Density functional studies of small platinum clusters

LETTER TO THE EDITOR

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Abstract.   We present results of a density functional theory study of the structure and energetics
of small Pt clusters. The method of calculation is based on the non-selfconsistent Harris
functional version of LDA (as formulated by Sankey and Niklewski, and generalized to include
d orbitals in the basis set), which produces excellent results for bulk Pt. We used a dynamical
quenching algorithm to obtain minimum-energy structures of Pt_n clusters for $n = 2$–6. The
clusters with $n = 4$–6 are shown to be planar. For Pt_{13} we found that there is a variety of
low-symmetry geometries that are lower in energy than the icosahedral and cubo-octahedral
structures. We also compute the vibrational states of $n = 2$–4, and show that the calculated
vibrational frequency and bond energy of the Pt dimer are in good agreement with experiments.

The study of small clusters is intrinsically interesting because they often exhibit structures
and properties different from those of the bulk, due to their high ratio of surface area to
volume. Transition metal clusters are of special interest because they are used to catalyse
reactions; for example, small clusters of Pt, Rh, and Pd are used in automotive exhaust
systems to reduce toxic pollutants such as CO, NO, and hydrocarbons. Pt clusters are
considered to be one of the most important materials for the heterogeneous catalysis of
hydrogenation because of their small hydrogenation energy compared with other metal
clusters [1]. Determining the shape and the microstructure of small metal particles is
important because it is a major feature in controlling the catalyst's activity. In particular,
it is possible that very small transition metal clusters have unusual structures and therefore
unusual activities. Quantum mechanical theoretical studies of Pt clusters are however scarce,
reflecting the difficulty of treating the compact d orbitals present in transition metals. The
purpose of this letter is to provide a systematic *ab initio* study of the structure and energetics
of small Pt_n clusters for $n = 2$ to 6, and for $n = 13$, which is of particular interest since
it is the first atomic-shell closing of both the icosahedral (ICS) and cubo-octahedral (COS)
structures.

   Our calculations are based on the non-selfconsistent Harris functional version [3] of the
local density approximation (LDA), within density functional theory (DFT). In particular,
we extended the method of Sankey and Niklewski [4] to include d orbitals in the basis set,
thus allowing the treatment of transition metals. One-electron wavefunctions are expressed
as linear combinations of s, p, and d pseudoatomic orbitals, which are computed by solving

the selfconsistent LDA equations for an isolated atom with the constraint of a confinement boundary R_c. We use the Ceperley–Alder exchange–correlation potential, and the non-local, norm conserving pseudopotentials of Bachelet, Hamann and Schluter [5]. The R_c chosen in this study is 5.5 au. The details of the method will be published elsewhere [6]. All the energies presented in this paper are calculated relative to the energy of a Pt pseudoatom with the same basis. The method was tested by calculating the bulk properties of Pt. The calculated band structure was in excellent agreement with results from augmented plane wave calculations at all high-symmetry points [6, 7], for the valence and lower conduction bands. The lattice constant and bulk modulus were found to be 3.92 Å and 2.631 Mbar respectively, which compare well with the experimental values of 3.92 Å and 2.783 Mbar. The calculated cohesive energy is 6.08 eV, bigger than the experimental value of 5.84 eV [8]. The error in the cohesive energy is mainly due to the reference energy of the pseudoatom, which is higher than the atomic energy because of the confinement boundary R_c [4]. Nevertheless, since this is a constant reference energy, relative energies between different structures are expected to be accurate.

We carried out molecular dynamics (MD) simulations to determine the optimal structure of the Pt clusters. We used a dynamical quenching algorithm, in which at each MD step the velocity components of those atoms going uphill (i.e., those for which the force components are opposite to the velocity components) are quenched to zero, while the atoms going downhill follow Newtonian dynamics. The calculated geometries of Pt_n are shown in figure 1, together with the binding energies per atom, in eV. The third column corresponds to the structures with the lowest energies.

