahedral structures are lowest in energy around Pd$_{13}$ and Pd$_{55}$, but computed energy differences between different isomers are small. This is also the case for $n$ around 147 and 309: ico147 is obtained 0.037 eV lower than cuboct147, and cuboct309 is 0.427 eV lower than ico309. The largest cohesive energy around 146 atoms is computed for oct146 as for aluminium. All that can be said is that DFT indicates a preference for octahedra for clusters larger than about 100 atoms. Decahedral packings are competitive in energy with other structures up to about 85 atoms.
Quantum chemical treatments

Properties computed for the larger clusters allow for an extrapolation towards the bulk. This yields $\varepsilon_{\text{coh,bulk}} = 3.59\text{eV}$, to be compared with the experimental value of $3.9\text{eV}$ (Wagman et al. 1982). A regression analysis of Pd–Pd bond distances as a function of the number of next neighbours leads to an extrapolated value (for 12 next neighbours) of $d_{\text{bulk}} = 2.816\text{Å}$, again not too different from the experimental result of $2.748\text{Å}$. Considering the many problems of a theoretical treatment mentioned earlier, we find a surprisingly close agreement with experiments.

We now turn to the ligand-stabilized clusters of Tran et al. (2000, 2001). First of all, the metal cores found there are less stable than the other clusters of the same size and the proposed pathways for syntheses are likewise high in energy. There are always other structures, which are up to 1 eV lower in energy. This neither disproves the pathways nor confirms the idea. The point is that interactions with ligands or solvent molecules can easily compensate 1 eV.

Ligand coverage, by CO and/or PR$_3$, has two main effects, which are very clearly displayed by the calculations. The first is a quenching of spins of the metal core, which has also been found for clusters of Ni (van Leeuwen et al. 1994). The second is a change in relative stability of Pd cluster cores on loading with CO. A most instructive example is Pd$_{19}$(CO)$_8$: for the bare Pd$_{19}$, the octahedron is 1 eV lower in energy than the bi-icosahedral core; for a large load with eight CO, the energetic order has reversed and the bi-icosahedral core is now 0.36 eV more stable (figure 5). This is a general trend: icosahedral clusters are stabilized relative to others by ligands such as CO or PR$_3$. The great influence of ligands is also shown by the fact that the binding energy of ligands to the core in [Pd$_{16}$(CO)$_{13}$(PMe$_3$)$_9$] is as large as the binding energy of Pd$_{16}$ itself.

DFT/BP86 calculations proved to be a useful tool in the exploration of the chemistry of ligand-stabilized Pd clusters. All results for structure constants and their trends, the pattern of ligand coverage and the energetic order of different isomers are in agreement with experiments.

Figure 5. Energy difference between octahedral and bi-icosahedral Pd$_{19}$ depending on the number of adsorbed CO units.
6. Tin cluster anions: from spherical to prolate to clusters of cluster structures

It is a typical feature of metal clusters—neutral or charged—that there are various isomers with an energetic separation of about 0.1 eV or even less. DFT procedures certainly can have errors of this size. As a consequence, no reliable determination of ground states or the energetic order of the most stable structures is possible. This goal can presently only be achieved by a combination of experiment and theory, since measurements alone are also inconclusive in general. In a combined approach, molecular electronic structure calculations are used to get candidate structures, and the computed properties are then compared with one or more measurements to determine the isomer that best fits all data. It is important that the structure search employs an unbiased procedure such as a GA. This type of procedure has been carried out for neutral Sn\textsubscript{n} (n = 6–20; Schäfer et al. 2008), where electric deflection measurements were combined with GA/DFT to determine structures. This was successful only for the smaller clusters up to Sn\textsubscript{11}. No agreement between experiment and theory could be achieved for the larger clusters, and it was concluded that these undergo rapid interconversion of isomers at temperatures down to 40 K. Tin cluster cations have been much investigated. On the basis of ion mobility measurements, it has been concluded that the morphology follows the pattern found for Si and Ge but not that of Pb (Shvartsburg & Jarrold 1999). Tin cluster anions have not been investigated as much as the cations; recent reviews of the literature can be found in Oger et al. (2009) and Lechtken et al. (in preparation). We just mention the recent work of Cui et al. (2006) in which the existence of a relatively stable Sn\textsubscript{12}\textsuperscript{2−} dianion with a perfect icosahedral structure was inferred from the photoelectron spectrum of KSn\textsubscript{12}.

