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# Theoretical study of the icosahedral to cuboctahedral structural transition in Rh and Pd clusters

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**Abstract.** The icosahedral to cuboctahedral structural transition in $Rh_N$ and $Pd_N$ clusters with closed atomic shells and increasing sizes ($N = 13$, 55, 147, 309, 561) is studied using a tight-binding description of the valence band including *sp* electrons as well as *d* electrons assuming an homogeneous relaxation, the effect of inhomogeneous relaxation being discussed by means of an empirical potential. The critical size at which the cuboctahedral and icosahedral clusters have roughly the same energy is similar for Rh and Pd. The potential energy profile for the Mackay transformation which distorts continuously a cuboctahedron into an icosahedron is also calculated. The cuboctahedral structure is found to be unstable for $N = 13$ but, for $55 \leq N \leq 561$, the potential energy profile exhibits an activation barrier which is expected to persist at least in some range of larger sizes. This explains the coexistence of both geometries at intermediate sizes. Finally the electronic structure of these clusters is also discussed.

**PACS.** 36.40.Ei Phase transitions in clusters – 71.24.+q Electronic structure of clusters and nanoparticles – 71.20.Be Transition metals and alloys

## 1 Introduction

In spite of the large number of theoretical and experimental studies, the atomic structure of small clusters is still the object of many investigations. When the size of the cluster decreases, most atoms become surface atoms with low coordination and are subject to forces which lead to an equilibrium atomic configuration possibly different from that of a fragment of the bulk phase. Furthermore the relative stability of two clusters depends on several fundamental quantities: the number of surface atoms, the orientation of facets and their relative energies, the stress inside the cluster etc. The determination of the atomic configuration of small clusters is however of a fundamental importance in addressing chemical and physical properties, such as catalysis or crystal growth, of any system. Unfortunately for the moment there exists no direct experimental technique to determine the structure of free clusters. The only really direct method for observing clusters is the High Resolution Electron Microscopy (HREM) [1–3] but of course it only concerns supported clusters where the substrate may play a role, and moreover the influence of the high-energy electron flux on the geometry of the clusters may induce radiation damage. This damage is drastically reduced in electron diffraction [4,5] and Extended X-ray Absorption Fine Structure (EXAFS) [6] experiments but the structural information is less directly obtained. In these experiments, clusters with five fold symmetry axes have been observed, whereas such axes are forbidden in perfect crystals. For instance, icosahedral aggregates have been found in a large number of experiments on rare gas clusters [7] and also on metals like Cu, Ag, Au, Ni, Pd, Pt and Co (for specific references see Ref. [8]). Moreover, the cluster sizes $N = 55$, 147, 309, 561 atoms of Ni and Co have revealed to be particularly stable [9] and have a closed icosahedral structure (*i.e.*, made of closed atomic shells). From the theoretical point of view and since the rare gases and all the metals quoted above have an FCC solid phase (save for Co which has however an FCC phase at high temperature), it is interesting to study the relative stability of the closed icosahedral clusters and FCC clusters which have the same sequence of number of atoms, *i.e.*, closed cuboctahedral structures.

Several studies of this type can be found in the literature. Pair potentials (Lennard-Jones or Morse) have been extensively used for rare gases [10–12]. For instance Doye and Wales [13] showed recently with a very simple Morse potential that a wide variety of scenario can be obtained depending only on the range of the potential. However, in metals and in particular for noble and transition metals, the interactions between atoms are not pairwise and energy calculations need either more elaborate potentials, containing at least a many body contribution, or *ab initio* methods. In spite of recent progress in the computer power and in the electronic structure codes, it remains very difficult to go beyond one hundred of atoms in the latter methods, especially for transition metal systems for which the precise description of *spd* valence electrons remains a hard task. As a consequence there are many *ab initio* results on 13 atom clusters, but very few for larger sizes.

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Among them Bernholc *et al.* [14] studied $\mathrm{Al}_{13}$ and $\mathrm{Al}_{55}$ and Jennison *et al.* [15] $\mathrm{Ru}_N$, $\mathrm{Pd}_N$ and $\mathrm{Ag}_N$ with $N = 55$, 135 and 140 using massively parallel computer codes. On the contrary, many empirical or semi-empirical potentials have been widely used to study the relative stability of closed cuboctahedral and icosahedral structures: Sutton-Chen potential [16], second moment potential [17–19], glue model [20], embedded atom model (EAM) [2,21–23], effective medium theory (EMT) [24]. Finally, intermediate between the above types of calculations, the tight-binding scheme is much less costly in computer time but still describes systems within the framework of quantum mechanics and allows to investigate cluster sizes which are presently out of reach of *ab initio* calculations. For instance Lathiotakis *et al.* [8] used this method to study $\mathrm{Ni}_N$ clusters up to $N = 55$. All these works agree in predicting the higher stability of the icosahedral structure at very small sizes.

Furthermore, Mackay [25] has quoted that it is possible to transform the cuboctahedron into an icosahedron by a simple continuous distortion. As we will see in the following this distortion preserves many of the symmetries of the cuboctahedron and one can think that the configuration space point follows a valley in the potential energy surfaces. Thus it is interesting to investigate if this transformation (or the inverse one) needs an activation energy or, in other words, if the cuboctahedron is unstable or metastable relative to this transformation at sizes for which the icosahedron is energetically favoured (or *vice versa*).