We start our discussion with the Pt_2 cluster. This is the only case of small Pt clusters that has been studied experimentally, to our knowledge. Jansson and Scullman [9] measured the vibrational spectrum of Pt_2 in an Ar matrix, and identified a well resolved single vibronic transition with vibrational frequency $\omega_e = 217.2$ cm^{-1}. Taylor *et al* [10] used resonant two-photon ionization spectroscopy of jet-cooled Pt_2 to find numerous vibronic bands of Pt_2. They determined the dissociation energy of Pt_2 to be 3.26 eV by looking at the change of the lifetimes of successive vibronic levels measured near the dissociation threshold. An abrupt drop was seen in the measured lifetimes at the vibronic level which corresponds to the dissociation. Gupta *et al* [11] were successful in detecting Pt_2 over the temperature range 2259–2736 K and estimated the dissociated energy to be in the range from 2.80 to 3.71 eV. Our calculations for Pt_2 give a well defined minimum-energy state with a bond length of 2.40 Å, and a binding energy of 3.30 eV. The ground state corresponds to a triplet. We also computed the vibrational frequency of the stretching phonon of the dimer, which was found to be $\omega = 218$ cm^{-1}. We see that our results for the dimer are in excellent agreement with the experimental data. Other authors have also calculated the properties of the Pt dimer. Balasubramanian [1] performed complete active space selfconsistent-field (CASSCF) calculations followed by first-order configuration interaction (FOCI) calculations with and without the spin–orbit interaction. He obtained a binding energy of 1.95 eV, significantly far from the experimental values. It seems evident that considerable additional electronic correlation is required for a better agreement with experiment. He obtained a bonding distance of 2.46 Å, and a vibrational frequency of 189 cm^{-1}, much further from the experimental value than our result. Ellis *et al* [12] calculated a binding energy curve for Pt_2 within the relativistic Dirac–Slater model, and found an equilibrium bond length of 2.33 Å and a binding energy of 5.8 eV, much higher than the experimental value. We conclude that our method yields the most accurate results for the structure and energetics of the Pt_2 cluster.

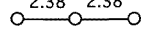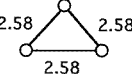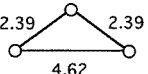The local minimum structures of Pt_3 are shown in figure 1. They are a linear chain,
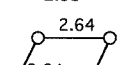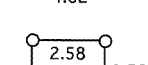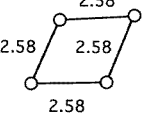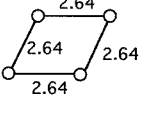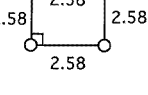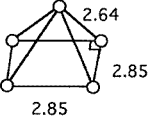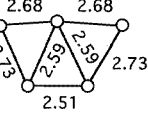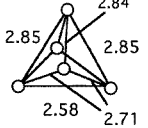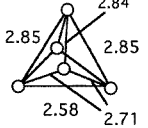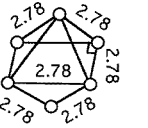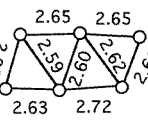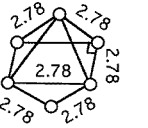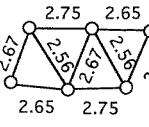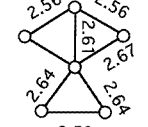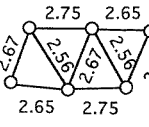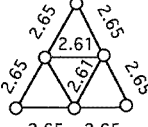
Figure 1. Minimum-energy structures of Pt_n, $n = 2$ to 6, with the corresponding binding energies per atom. The structures in the third column are believed to be most stable.

an isosceles triangle, and an equilateral triangle. The ground state of Pt_3 is found to be the equilateral triangle, with a bond length of 2.58 Å, and an energy which is about 0.24 eV/atom lower than the other metastable structures. We calculated the vibrational modes for the equilateral triangle, which were found to be at 145, 215, and 290 cm^{-1}.