For the determination of candidate structures, the TPSS functional was employed in combination with an effective core potential (ECP; Metz et al. 2000). The ECP accounts for core electrons 1s to 3d and includes scalar relativistic effects. The GA applied to generate candidate structures has been described in Sierka et al. (2007). Since computational demands for the GA are appreciable, a smaller split valence basis was used to obtain a population of neutral clusters. The final population was then reoptimized with the larger def2-TZVPP basis (Weigend & Ahlrichs 2005) for neutral clusters and anions.

Three experimental procedures were employed to determine anion cluster properties: ion mobility spectroscopy (IMS), collision-induced dissociation (CID; Weis et al. 2002) and trapped ion electron diffraction (TIED; Schooss et al. 2005). IMS measurements were done for up to 15 atoms; TIED was not possible for n ≤ 12 since intensities were too low. The computed structures served as input for the computation of cross sections measured in IMS and for reduced molecular scattering intensities obtained with TIED, which were then compared with experimental results. The CID yields relative intensities of different fragmentation channels, which can be compared with pathways suggested by computed reaction energies.

A comparison of all results from experiments and calculations reveals the following picture. The computed global minimum gives the best fit to IMS and TIED in virtually all cases up to n = 26. In some cases, however, several low-lying isomers separated by only 0.1–0.2 eV give equally good fits to cross
Quantum chemical treatments

sections and/or scattering intensities. This is the case for Sn_{14}^- and one can establish neither the global minimum structure nor whether there is a mixture of different isomers. In some cases, the best fit for TIED is obtained by assuming a mixture of isomers. For Sn_{24}^-, no low-energy structure was obtained that gives a representation of TIED scattering intensities. The most probable reasons for this failure are: the GA did not locate the ground state in more than 300 generations carried out; the TPSS functional does not yield a local minimum near the true ground state.

The small tin cluster anions up to Sn_{12}^- have compact quasi-spherical structures such as a pentagonal bipyramid (D_{5h}) for Sn_{7}^-, a tricapped trigonal prism (C_{s} symmetry, Jahn–Teller-distorted D_{3h}) for Sn_{9}^-, a bicapped tetragonal anti-prism (D_{4d}) for Sn_{10}^- and a distorted hollow icosahedron (C_{5v}) for Sn_{12}^-.

The TTP and BTA are closely related since the TTP can also be viewed as a (mono-)capped tetragonal anti-prism. The low-energy structures of Sn_{18}^-, which provide a good fit of TIED data, consist of two TTPs; those of Sn_{20}^- are composed...
of two BTAs. For Sn$_{23}$, we find three low-energy structures consisting of two BTA units linked by three additional atoms (figure 6). In all cases ($n = 18, 20$ and $23$), the bonding between subunits appears to be quite floppy, and the relative orientation of TTP or BTA units is not rigidly fixed. The lowest-energy isomer of Sn$_{25}$, which yields an almost perfect match of TIED results, is composed of an Sn$_{15}$ unit (very similar to the structure of Sn$_{15}$) and a 10-atomic BTA. The structure for Sn$_{20}$ has also been proposed for neutral Sn$_{20}$ (Schäfer et al. 2008).

The tendency of tin to form clusters of clusters is connected with features of the cohesive energy as a function of cluster size $n$, which has already been pointed out by Majumder et al. (2001). The cohesive energy $\varepsilon_{\text{coh}}$ increases steeply for small $n$ and reaches a value corresponding to 90 per cent of the bulk already for $n = 7$ or 10 (figure 7). This behaviour contrasts with that found for other metals discussed in this paper, where such a large fraction of the bulk cohesive energy is not even reached for 100 atoms. As a result of the stability of Sn$_9$ and Sn$_{10}$, it is favourable to simply form dimers of these units. This feature is also reflected by CID results, which show a preference for dissociation into clusters and not a loss of one or two atoms. An extrapolation of computed cohesive energies for $n = 11$–26 yields $\varepsilon_{\text{coh,bulk}} = 3.16 \text{ eV}$, while the experimental value is $3.14 \text{ eV}$ (Wagman et al. 1982).