We have recently set up a new tight-binding model [26] using an orthogonal *spd* basis set from which, contrary to analytical potentials, the electronic structure and the corresponding total energy for any position of the atoms can be derived. This tight-binding model was shown to be able to reproduce very accurately the electron energy levels as well as the total energy of surfaces and very small clusters. In this paper we will apply it to the study of the relative stability of closed cuboctahedral and icosahedral clusters $\mathrm{Rh}_N$ and $\mathrm{Pd}_N$ ($N$ = 13, 55, 147, 309, 561) and the potential energy profile of the Mackay transformation which, at least to our knowledge, has not been calculated yet. The paper is organized as follows. In Section 2 we present a brief summary of the model. Section 3 is devoted to the relative stability of the two structures as a function of the cluster size and atomic relaxation effects are discussed. The local densities of states are discussed in Section 4 on the example of $\mathrm{Rh}_N$. Section 5 presents the study of the variation of the potential energy during the Mackay transformation. Finally conclusions are drawn in Section 6.

## 2 The model

The tight-binding model used has been described in details in a previous paper [26], thus we will only recall its main features. The Hamiltonian is defined by its matrix elements in an orthogonal basis set built from $s$, $p(x, y, z)$, $d(xy, yz, zx, x^2 - y^2, 3z^2 - r^2)$ valence atomic orbitals $|i\lambda\rangle$ centered at each atomic site $i$. The intersite elements (hopping integrals) are determined from the ten Slater Koster hopping integrals $(ss\sigma, sp\sigma, sd\sigma, pp\sigma, pp\pi, pd\sigma, pd\pi, dd\sigma, dd\pi, dd\delta)$. A simple exponential decay of these elements with distance is assumed and three center integrals are neglected. Following reference [27] the on-site terms of the Hamiltonian are defined in such a way that the total energy is obtained by summing up the occupied energy levels. This means that the usual repulsive contribution is accounted for by a dependence on the atomic environment of the on-site terms that we write in the simple form [27] $(\lambda = s, p, d)$:

$$\varepsilon^0_{i\lambda} = a_\lambda + b_\lambda \rho_i^{2/3} + c_\lambda \rho_i^{4/3} + d_\lambda \rho_i^2 \tag{1}$$

with

$$\rho_i = \sum_{j \neq i} \exp\bigl(-p_\rho (R_{ij}/R_0 - 1)\bigr). \tag{2}$$

The parameters of the model are determined by a non-linear least mean square fitting on *ab initio* band structure and total energy curves of two different crystallographic structures (FCC and BCC) at several interatomic distances and their values for palladium and rhodium have been given in our previous publications [26,28].

One should note that these parameters are obtained from systems in which all atoms are geometrically equivalent therefore with no charge transfers. When they are used to study systems presenting inequivalent atoms, unrealistic charge transfers occur, as expected since this is a well-known drawback of non-self consistent tight-binding methods. In metallic systems a very efficient screening of the electrons induces an almost perfect charge neutrality of each individual atom, therefore we have adopted the simplest possible approximation that consists in adding a shift $\delta V_i$ to the on-site terms in order to ensure the local charge neutrality. Since this potential arises from electron-electron interactions, one should not forget to subtract the corresponding double counting term in the expression of the total energy which is then written as:

$$E_{\mathrm{tot}} = \sum_{nocc} \epsilon_n - N_{\mathrm{val}} \sum_i \delta V_i \tag{3}$$

where $N_{\mathrm{val}}$ is the total number of valence *spd* electrons per atom of the metal.

## 3 Relative stability of cuboctahedra and icosahedra

The cuboctahedron and the icosahedron are two very interesting polyhedra, the first one is an Archimedean solid whereas the second one belongs to the class of the five Platonic solids. Besides these historical classifications and their rather different apparent geometrical shapes, cuboctahedra and icosahedra are very closely linked, since a cuboctahedron formed of rigid rods can be transformed

**Table 1.** The nearest neighbour bond length at equilibrium and the binding energy per atom of cuboctahedral and icosahedral $\mathrm{Rh}_N$ and $\mathrm{Pd}_N$ clusters with closed atomic shells as a function of the number of atoms $N$ for homogeneously relaxed clusters.

| Rh | cuboctahedron | | icosahedron | | |
|---|---|---|---|---|---|
| $N$ | $R$ (Å) | $E^{\mathrm{hom}}_{\mathrm{cubo}}$ (eV/atom) | $R_{\mathrm{r}}$ (Å) | $R_{\mathrm{t}}$ (Å) | $E^{\mathrm{hom}}_{\mathrm{ico}}$ (eV/atom) |
| 13 | 2.613 | 3.472 | 2.556 | 2.688 | 3.748 |
| 55 | 2.656 | 4.355 | 2.593 | 2.726 | 4.457 |
| 147 | 2.671 | 4.751 | 2.606 | 2.740 | 4.812 |
| 309 | 2.679 | 4.970 | 2.615 | 2.749 | 4.998 |
| 561 | 2.683 | 5.111 | 2.620 | 2.755 | 5.119 |
| $\infty$ | 2.694 | 5.780 | 2.643 | 2.779 | 5.666 |

