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Hartree–Fock–Slater Linear Combination of Atomic Orbital Calculations of the Valence Electron Distribution in Neutral and Charged Ir Clusters

W. Ravenek,

Department of Theoretical Chemistry, Free University of Amsterdam, De Boelelaan 1083,
1081 HV Amsterdam, The Netherlands

A. P. J. Jansen, and R. A. van Santen*

Laboratory of Inorganic Chemistry and Catalysis, Technical University of Eindhoven, P.O. Box 513,
5600 MB Eindhoven, The Netherlands *(Received: October 25, 1988)*

Hartree–Fock–Slater LCAO calculations have been performed for two clusters, viz., Ir_4 and Ir_{10}. The average atomic configurations are found to be $(5d)^{8.28}(6s)^{0.66}(6p)^{0.06}$ for the Ir_4 cluster and $(5d)^{8.10}(6s)^{0.86}(6p)^{0.02}$ for the Ir_{10} cluster. The larger number of d holes computed for the Ir_{10} cluster contradicts observations of the white line edges of EXAFS of small particles, which indicate a larger d-hole density on smaller particles. Comparison with d hole density calculations on clusters having a core hole demonstrates that this apparent discrepancy is due to polarization–relaxation of the ionized clusters. The atomic configuration on the ionized atom for the Ir_4^+ cluster is found to be $(5d)^{9.13}(6s)^{0.01}(6p)^{0.44}$, and the average atomic configuration on the ionized atoms of the Ir_{10}^+ cluster is $(5d)^{9.32}(6s)^{0.46}(6p)^{-0.03}$. The electron populations are based on population analysis. One observes a larger number of holes on the ionized atom of the Ir_4 cluster compared to that of the Ir_{10} cluster. The observed inversion in d-hole density clearly derives from the larger polarizability of the larger particle.

Introduction

A fundamental question in heterogeneous metal catalysis deals with the possibility that intrinsic metal particles properties can be changed by interaction with the support. A recent discussion on this subject can be found in the book by Boudart and Djega-Mariadassou.[1] The so-called Schwab effect of the second kind is introduced. It describes a modification of the catalytic activity due to the alteration of the electron density of cluster atoms because of charge transfer or polarization at the interface between a very small cluster and a support.

Catalytic[2,3] and spectroscopic studies[4–6] strongly suggest such an effect to be present in Pt–Y sieves, containing in addition to Pt different alkali-metal or alkaline-earth cations. Rabo[2] has suggested that if highly charged cations are present, the Pt clusters appear to be electron deficient, due to polarization of the clusters by the strong electrostatic fields.[2]

Two spectroscopic observations can be considered a key to the deduction that the metal clusters appear electron deficient: the atom–atom distances between the Pt atoms in a cluster embedded[6] in the micropores of the zeolite which are shorter than the bulk atom–atom distance and the edge spectra of the EXAFS measurements on similar embedded clusters.[5]

White line areas of L_{III} absorption edges of 3-nm Pt clusters reduced by H_2 in PtNa–Y are reported as well as those of 1-nm-size clusters. One deduces a larger number of d holes in the small clusters compared to the number of d holes in the large cluster. Comparison with data of 1-nm Pt clusters in a PtNaCe–Y zeolite indicates a larger number of d holes in clusters incorporated in the micropores of a zeolite containing Ce than in one with only Na ions.

Other interpretations than charge deficiency of the clusters can be given to explain the shorter atom–atom distances and the behavior of the number of d holes with particle size.

TABLE I: Exponents of the Core and Valence STO's

type	exp		type	exp	
1s	26.55	core	3d	22.15	core
2s	26.55	core	4d	10.65	core
3s	22.40	core	4f	7.59	core
4s	8.85	core	5d	1.55	valence
5s	6.95	core	5d	2.75	valence
2p	35.24	core	5d	4.75	valence
3p	18.47	core	6s	1.30	valence
4p	9.99	core	6s	2.35	valence
5p	4.57	core	6p	1.81	valence

Earlier theoretical work on small copper particles[7] using the Hartree–Fock–Slater LCAO method has clearly demonstrated that in Cu particles the Cu–Cu distance becomes shorter than in the bulk metal. This is due to the decreased number of Cu–Cu atom neighbors, leading to less localization energy[8] with a shortening of the Cu–Cu distances as a result. Similar decreases in metal atom distances have been observed on metal surfaces compared to values in the bulk of the metal.[9] Also, on metal surface changes in the d-band hole density as compared to that in the bulk of the metal have been discussed.

Both Cyrot-Lackman et al.[10] and Saillard et al.[11] have argued that the decreased d valence electron bandwidth at the surface as compared to that of the bulk metal electrons leads to an increased d valence electron band filling. The d valence electron bandwidth at the surface is decreased compared to that of the bulk because of the decreased degree of delocalization since atoms at the surface have fewer neighbors than those in the interior.