The most stable structure for Pt_4 is found to be a rhombus of C_{2v} symmetry, with a bond length of 2.64 Å and an angle of 58°, and a binding energy of 2.56 eV/atom. The vibrational frequency modes are calculated for this ground state structure. The positions of the peaks are at 33, 86, 105, 128, 152, 216 cm^{-1}. The other metastable structure is a square with a side length of 2.58 Å, whose energy is slightly higher than the rhombus by about 0.05 eV/atom. Our results agree with more accurate calculations carried out by Dingguo Dai and Balasubramanian [2] on the Pt_4 clusters. Using a modified version of the CASSCF–FOCI, they found that a rhombus was the ground state structure and a tetrahedron and a square were metastable structures. In our calculations the tetrahedron structure was unstable. Ellis *et al* [12] also studied the Pt_4 clusters using an *ab initio* generalized valence bond method within the relativistic effective core potential and a double-zeta basis. But they found the square to be favoured over the rhombus by 0.48 eV/atom. Ellis *et al* referred to the bonds of the rhombus as metallic, because this type of bond was frequent in metallic systems such as Li, Na, and Ag, and to the bonds of the square as covalent, because it was formed by the overlapping of the sd hybrids analogous to that of the carbon–carbon bonds

of organic molecules. In terms of their language, our results suggest that a strong metallic phase already starts to appear at this cluster size.

The minimum-energy structure of Pt_5 was found to be a planar C_{2v} structure. It has a W shape with a side length of 2.73 Å, as shown in figure 1. A pyramid and a trigonal bipyramid are also found to be metastable structures. The pyramid is higher in energy by 0.06 eV/atom than the trigonal bipyramid, which is about 0.1 eV/atom higher in energy than the ground state C_{2v} structure.

For Pt_6, we found the most stable structure to be a planar triangular configuration with C_{3v} symmetry, which consists of four small triangles as shown in figure 1. The bond length between atoms sitting at the side of the exterior triangle is 2.65 Å, while that of the interior small triangle is 2.61 Å. The other metastable structure is a distorted pentagon (planar) structure (second column in figure 1). Its energy is about 0.1 eV/atom higher than the ground state structure. A ladder-like structure (first column in figure 1) is also found as a metastable structure. Its shape is like a W with one more atom added at the side of the W. It is not quite planar, but slightly twisted like a helix. A similar planar-like structure is also found to be a local minimum with an energy close to the other planar structure. The bipyramid with D_{3d} symmetry is another local minimum, but its energy is found to be the highest among its isomers, 0.33 eV/atom higher than the ground state structure.

To summarize the results for the Pt_n clusters to 2 to 6 atoms, planar structures are preferred for $n = 4$–6. The binding energy of the clusters monotonically approaches the bulk binding energy, but there is a decrease in the slope of the binding energy curve at $n = 4$ and 5. These are the sizes at which fragmentation would be more likely to occur into fragments of smaller sizes, so they should be the least frequent sizes for the small clusters.

Larger clusters have also been investigated by several groups using empirical potentials [13]. Pt_{13} is particularly interesting because it represents the first atomic-shell closing of both the ICS and COS structures. Sachdev *et al* used the embedded atom method (EAM) to study Pt clusters of 5 to 60 atoms and found that the minimum-energy structure of Pt_{13} was highly distorted. On the other hand, Garcia-Rodeja *et al* using a different EAM potential found the ICS to be the minimum-energy structure. Uppenbrink and Wales used another EAM potential and found that the minimum-energy structure was the ICS. They also reported that there were many highly distorted structures which were very close in energy to the ground state ICS. Yang and DePristo used corrected effective medium theory to perform MD simulations using two different interatomic potentials. One of them predicted the ICS as the minimum and the other an open and distorted structure. The true structure of Pt_{13} is therefore under dispute.