| Pd | cuboctahedron | | icosahedron | | |
|---|---|---|---|---|---|
| $N$ | $R$ (Å) | $E^{\mathrm{hom}}_{\mathrm{cubo}}$ (eV/atom) | $R_{\mathrm{r}}$ (Å) | $R_{\mathrm{t}}$ (Å) | $E^{\mathrm{hom}}_{\mathrm{ico}}$ (eV/atom) |
| 13 | 2.625 | 2.680 | 2.578 | 2.711 | 2.825 |
| 55 | 2.690 | 3.093 | 2.628 | 2.763 | 3.148 |
| 147 | 2.711 | 3.309 | 2.652 | 2.788 | 3.333 |
| 309 | 2.724 | 3.442 | 2.660 | 2.797 | 3.446 |
| 561 | 2.731 | 3.527 | 2.667 | 2.804 | 3.521 |
| $\infty$ | 2.751 | 3.923 | 2.691 | 2.830 | 3.882 |

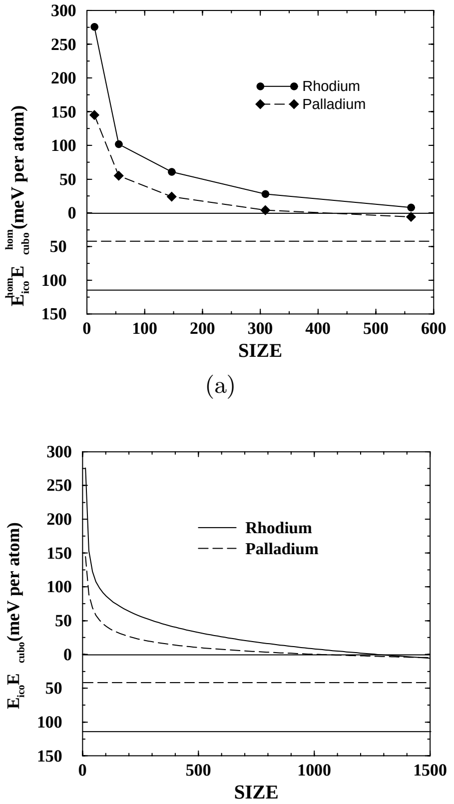
simply into an icosahedron. The cuboctahedral clusters are built on the basis of a fixed FCC lattice, and from this transformation an icosahedral cluster with the same number of atoms is obtained. These two closed structures are particularly stable at intermediate sizes. Of course at mesoscopic sizes the Wulff polyhedron is expected to be the most stable [24] since it satisfies the Wulff condition of minimization of surface energy at constant volume, but this condition only applies for large sizes when edge and vertex effects become negligible. At intermediate sizes of a few thousand atoms (sometimes up to $10^5$ atoms) a large variety of shapes can be observed [1,3] and among them particles with cuboctahedral or icosahedral symmetry.

In this section we will focus our attention on the relative stability of closed cuboctahedral and icosahedral clusters of palladium and rhodium when size increases. In a previous publication [28] we studied the magnetic behavior of small palladium and rhodium clusters of various shapes and sizes, however we did not perform calculations on large clusters since the magnetic moment of rhodium clusters disappears for sizes of more than 100 atoms, whereas palladium clusters are hardly magnetic. From our results it also appeared that magnetism does not play an important role in the relative stability of cuboctahedral and icosahedral clusters of these elements even at small sizes. Therefore spin polarization will be neglected in the present work.

Most of the calculations are based on the self-consistent tight-binding model described in the previous section. Within this model the only geometrical optimization that we consider is the "breathing mode" relaxation which leads to an homogeneous contraction of the clusters. We will check in the following the limits of validity of this simple optimization by using an analytical empirical potential. However, an unconstrained relaxation would be feasible in our model, but much more time consuming. In all calculations a finite Fermi temperature (0.01 eV) was used to attain convergency without any computational difficulties, we checked that this Fermi broadening of the energy levels did not affect the relative energies of the two geometries. The convergency of the local potentials $\delta V_i$ has been considered to be achieved when the net charge on each atom is less than $5 \times 10^{-2}$ electron and the difference in energy per atom of three consecutive iterations less than $5 \times 10^{-4}$ eV. We performed calculations on all $\mathrm{Pd}_N$ and $\mathrm{Rh}_N$ icosahedral and cuboctahedral clusters ranging from the smallest, $N = 13$, to $N = 561$ (*i.e.* $N = 13, 55, 147, 309, 561$).

In the cuboctahedron all atoms have the same first neighbour distance, $R$, which is slightly contracted compared to the bulk one, $R_0$, this contraction decreasing monotonically when size increases (see Tab. 1). In the icosahedron there are two characteristic distances: the radial nearest-neighbour distance, $R_{\mathrm{r}}$, (*i.e.*, the distance between atoms belonging to two adjacent shells) and the intrashell nearest neighbour distance, $R_{\mathrm{t}}$, which is about 5% larger than the former ($R_{\mathrm{t}} = r_{\mathrm{ico}} R_{\mathrm{r}}$ with $r_{\mathrm{ico}} = (2(1 - 1/\sqrt{5}))^{1/2} \approx 1.05146$). At equilibrium we find that $R_{\mathrm{r}}$ ($R_{\mathrm{t}}$) is slightly smaller (larger) than the value of $R$ in the corresponding cuboctahedron and $(R_{\mathrm{r}} + R_{\mathrm{t}})/2 \simeq R$ (see Tab. 1).