On the basis of these predictions one would expect for small particles of group VIII metal atoms that the average d-hole density should be smaller than that of large particles. This appears to be contradictory to observations. As a consequence one may be inclined to suppose an electron deficiency on the smaller cluster. The results of the HFS-LCAO calculations presented here for tetrahedral Ir_4 and Ir_{10} clusters demonstrate that the relative areas

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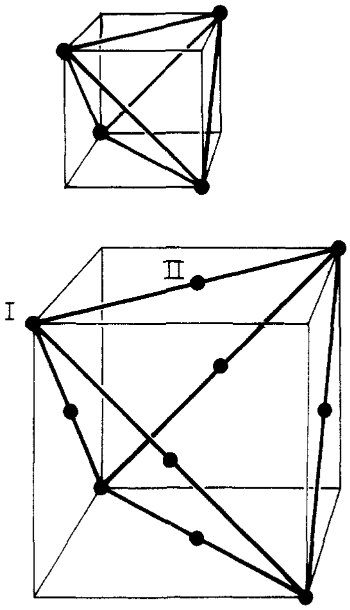

Figure 1. Structure of the neutral clusters. The distance between nearest neighbors in both clusters is 5.131 bohr.

TABLE II: Gross Occupation Numbers for the Neutral Clusters

	Ir_4	Ir_{10} I	Ir_{10} II	Ir_{10} av
s	0.66	0.93	0.82	0.86
p	0.06	0.10	−0.04	0.01
d	8.28	8.24	8.05	8.13

of the white lines observed for hydrogenated Pt particles are consistent with charge neutrality of the particles.

We have chosen to do calculations on Ir particles rather than on the Pt particles for which experimental data are available, since adsorbed hydrogen reduces the d valence electron density on the Pt clusters, making them Ir-like. As will become clear from our results, similar conclusions would be derived for neutral Pt particles as for the Ir particles studied by us. In a later paper the effect of the cations will be considered.

Computational Details

The calculations on the Ir clusters were performed by using the nonrelativistic HFS-LCAO method with frozen cores for the Ir atoms up to 4f inclusive. A Cartesian STO basis was used with single-ζ core functions for core orthogonalization and triple-ζ 5d, double-ζ 6s, and single-ζ 6p functions. This gave a total of 39 core and 23 valence functions per atom. The exponents are given in Table I. The number of holes in the d band of the clusters was analyzed via a Mulliken population analysis and by looking at the gross orbital population. For the neutral clusters the effective core charge was set equal to the number of valence electrons in an Ir atom (=9). For the positive clusters the effective core charge was increased by 1 for one of the Ir atoms, thus modeling a core hole as it is created in EXAFS. All calculations were performed with the vectorized version of the HFS-LCAO program on the Cyber 205 at SARA, Amsterdam. The electronic configurations were selected according to the Aufbau principle.

The (neutral) Ir_4 and Ir_{10} clusters were both given tetrahedral symmetry (point group T_d; see Figure 1). In the Ir_4 cluster all Ir atoms are equivalent. In the Ir_{10} cluster the atoms at the corners (type I) will in general differ from those at the midpoints of the edges (type II). Creating a core hole lowers the symmetry (see Figure 2). The symmetry of the Ir_{10}^+ cluster depends on the position of the atom on which the core hole is created. If it is created on a corner atom, then the point group of the cluster becomes C_{3v}, and there will be four types of atoms. If it is created on an edge atom, the point group is C_{2v}, and there will be five types of atoms. The type designation in subsequent tables refers to Figures 1 and 2.

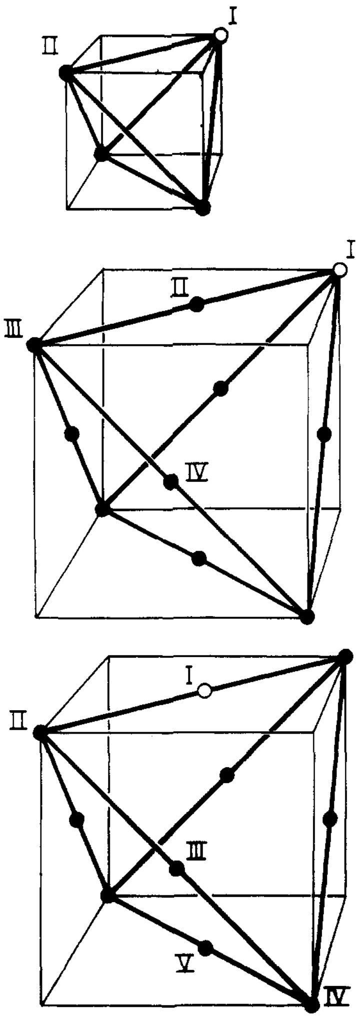

Figure 2. Structure of the positively charged clusters. The open circles depict the atoms with a core hole. The distances between the atoms are the same as for the neutral clusters.

