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# Extending the cluster scaling technique to ruthenium clusters with hcp structures

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## ABSTRACT

Using density functional techniques at the level of the generalized gradient approximation, we addressed structural, energetic, and electronic properties of ruthenium clusters with hexagonal close-packed structural motifs and sizes between ~1 and ~2 nm. We discuss the construction principles of model clusters with hcp structures and examine the evolution of various properties with respect to cluster size. We compare the scaling behavior with that of ruthenium clusters of similar sizes, but with face-centered cubic structures. Thus, we extended the scaling technique, well established for clusters of transition metals with face-centered cubic structures, to hexagonal closed-packed ones. For the model clusters explored, the examined properties scale well with cluster size. For example, a clear energy preference develops for hexagonal over cubic structures of ruthenium particles. Furthermore, we studied the differences in the scaling behavior as described by an all-electron treatment with localized basis functions and a projector augmented wave plane-wave method.

## 1. Introduction

Similar to the other elements of the platinum group, ruthenium shows outstanding catalytic properties [1–9]. Important examples for this catalytic activity are the Fischer–Tropsch process [2,6], the synthesis of ammonia [3,6], photochemical water splitting [7], the oxidation of carbon monoxide [5,8], the methanation of $CO_2$ [4], and the hydrodeoxygenation of aromatic compounds [9]. Ru nanoparticles with diameters of about 2–6 nm as employed in some of the aforementioned experiments clearly are beyond the reach of quantum chemistry studies by density functional theory (DFT) calculations. Smaller $Ru_n$ model clusters with nuclearities in the order of $n = 10^1$–$10^2$ are more amenable to studying size dependent properties of such nanoparticles (NPs), which then can be extrapolated to the desired size range using suitable scaling relations [10–22].

Bare clusters of specific nuclearities $n > 50$ of late transition metal elements are often difficult to isolate in experiments. In consequence, experimental references are rather sparse for such systems. Thus, a comparison with results from theoretical approaches like DFT is mostly limited to bulk materials which are easily accessible in experiments. Cluster scaling methods, connecting properties of moderately large clusters ($n \approx 10$–$300$) to those the corresponding bulk material, have extensively been applied to $Ni_n$, $Pd_n$, and $Au_n$ clusters [10–20,22,23]. In such studies the scaling behavior of various properties of metal clusters $M_n$ with increasing nuclearity $n$ have been examined, benefitting from an extrapolation to the bulk limit, e.g. via a suitable size parameter (Section 2.2) [10–16,18–20,22].

The cluster scaling approach allows one to obtain a physically motivated average of a series of results as well as to examine the scalability of the property under study [10–20,22]. While larger Ruthenium clusters were studied in the past by parameterized methods [24], thus far a systematic theoretical study of larger $Ru_n$ clusters with up to several hundreds of atoms by accurate DFT calculations is still lacking, likely due to the hexagonal close-packed (hcp) structure of the ruthenium bulk material [25]. Ru NPs beyond a certain size will behave likewise, despite the reported preference for cubic structures for smaller $Ru_n$ clusters with $n < 64$ [26,27]. Compared to NPs of elements with face-centered cubic (fcc) bulk structures, the construction principles of clusters of hcp metals like Ru are somewhat more complicated. In addition, the hcp structure becomes favored only beyond a certain cluster size due to the aforementioned preference for cubic motifs in smaller $Ru_n$ species [28].

The present DFT study addresses the evolution of structural, energetic, and electronic properties of ruthenium NPs with increasing cluster size. To this end we examined the scaling behavior of two series of NPs $Ru_n$, one series following the hcp motif, the other one the fcc motif. Furthermore, we compare the results of plane-wave DFT calculations

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with those obtained from an all-electron scalar-relativistic treatment using localized basis functions to examine possible variations arising from these computational methodologies.

## 2. Theoretical methods

### 2.1. Computational details

All DFT calculations were carried out with the generalized-gradient approximation PBE (suggested by Perdew, Burke, and Ernzerhof [29]) to the exchange–correlation (xc) functional. The program PARAGAUSS [30], an implementation of the Gaussian-type orbital fitting-function density functional method [31,32] (LCGTO-FF-DF) was used for the all-electron (AE) calculations of this study. Scalar relativistic effects were accounted for by means of the second-order variant of the approximation due to Douglas, Kroll, and Hess [33,34]. For Ru, we employed a Gaussian-type orbital basis set [35] that features the contraction $(18s,13p,9d) \rightarrow [8s,6p,4d]$; the contraction coefficients were constructed from atomic eigenvectors. An auxiliary basis set used to represent the Hartree potential was generated from this orbital basis following an established prescription [31,32]. For the numerical integration of the xc terms, we used a superposition [36] of spherical, atom-centered, Lebedev-type grids [37], each with a radial grid containing 177 shells. All structures were optimized with an angular grid locally exact for spherical harmonics up to angular momentum $L = 17$. The final energies were then obtained with a grid accurate up to $L = 19$. While the structural changes induced by this larger grid are below 0.01 pm, $L = 19$ was found to be essential for correctly reproducing the energy differences between hcp and fcc structures (Section 3.2). Test calculations on even larger grids indicated that with $L = 19$ energies are stable within 1 kJ/mol. The electronic structure of all cluster models was converged under constraints of appropriate point-group symmetries (Section 2.2) until the maximum changes in the density matrix were below $10^{-7}$. Furthermore, a Fermi-type fractional occupation number approach [31] with a broadening parameter of 0.01 eV was employed to ease the convergence. The geometric structures were relaxed with the utility suite PARATOOLS [38] until all atomic forces were below $10^{-5}$ au. Henceforth the results of the calculations with the all-electron approach described above will be labeled as AEGTO.