The binding energy per atom (positive) of $\mathrm{Rh}_N$ and $\mathrm{Pd}_N$ cuboctahedrons and icosahedrons of increasing sizes



(a)

(b)

**Fig. 1.** (a) The difference of binding energy (per atom) between the homogeneously relaxed icosahedral and the cuboctahedral clusters $\mathrm{Rh}_N$ and $\mathrm{Pd}_N$ as a function of $N$, calculated with the tight-binding model. (b) Same difference as in (a) but the effect of an inhomogeneous relaxation, calculated with an empirical model, has been added. The horizontal lines give the asymptotic value when $N \to \infty$. The curves joining the calculated points are a guide for the eyes, they do not give the energy difference for intermediate sizes.

and the corresponding difference in binding energy per atom between these two clusters are given respectively in Table 1 and Figure 1a. Clearly for both elements the icosahedron is the preferred structure at small sizes, and the critical size at which the relative stability becomes favorable to cuboctahedrons is larger for rhodium than for palladium. This critical size is $N = 561$ for $\mathrm{Pd}_N$ clusters. For $\mathrm{Rh}_N$ it is larger and we expect it to be attained for $N = 923$. In Table 1 we have also given the binding energy per atom of cuboctahedral and icosahedral $\mathrm{Pd}_N$ and $\mathrm{Rh}_N$ when $N$ tends to infinity. The binding energy per atom of an infinite cuboctahedron is just the cohesive energy of the corresponding bulk FCC metal. Let us consider now an icosahedron with an arbitrary large number of atoms. It is well-known that an icosahedron can be built from 20 identical tetrahedra possessing a common vertex and connected with each other through adjacent faces, forming twinning planes [29]. Each tetrahedron, with 4 faces of (111) type, has a slightly distorted FCC structure. It can be considered as made of (111) planes, parallel to its external face, with an ABC stacking sequence but the distance between nearest neighbours inside these planes is $\simeq 5\%$ larger than the distance between nearest neighbour atoms belonging to two adjacent planes. In the limit of large $N$, not only the weight of surface atoms vanishes as for the cuboctahedron but also that of the twinning planes. Thus the binding energy per atom of an infinite icosahedron is the cohesive energy of a distorted bulk FCC structure. This cohesive energy is minimized with respect to $R_{\mathrm{t}}$, the ratio $R_{\mathrm{t}}/R_{\mathrm{r}}$ being kept to the value $r_{\mathrm{ico}}$. It is found that the minimum occurs when the atomic volume of the distorted structure is almost equal (actually very slightly larger) to the atomic volume of the perfect FCC crystal as expected from elasticity theory.

From Figure 1a it appears that rhodium and palladium have a rather similar behaviour save for a scaling factor. For small sizes the energy difference between the two geometries is larger (in favor of icosahedrons) for $\mathrm{Rh}_N$ than for $\mathrm{Pd}_N$ and at the infinite limit this energy difference is almost three times larger (in favor of cuboctahedron) for rhodium (114 meV) than for palladium (41 meV).

Let us recall that all the results presented above have been obtained by assuming an homogeneous atomic relaxation of the clusters. However a rigorous treatment must involve an unconstrained relaxation, *i.e.*, an inhomogeneous radial relaxation as well as tangential displacements. In particular it is well-known that icosahedrons have a rather peculiar relaxation around the central atom [10,15,19] with a compression, increasing with size, of the innermost shells. We have first checked this specific behaviour on the example of 55 atom clusters by allowing independent relaxations of the two atomic shells, using our tight-binding model. In order to define the positions of these two shells, let us consider an atomic row going from the central to a vertex atom. We call $d_{01}$ the distance between the former atom and its first nearest neighbour along this row and $d_{12}$ the distance between this neighbour and the latter atom. The corresponding relaxations are defined as $\Delta d_{01}/R_0 = (d_{01} - R_0)/R_0$ and $\Delta d_{12}/R_0 = (d_{12} - R_0)/R_0$. We indeed find that the relaxation is very different for the two geometries. For instance in $\mathrm{Pd}_{55}$ rather large compressions ($\Delta d_{01}/R_0 = -4.5\%$) about the central atom are obtained while surface relaxations are more modest ($\Delta d_{12}/R_0 = -3.6\%$) in the icosahedron. In contrast, the FCC cluster has a small internal compression ($-1.1\%$) but larger surface relaxations ($-3.1\%$). These results are in agreement with the *ab initio* calculations of Jennisson *et al.* [15] and in both cases the energy difference with the homogeneously contracted cluster is less than 1 meV per atom, *i.e.*, at least one order of magnitude smaller than the typical energy difference between cuboctahedron and icosahedron with 55 atoms.