We have tried to elucidate the issue by performing *ab initio* calculations of the energetics of the Pt_{13} cluster. We first examined the ICS and the COS structures. The COS is characterized by the presence of square (100) and triangular (111) facets on the surface, and it is the same as the fcc structure of the bulk crystal (see figure 2). The ICS is characterized by having only (111) facets on the surface. In both casts one central atom is surrounded by the other 12 outer atoms. For clusters made of rare gases, which exhibit a short-range and isotropic interatomic potentials, the ICS is expected to be a more stable structure than the COS due to its compactness, which leads to a smaller surface energy contribution. However, this is not necessarily true for metal clusters because their bonding is more complex [14].

We first compare the energies of the ideal ICS and COS of Pt_{13} clusters relaxed without allowing any symmetry breaking. The two structures were very close in energy, with the COS slightly lower than the ICS by 0.005 eV/atom. However, when symmetry breaking was allowed the ICS and COS structures went through the Jahn–Teller distortions lowering their energies by 0.009 and 0.002 eV/atom from their ideal structures respectively, and
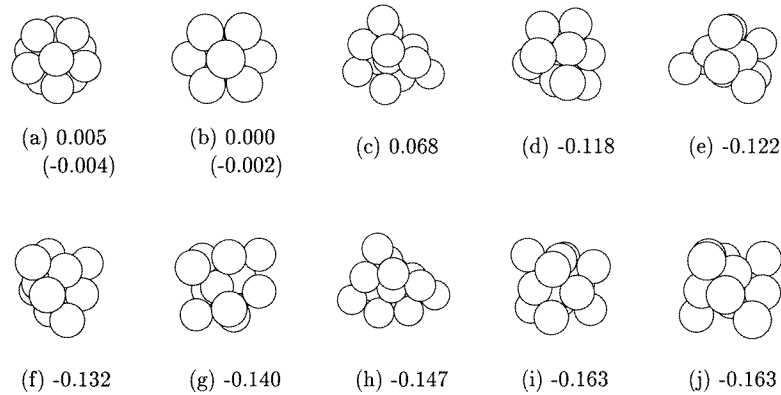
Figure 2. Different geometries for the Pt_{13} cluster and their energies shown in eV/atom relative to the ideal COS. (a) and (b) are the ICS and COS, respectively. The top and bottom (parenthesis) values are the energies of the ideal and the Jahn–Teller distorted structures respectively. (c)–(j) are local minimum amorphous structures. (j) has the lowest energy, and (c) has higher energy than the ideal COS.

at the end the ICS was found to be lower in energy than the COS by 0.002 eV/atom. Our calculations showed that the highest occupied levels of the ideal COS and ICS were threefold and fivefold degenerate without considering spin degeneracy respectively. Upon the Jahn–Teller relaxations these levels split into individual levels leaving no degeneracy at the highest occupied levels. The magnitude of the geometrical distortions was small, with bond lengths changing less than 0.12 Å in both cases.

To search for other possible structures, the ideal configurations of the 13-atom ICS and COS clusters were annealed at 8000 K until they become completely disordered. Then we performed a dynamical quench of the clusters from various stages of the simulated annealing trajectories. Surprisingly, we found many low-symmetry structures lower in energy than the ideal ICS and COS. We carried out eight quenchings starting from different initial configurations, producing eight low-symmetry structures which are shown in figure 2. Seven of these structures have lower energies than the ideal ICS and COS, the lowest being 0.16 eV/atom below. They are all quite distorted, and some are more open that others. We also studied the radial distribution function for these local minima. Amorphous structures were distinguished from the perfect ICS and COS structures by having double humps at second peaks around 5 Å (see figure 3), which also occurs in metallic glasses but not in metallic liquids [15].