In addition, we carried out plane-wave calculations with the program VASP, version 5.3 [39,40]. The projector augmented wave (PAW) approach [41,42] was employed for describing the core electrons. An energy cutoff of 400 eV was used for the plane-wave representation of the orbitals. In all cases, the Brillouin zone was sampled at the **Γ**-point. In the case of the extended bulk systems **k**-point grids were centered at the **Γ**-point, 21 × 21 × 13 for hcp and 21 × 21 × 21 for fcc. Both bulk structures were calculated in their respective crystallographic unit cells. The Ru atom and all clusters were modeled in unit cells large enough to ensure a nearest-neighbor distance of at least 15 Å in all directions between separate images. Dipole corrections were added to account for electrostatic interactions between these images [43]. Also in the case of the plane-wave calculations the electronic levels were broadened by a Fermi–Dirac function, using a broadening parameter of 0.001 eV [44]; subsequently the results were extrapolated to 0 eV. The electronic structures of all systems were converged until the changes in the total energy were below $10^{-5}$ eV. The geometries were optimized until forces on all atoms were below $\sim 3 \times 10^{-4}$ au. In the following the results of these calculations are designated as PAWPW.

### 2.2. Scaling procedure and cluster models

While providing information on the scalability of many physical properties $X$ of clusters $M_n$ with increasing nuclearities $n$, cluster scaling approaches [10–20,22] also allow one to extrapolate computational results for such properties to their respective bulk limit.

Cluster scaling may be motivated as follows. Individual atoms of a cluster are located in various environments. While the core part of a cluster can be expected to exhibit similarities to the corresponding bulk material, atoms in the cluster surface are subject to distinctively different surroundings [45]. However, any property of a given cluster is determined by its electronic structure and therefore, in a metal system, by all of its atoms [10,11,16,46,47]. Beyond a certain cluster size, in the so-called scalable regime [48], many physical properties can be considered as result of additive contributions of bulk and surface atoms. To the extent that these fractions of atoms scale with the volume and the surface, respectively, of the cluster, the property $X$ per atom will show a linear dependence on the surface-to-volume ratio of the cluster [10–20,22]. The volume of a cluster can be taken to be proportional to n. The surface of sufficiently large clusters scales as $n^{2/3}$, hence the surface-to-volume ratio scales as $n^{-1/3}$. Thus the size-dependence of a linearly scalable property $X$ is given as

$$X(n) \approx k_X \cdot n^{-1/3} + X_\infty. \quad (1)$$

From a series of cluster models one determines the slope $k_X$ and the offset $X_\infty$ (i.e. the bulk limit) as the result of a least-squares fit [11–20, 22].

For a good scaling behavior it is beneficial if the cluster models examined show a close structural similarity, in particular to cut-outs of the bulk crystal structure. Furthermore, electronic situations not present in the bulk have to be avoided. Clusters of related structural motifs were selected to facilitate scalability. Increasingly larger models for cluster scaling were mostly constructed in terms of shells of atoms. In the targeted nuclearity range, $50 < n < 330$, the fcc-type cluster models $M_n$ studied are the atom-centered, cuboctahedral systems $Ru_{55}$, $Ru_{147}$, and $Ru_{309}$ (Fig. 1a) as well as the octahedron-centered clusters $Ru_{116}$ and $Ru_{260}$ (Fig. 1c), which are of truncated octahedral shape.

Additional truncated octahedral structures were generated by adding atoms on the (001)-type facets of the aforementioned systems, to yield the atom-centered models $Ru_{79}$ and $Ru_{225}$ (Fig. 1b) and the octahedron-centered system $Ru_{140}$ (Fig. 1c). All these models exhibit $O_h$ symmetry, reflecting the local topology of the fcc crystal structure. Although not related to bulk materials, we also examined the icosahedral clusters $Ru_{55}$ and $Ru_{147}$ (Fig. 1d) as examples of another type of highly symmetric particles. These latter species are also studied to confirm earlier findings [49] that icosahedral $Ru_n$ structures are not preferred over clusters with lower symmetry.

For hcp-type $Ru_n$ systems we established a similar construction scheme as for the fcc clusters. fcc and hcp crystal structures differ mainly in the lower local symmetry of the latter. Compared to fcc cluster centers (occupied by a single atom or octahedron), four types of centers can be defined for cluster models of an hcp material (Fig. 2). From a single atom as cluster center a series of systems with $D_{3h}$ symmetry can be constructed in the target range of nuclearities: $Ru_{57}$, $Ru_{153}$, and $Ru_{323}$ (Fig. 2a); $Ru_{323}$ was studied only with PAWPW calculations. Starting with a triangle $Ru_3$ at the center, one arrives at two series of clusters that differ in the position of the adjacent (0001)-type layers. These second layers are either located with a single atom or another $Ru_3$ triangle on-top of the central triangle; all clusters again are of $D_{3h}$ symmetry. Examples of the former series are the clusters $Ru_{87}$ and $Ru_{210}$ (Fig. 2b), examples of the latter $Ru_{89}$ and $Ru_{214}$ (Fig. 2c). Finally, the cluster center can also be located between two (0001) layers, hence comprise a $Ru_6$ octahedron, "lying" on one of its faces. We studied only a single structure of this type, the cluster $Ru_{114}$ with $D_{3d}$ symmetry (Fig. 2d).

## 3. Results and discussion

### 3.1. Structural aspects

We start the scaling analysis of cluster properties of $Ru_n$ clusters with the average nearest-neighbor distance $d_{av}$. Table S1 of the SD provides

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