7. Binary metal clusters

Properties of homoatomic clusters mainly depend on their size. Clusters consisting of more than one type of atom have a second parameter that can be varied: the composition. For potential applications, this is an opportunity, as this might lead to tunable properties. For the theoretical treatment, this is a challenge, as the number of possible distributions of the different atom types for a given cluster increases exponentially with cluster size, e.g. like $2^N$ for binary $N$-atomic clusters. Explicit calculation of all possible distributions is possible only for small clusters;
Quantum chemical treatments

for larger systems, approximate treatments have to be developed, which may be used for screening the plethora of possibilities for promising candidates (Weigend et al. 2004).

Such a screening can be carried out via perturbation theory: the heteroatomic (binary) system $B_nA_{N-n}$ is regarded as a homoatomic system $A_N$ plus perturbation by $n$ atoms of type $B$. For system $A_N$ (with $n_e$ electrons and energy $E^A$), the energy change when replacing one atom of type $A$ (nuclear charge $Z_A$) with one atom of type $B$ ($Z_B = Z_A + \Delta Z$) at position $R_i$ in first order is

$$\Delta E^A_i = \left. \frac{\partial E^A}{\partial Z} \right|_{R_i} \Delta Z + \left. \frac{\partial E^A}{\partial n_e} \right|_{R_i} \Delta n_e. \quad (7.1)$$

This straightforwardly leads to an estimate for the stability $E^A_{\text{est}}$ of a binary $B_nA_{N-n}$ with respect to the homoatomic species $A_N$:

$$E^A_{\text{est}} = \Delta Z \sum_{i=1}^{n} [U^A(R_i) - \bar{U}^A], \quad (7.2)$$

where $U^A(R_i)$ is the electrostatic potential of system $A_N$ at the position of the B–A-replaced atom, calculated without the charge of this nucleus, and $\bar{U}^A$ is the mean value of $U^A(R_i)$ over all $N$ atom positions $R_i$.

Energetically most favourable distributions (for fixed geometry) now may be obtained as follows:

1. Calculation of the energy and wave function of $A_N$ (and/or $B_N$) and of the electrostatic potential $U(R_i)$ at the positions of the $N$ nuclei.
2. Calculation of $E_{\text{est}}$ for all distributions according to equation (7.2).
3. Explicit calculation of the most favourable distributions due to $E_{\text{est}}$.

The first step is just a single DFT calculation and the second one formally scales like $2^N$, but for each of the $2^N$ distributions it only consists of the addition of $N$ numbers at most. If one is interested only in the most favourable distributions (lowest $E_{\text{est}}$), scaling for this step can be much reduced by sorting $U^A(R_i)$ with respect to their size.

As an example, we present the application of this method to Pt$_{n}$Ir$_{13-n}$. For both Pt$_{13}$ and Ir$_{13}$, the $C_s$ symmetric structure shown in figure 8a is (at least) a local minimum, which is more stable than the icosahedral cluster by about 3 eV for both metal types. For this structure, $E_{\text{est}}$ was calculated for all distributions (see figure 8b). For the most favourable systems (below the line, figure 8b), $E_{\text{est}}$ finally was compared to the relative stability $E_{\text{rel}}$ with respect to decomposition to homoatomic species:

$$E_{\text{rel}}^{\text{SP/opt}}(A_{N-n}B_n) = E_{\text{rel}}^{\text{SP/opt}}(A_{N-n}B_n) - \frac{[(N - n)E(A_N) + nE(B_N)]}{N}. \quad (7.3)$$