However it is not clear that these results are still valid for larger clusters and with a fully (except for symmetry) unconstrained relaxation. As previously mentioned, this could be investigated in the framework of our tight-binding model but, in view of the computing time needed for a systematic study, we have used the following empirical potential:

$$E_{\text{tot}} = A \sum_{i,j,j\neq i} \exp\big(-p(R_{ij}/R_0 - 1)\big) - \xi \sum_i \Big(\sum_{j\neq i} \exp\big(-2q(R_{ij}/R_0 - 1)\big)\Big)^{\alpha} \quad (4)$$

with a smooth cut-off function beyond the fourth neighbors. Note that this potential differs from the conventional second moment potential in which $\alpha = 1/2$. Indeed it is well-known [30] that it is impossible to get both the cohesive and the surface energies correctly with $\alpha = 1/2$. This is a serious problem when dealing with clusters in which the atomic structure is determined by the competition between surface and bulk effects. Furthermore, another exponent ($\alpha = 2/3$) has been proposed in the literature [31] to account for higher moments and charge neutrality requirements. In the particular case of Rh and Pd we have found that, with $\alpha = 3/4$, we have been able to reproduce quite accurately the *ab initio* cohesive energy curve versus atomic spacing and the surface energies of the three lowest index surfaces ((111), (100), (110)) while keeping reasonable values for the elastic constants $C$ and $C'$. The corresponding parameters are $A = 0.334$ eV (0.259 eV), $\xi = 1.393$ eV (1.026 eV), $p = 9.53$ (9.86), $q = 2.48$ (2.83) for Rh (Pd). With this potential, we have optimized the interatomic distances of the cuboctahedral and icosahedral $\text{Rh}_N$ and $\text{Pd}_N$ clusters in three different ways up to $N = 1415$:

(i) the breathing (or homogeneous) mode,
(ii) purely radial but inhomogeneous atomic displacements,
(iii) displacements with radial as well as tangential components.

We have found that the tangential relaxation has a negligible effect on the total energy of the clusters. When comparing the inhomogeneous radial relaxation to the breathing mode, we have found that the binding energy per atom at equilibrium in the cuboctahedral clusters is almost unchanged (by less than 1 meV) while, as expected, it is increased significantly in the icosahedral clusters.

Let us call $\Delta E^{\text{hom}}(N) = E^{\text{hom}}_{\text{ico}}(N) - E^{\text{hom}}_{\text{cubo}}(N)$ the binding energy difference between the homogeneously relaxed icosahedron and cuboctahedron of size $N$ and $\Delta(N)$ its variation due to allowing inhomogeneous radial relaxation instead of the breathing mode. The latter quantity obviously vanishes for $N = 13$ and our calculations using the empirical potential show that $\Delta(N)$ is positive and increases with size but saturates at large $N$.

The most simple way to improve our tight-binding results for $\Delta E^{\text{hom}}(N)$ is to add the value of $\Delta(N)$ deduced from the empirical potential. Then it is seen that a precise determination of the critical size at which the cuboctahedron becomes more stable than the icosahedron would require tight-binding calculations at sizes larger than $N = 561$. In order to avoid lengthy calculations, we have adopted the following extrapolation procedure. First we have fitted the data for $\Delta E^{\text{hom}}(N)$ and $\Delta(N)$ obtained by means of the empirical model in the range $13 \leq N \leq 561$ using analytical expressions of the form:

$$f(N) = a_0 + a_1 N^{-1/3} + a_2 N^{-2/3} + a_3 N^{-1} \quad (5)$$

the second, third and fourth terms account for surface, edge and vertex effects, respectively. We have verified that these expressions reproduce very accurately the calculated data up to $N = 1415$ derived from the empirical model. Then, an analytical expression as equation (5) was found to fit perfectly the tight-binding data of $\Delta E^{\text{hom}}(N)$ up to $N = 561$. The above arguments show that this fitted expression can be used confidently to extrapolate the tight-binding data for this last quantity well beyond $N = 561$. The results obtained by adding $\Delta(N)$ to it are given in Figure 1b. This modifies the critical size to $N_{\text{c}} = 1415$ both for Rh and Pd.

In conclusion, due to the effect of a complete relaxation the number of closed atomic shells necessary to make the FCC cuboctahedron more stable than the icosahedron is increased by one or two.

## 4 Local densities of states

One of the advantages of our model is its ability to give not only the total energy but also the detailed electronic structure with a reasonable amount of computer time. In particular, the local density of states (LDOS) on site $i$, defined as:

$$n_i(E) = 2 \sum_{n,\lambda} c^*_{i\lambda}(\epsilon_n) c_{i\lambda}(\epsilon_n) \delta(E - \epsilon_n) \quad (6)$$

where $c_{i\lambda}(\epsilon_n)$ is the component of the eigenstate of energy $\epsilon_n$ on the orbital $\lambda$ centered at site $i$, are easily obtained. They are very interesting quantities since they give some indication on the localization of electronic states and on the possible occurrence of local magnetism. Let us first illustrate this possibility on the example of a large cluster $\text{Rh}_{309}$, for both geometries. The results are presented in Figure 2 for the central atom (a), one atom of the first atomic shell (b), the central atom of the square facet (of type (100)) of the cuboctahedron which becomes an edge atom in the icosahedron as a result of the Mackay transformation (c) (see Sect. 5), a vertex atom (d) and an atom inside a triangular facet (of type (111)) (e). The LDOS of the icosahedron have more structures than the corresponding LDOS of the cuboctahedron. Indeed the icosahedron has more symmetry elements than the cuboctahedron and consequently a higher degree of degeneracy in its electronic levels. This effect is particularly striking on the central atom. Actually this atom, being a center of symmetry of the cluster, has a very peculiar LDOS since the antisymmetric wave functions have no weight on it, whereas the weight of the symmetric ones is enhanced. This is clearly seen in Figure 3 in which we present the evolution with size of the LDOS on the central atom of $\text{Rh}_N$ cuboctahedral clusters. One can note that even at a size as large as 309 atoms, this LDOS remains very different from the bulk one. On the contrary the LDOS (b),