According to our calculations, it appears that there is no well defined minimum-energy structure for Pt_{13}, but a variety of disordered configurations with very similar energies. Although there is no direct evidence from experimental information, we argue that this is consistent with experimental studies on nanoscale Pt clusters. Yeon-wook Kim *et al* [16] conducted experiments to solidify small liquid droplets of 15 different pure metals at a high cooling rate of about 10^6 K s^{-1}. They found that the pure metals solidified from the melted liquid droplets of size 10–60 nm in diameter would form either crystalline or amorphous phases. They observed that bcc metals were more likely to solidify in an amorphous phase than the fcc or hcp metals. Pt clusters were always found to be crystalline. But the smallest droplet size they considered is 10 nm in diameter, which corresponded to at least ten thousand atoms. On the other hand, Contrata *et al* [17] studied smaller Pt clusters
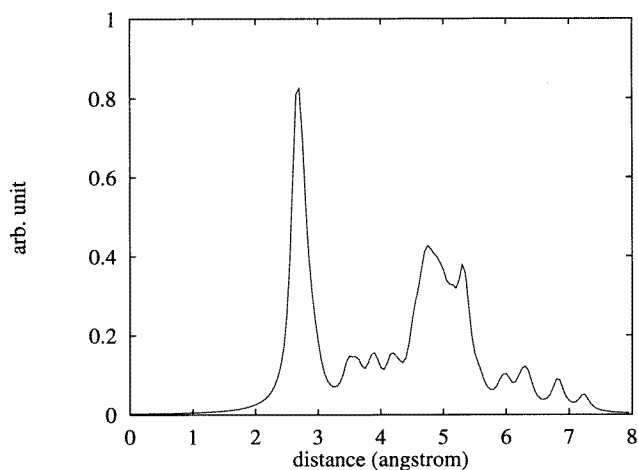
Figure 3. The radial distribution function of an amorphous Pt_{13} cluster, (j) of figure 2, obtained with a Lorentzian broadening of 0.1 Å.

using a scanning transmission electron microscope (STEM). They found that clusters less than 4 nm in diameter were disordered upon electron bombardment from the STEM and remained amorphous on carbon and silica substrates for 20 min and 24 h, respectively. Later Vanfleet and Mochel [17] repeated the same experiment in a higher-quality vacuum chamber and found that the clusters remained amorphous for over a week [17]. The Pt_{13} cluster is less than 1 nm in diameter, so it is reasonable to assume that the disordered phase will be stable at this cluster size as suggested by the experiments and our calculations.

It would be interesting to study how the cluster structures approach that of the bulk as the size increases. In our previous study of Al clusters [7], the minimum-energy structure of Al_{13} was ICS (slightly distorted due to the Jahn–Teller effect), Al_{55} was a distorted ICS structure, and Al_{147} was a distorted COS. Since Pt exhibits an amorphous structure for 13-atom clusters, and beyond a certain size the fcc structure should be favourable over any other (since it corresponds to the equilibrium crystal phase), it would be interesting to calculate at what size it would start to exhibit a bulklike fcc character. The method used in this letter would permit such a study, which is being presently considered.

A convenient framework for understanding the difference of structure between the Al_{13} and the Pt_{13} clusters can be provided by the concept of sharing electrons between energy levels of an atom. Considering the energy levels of a central atom in the cluster, an Al atom is more tolerant for high coordination since there are many unfilled sp states. In contrast, the central Pt atom has nearly full sd states. Therefore, the central Pt atom, which shares electrons with the outer atoms, should behave differently from Al. In fact, we found that the charge of the central atom of the perfect ICS of Al_{13} is 3.65 e, which is 0.65 e greater than the atomic valence charge of 3 e. On the other hand, that of the perfect ICS of Pt_{13} was found to be 8.4 e, which is 1.6 electrons smaller than the initial atomic valence charge of 10 e. This preference of the central atoms for a lower shared charge suggests that a lower-coordination structure such as the open amorphous configurations found in this work would be preferred for Pt_{13}. We found that in these amorphous structures the electron charge is more evenly distributed among the atoms, which stabilizes the cluster.

In conclusion, we have presented the results of a systematic *ab initio* study of small

Pt clusters. The results show excellent agreement with the experimental data available for the Pt dimer, and show that the Pt clusters with fewer than six atoms prefer planar geometries. For Pt_{13} our results suggest a preference for disordered structures far from the crystalline-like ordering, which is consistent with experiments on Pt nanoclusters.

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