Here SP/opt refers to single-point energies or energies after optimization of structure parameters for $A_{N-n}B_n$, respectively (see figure 8c,d). The correlation of $E_{\text{est}}$ with both $E_{\text{rel}}^{\text{SP}}$ and $E_{\text{rel}}^{\text{opt}}$ is surprisingly good. The technique may be used as a screening method, but it also improves the understanding of clusters consisting of two different metal atom types of similar atomic number. In Pt–Ir clusters, the
element with the higher atomic number, Pt, occupies the outer positions, whereas Ir is located on inner positions. This trend can be seen in figure 8, as well as for other Pt–Ir systems like, for example, Pt$_n$Ir$_{55-n}$ ($D_{5h}$ symmetry), for $E_{\text{rel}}$ as well as for $E_{\text{est}}$. As $E_{\text{est}}$ depends only on the electrostatic potential, this quantity is sufficient for rationalizing the preferred sites for Ir/Pt. As illustrated previously for the Mg clusters (figure 3), the low-lying cluster orbitals are located rather inside the cluster, whereas the higher-lying orbitals are rather on the cluster surface. For electron-rich clusters, one thus expects a surplus of electrons at the cluster surface and thus a more negative electrostatic potential, which according to equation (7.2) leads to the observed preference of outer positions for atoms with higher atomic number. For electron-poor compounds, in contrast, only the lowest cluster orbitals are occupied. The electrostatic potential for positive charges thus is more attractive at the cluster centre and the element with the higher atomic number is expected to be located more readily at inner positions. In fact, due to both experimental and quantum chemical results, for icosahedral Al$_{12}$Si, the silicon atom is at the central position.

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8. Conclusions

The treatment of clusters of metal atoms is a challenge for molecular electronic structure theory. The most demanding problems are: electronic states are of the multiple reference type, there are typically a number of isomers separated by only a few 0.01 eV and it is non-trivial to determine the structure of all low-energy isomers. DFT procedures have been proved to cope quite successfully with the first two problems; they predict changes in packing and shape of clusters as a function of cluster size, at least in a semi-quantitative way. The binding energies of small clusters and the cohesive energy of the bulk phase, where comparison with experiments is possible, are also reproduced with errors of about 0.1 eV. This accuracy is not sufficient to predict the correct order of low-lying states; an error of about 0.01 eV in relative energies would be highly desirable. This could probably be achieved by improved functionals, and their development and validation have to be based on reliable experimental data, which are presently not available in sufficient quantity. Finally, it is highly desirable to study unbiased structure search procedures and to improve their efficiency.

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References


Drebov, N. & Ahlrichs, R. In preparation. Structures of Al\(_n\), its anions and cations up to \(n=34\). A theoretical investigation.


Gagliardi, L & Roos, B. 2005 Quantum chemical calculations show that the uranium molecule U\(_2\) has a quintuple bond. Nature 433, 848–851. (doi:10.1038/nature03249)


F. Weigend and R. Ahlrichs

Jones, R. O. 1993 Simulated annealing study of neutral and charged clusters—Aln and Gann.


Köhnlein, H., Purath, A., Baum, E., Krossing, I., Stösser, G. & Schnöckel, H.
2001 Synthesis and characterization of an Al3− cluster with 51 naked Al atoms: analogies and differences to the previously characterized Al27− cluster.


Majumder, C., Kumar, V., Mizuseki, H. & Kawazoe, Y. 2001 Small clusters of tin: atomic structures, energetics, and fragmentation behavior.

Martin, T. P. 1996 Shells of atoms.


Meier, U., Peyerimhoff, S. D. & Grein, F. 1990 Ab initio MRD-CI study of neutral and charged Ga2, Ga3 and Ga4 clusters and comparison with corresponding boron and aluminum clusters.


Perdew, J. P. 1986 Density-functional approximation for the correlation energy of the inhomogeneous electron gas.


Schäfer, A., Horn, H. & Ahlrichs, R. 1999 Fully optimized contracted Gaussian basis sets for atoms Li to Kr.

Schäfer, S., Assadollahzadeh, B., Mehring, M., Schwerdtfeger, P. & Schäfer, R. 2001 Structure and electric properties of SnN clusters (N = 6–20) from combined electric deflection experiments and quantum theoretical studies.


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