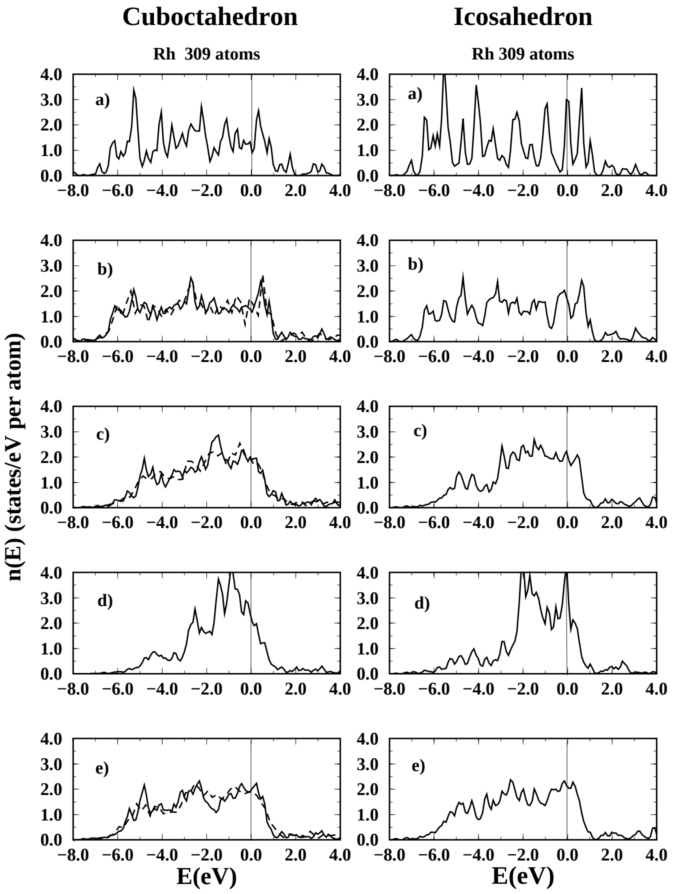


**Fig. 2.** The local densities of states at some specific sites of cuboctahedral and icosahedral $Rh_{309}$: (a) the central atom; (b) an atom in the first atomic shell; (c) an atom in the center of the square facet of the cuboctahedron which becomes an edge atom of the icosahedron in the Mackay transformation (see Fig. 3b); (d) a vertex atom; (e) an atom inside the triangular facets. The dashed lines in the cuboctahedral structures give the bulk density of states (b) and the LDOS on infinite (100) and (111) surfaces in (c) and (e), respectively. The discrete levels have been broadened by a Fermi function of with 0.05 eV.

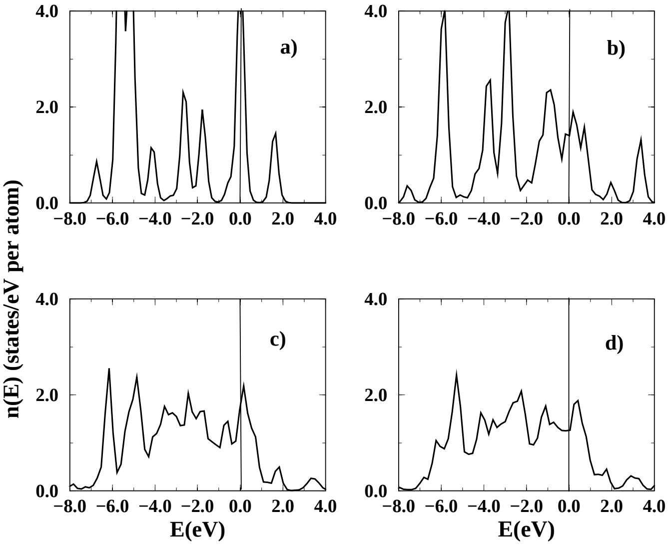


**Fig. 3.** The evolution with size of the local density of states at the central atom for cuboctahedral $Rh_N$ clusters: (a) $N = 13$, (b) $N = 55$, (c) $N = 147$, (d) $N = 309$. The discrete levels have been broadened by a Fermi function of with 0.1 eV.

(c), (e) shown in the left panel of Figure 2 are already quite close to those of the bulk, the (100) and the (111) surfaces, respectively. As expected the mean width of the LDOS increases with the local coordination number, the narrowest being that of the vertex atoms (d).

As pointed out in Section 3, experiments have shown that $Rh_N$ clusters have a noticeable magnetic moment up to $N \simeq 100$. Our results suggest however that on some specific sites of the icosahedral $Rh_{309}$ a magnetic moment may subsist. From simple arguments based on the Stoner criterion with a Stoner parameter $I = 0.69$ eV [28] we can deduce that this could occur on the vertex atoms, and perhaps on the central atom.

## 5 Mackay transformation

Let us now precise how a cuboctahedron can be transformed into an icosahedron. In this transformation [25] one of the diagonals of each square face of the cuboctahedron is contracted to the length $r_{\text{ico}} d_{\text{r}}$, $d_{\text{r}}$ being the length of the edges of the cuboctahedron (equal to its radius) while at the same time this face is folded following the same diagonal so as to form two equilateral triangles of edges $r_{\text{ico}} d_{\text{r}}$. The corresponding displacements of the vertices are shown in Figure 4 in which the axes of the coordinate frame have been chosen normal to the square faces of the cuboctahedron (cubic axes of the FCC lattice). It is easily seen that this transformation is a highly symmetric one since the three coordinate planes remain symmetry planes during the transformation. Once the displacements of the atoms located at the vertices are known, the displacements of all atoms in the cluster are easily derived.

In this section we calculate the variation of the total energy per atom during the distortion as a function of the size of the cluster using the *spd* tight-binding model. Each atom is displaced by a fraction $f$ of its total displacement and for each value of $f$ an homogeneous relaxation is performed so as to minimize the total energy. In view of the simplicity of this distortion which preserves many symmetries, it is expected that the corresponding path is a good candidate for this transformation.

The results for $Rh_N$ clusters are shown in Figure 5. It is seen that the 13 atom cuboctahedron is unstable, *i.e.*, it spontaneously transfers to an icosahedron. For $N = 55$, 147 and 309 the energy profile is not monotonic but presents a maximum around $f = 0.45$. Consequently, the cuboctahedron is metastable, at least relative to this transformation, with an activation energy of 15 meV for $N = 55$, 55 meV for $N = 147$ and 76 meV for $N = 309$. The activation energy for the inverse transformation (ico → cubo) is 116 meV both for $N = 55$ and 147, and 104 meV for $N = 309$. The $Pd_N$ clusters present an analogous behaviour. For $N = 13$ the cuboctahedron

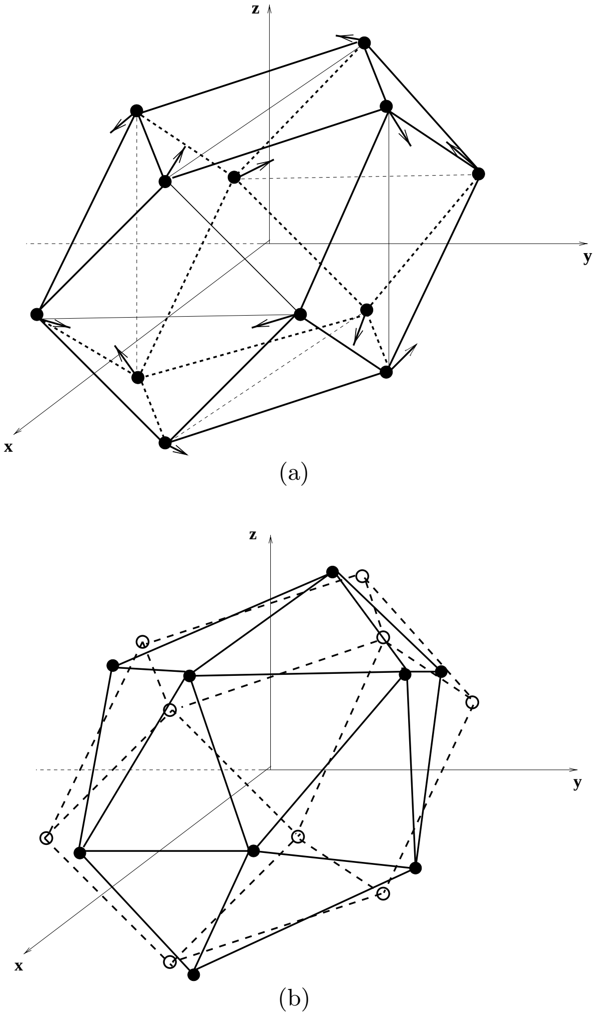


**Fig. 4.** (a) Atomic displacements transforming a cuboctahedron into an icosahedron with the same radial distance. (b) The resulting icosahedron.

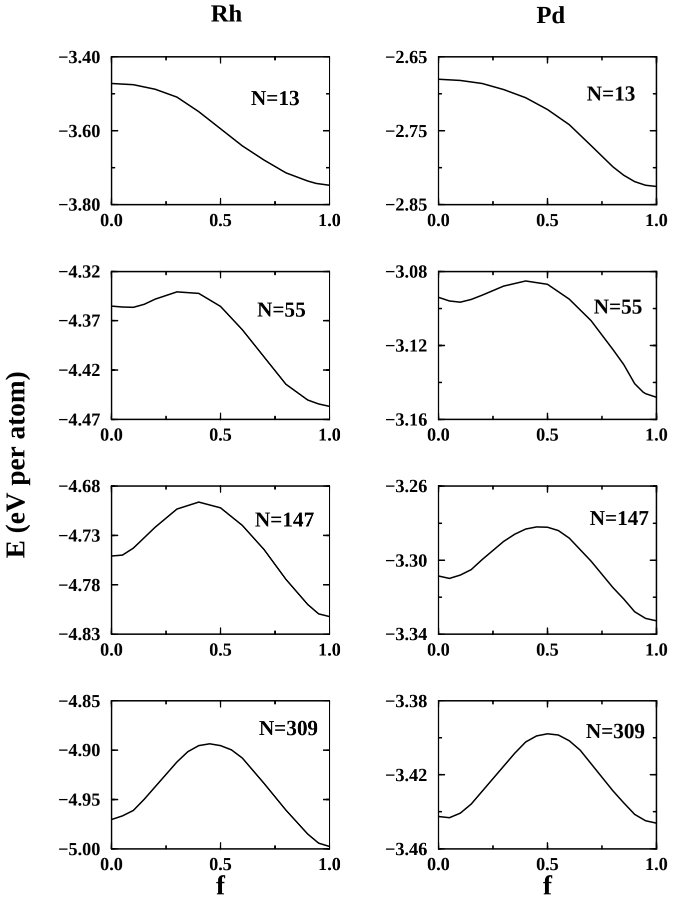


**Fig. 5.** The evolution of the potential energy profile of homogeneously relaxed $\mathrm{Rh}_N$ and $\mathrm{Pd}_N$ clusters during the Mackay transformation for increasing values of $N$. $f$ is a fraction of the displacements shown in Figure 3a: $f = 0$ and 1 correspond to the perfect cuboctahedron and icosahedron, respectively.

is also unstable. For $N = 55$, 147, and 309 atoms the cuboctahedron is metastable and slightly distorted. Its transformation to a perfect icosahedral structure needs an activation energy of 12 meV for $N = 55$, 28 meV for $N = 147$ and 45 meV for $N = 309$. The activation energies involved in the inverse transformation are 61 meV for $N = 55$, 51 meV for $N = 147$ and 48 meV for $N = 309$.

It is worthwhile to emphasize that for both elements the potential energy profile has a maximum even when the cuboctahedron and the icosahedron have roughly the same energy and it can be inferred that this maximum will still exist at least in some range of larger sizes. This could explain why icosahedral clusters may be observed at sizes for which the cuboctahedron should be energetically favoured. In addition, note that the activation barrier (per atom) for the transition ico → cubo decreases with size.

In addition, we have seen in Section 3 (Tab. 1) that the optimum radial distance of the icosahedron is always smaller than that of the cuboctahedron with the same number of atoms. Our calculations show that during the Mackay transformation the radial distance contracts monotonically.

Finally, let us discuss the effect of inhomogeneous radial relaxations with the help of the empirical potential determined in Section 3. First we have verified that for an homogeneous contraction the empirical potential leads to results extremely similar to those obtained with the tight-binding model, *i.e.*, the cuboctahedron is unstable for $N = 13$ and metastable at larger sizes. Furthermore, the potential energy barrier between the two structures has the same shape and a similar height with a saddle point around $f = 0.45$. Then the lowering of the total energy per atom due to inhomogeneous radial relaxation has been calculated for $f = 0$ (perfect cuboctahedron), $f = 0.45$ (saddle point), $f = 1$ (perfect icosahedron). It almost vanishes for $f = 0$, is quite small for $f = 0.45$ (for instance 7 meV for $\mathrm{Rh}_{309}$) and, as discussed in Section 4, becomes significant but less than $\simeq 20$ meV for $f = 1$. As a conclusion, we can state that inhomogeneous relaxations do not induce drastic changes, they only slightly modify the activation energies.

## 6 Summary and conclusions

We have presented a systematic study of cuboctahedral and icosahedral clusters of Rh and Pd with closed atomic shells as a function of their number of atoms, in the framework of a tight-binding method using a *spd* basis set, assuming an homogeneous relaxation. This method has allowed us to consider large sizes which are presently unreachable by *ab initio* calculations and to obtain the corresponding electronic structure which is ignored when using (semi)empirical potentials. Nevertheless, we have used such a potential to discuss the effect of a complete, except for symmetry constraints, relaxation,

Total energy calculations have shown that at small sizes the icosahedron is the most stable structure and that, due to inhomogeneous radial relaxation, the size at which the cuboctahedron becomes energetically favoured is comparable for the two metals (around $N = 1415$). The analysis of the local densities of states reveals that the central atoms have a very peculiar behaviour for symmetry reasons even at a size as large as $N = 309$. In addition from their values at the Fermi level it can be inferred that, even though magnetism is not detectable in $\mathrm{Rh}_N$ for $N \geq 100$, some specific sites may still carry a magnetic moment, for instance the vertex atoms in the icosahedral $\mathrm{Rh}_{309}$.

Finally the study of the potential energy profile during the Mackay transformation which distorts continuously a cuboctahedron into an icosahedron has shown that the cuboctahedron is unstable for $N = 13$ whereas it becomes metastable at intermediate sizes. This result could explain the experimentally observed coexistence of both geometries in some range of sizes.

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