TABLE III: Gross Occupation Numbers for the Ir_4^+ Clusters

	I	II	av
s	0.44	0.66	0.61
p	0.01	0.09	0.07
d	9.13	8.05	8.32

TABLE IV: Gross Occupation Numbers for the Ir_{10}^+ Clusters

C_{3v}	I	II	III	IV	av
s	0.46	0.79	0.75	0.77	0.74
p	0.03	0.04	0.11	0.00	0.05
d	9.37	8.03	8.21	8.02	8.22

C_{2v}	I	II	III	IV	V	av
s	0.47	0.64	0.76	0.76	0.75	0.70
p	−0.07	0.09	0.02	0.12	0.01	0.04
d	9.29	8.28	8.07	8.20	8.01	8.26

Results

The Neutral Clusters. The gross populations of the neutral clusters can be found in Table II. The electronic configuration of the Ir_4 cluster was found to be $a_1^4e^8t_1^6t_2^{18}$. The number of holes in the d band, 1.72, is what one expects for Ir atom with a low coordination number. Actually, two configurations were converged for the Ir_{10} cluster, neither of which satisfied the Aufbau principle. However, configuration $a_1^8e^{16}t_1^{24}t_2^{42}$ was very close. The gross populations in Table II for Ir_{10} corresponds to this configuration. The difference in the number of holes in the d band for atoms I and II corresponds to the difference in the coordination number. The corner atoms of Ir_4 and Ir_{10} have a more or less equal number of holes.

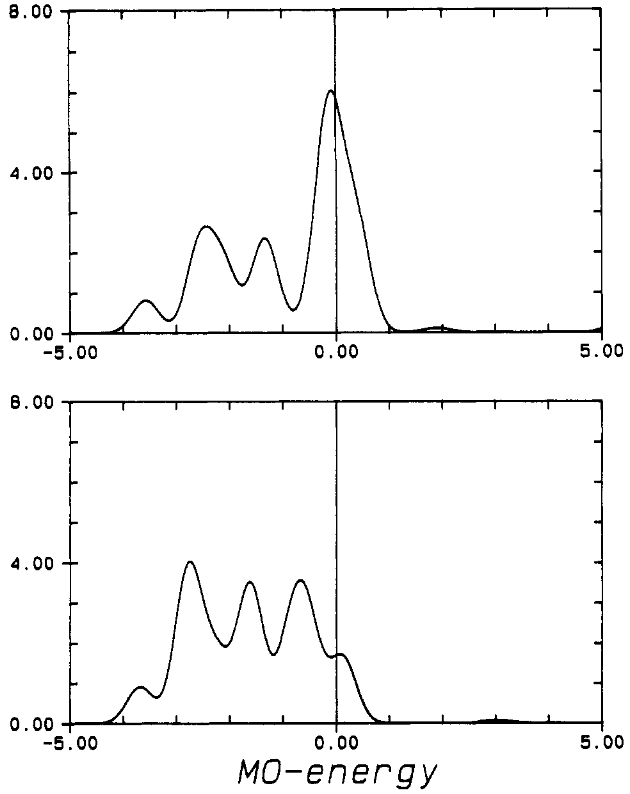

Figure 3. Local density of states (LDOS) of the d band at the atom with the core hole in the 4-cluster. The upper plot shows the LDOS before the core hole is created, i.e., Ir_4. The lower plot shows the LDOS afterward, i.e., Ir_4^+. The curves have been attained by convolutions of the sum of delta functionals that represents the true LDOS with a Gaussian distribution with width $\sigma = 0.25$ eV.

The Positive Clusters. The gross population of the positive clusters can be found in Tables III and IV. The electronic configurations of these cluster are $a_1^{10}a_2^{2}e^{24}$ (for Ir_4^+), $a_1^{30}a_2^{17}b_1^{22}b_2^{21}$ (for Ir_{10}^+ with C_{2v} symmetry) and $a_1^{22}a_2^{8}e^{60}$ (for Ir_{10}^+ with C_{3v} symmetry). The number of valence electrons is the same as for the neutral clusters as a core electron has been removed. We see that there is a drastic change in the d-band occupation on the ionized atom. This change is less in the 4-cluster (0.86 electron) than in the 10-cluster (on the average 1.19 electrons). As a result, the number of holes in the d band on the ionized atom is less in the 10-cluster (0.68 on average) than it is in the 4-cluster (0.88). This is in contradiction to the neutral clusters where these numbers are 1.87 and 1.73, respectively.

The white line edges of EXAFS spectra, on the other hand, showed that the larger cluster had fewer holes. This confirms that the EXAFS spectra should be compared with calculations on ionized clusters. Also, the average occupation of the d band is larger in the positive clusters. As shown in Figure 3, this is a consequence of the shift to lower energies with respect to the Fermi level of the d band. The sd hybridization must consequently also change, yielding greater d character for the occupied states. The effect is larger in the 10-clusters than in the 4-cluster as their polarizability is larger. The d band also becomes wider because the states are shifted in various amounts due to the inhomogenity of the electric field from the core hole.

Comparing the polarizability of the two 10-clusters, we note the following. The change in the number of d electrons is greater for the edge atoms than for the corner atoms, as the electron cloud has to shift less when an edge atom is ionized. The larger number of d valence electron holes on the edge atom than the corner atom in the ground state agrees with the observations on surfaces mentioned in the Introduction. The atoms with broadest local electron energy density of states distribution have the larger number of d valence electron holes because a larger fraction of the electron energy density is above the Fermi level. As a result the number of d electrons on the ionized atom is greater if it is a corner atom than if it is an edge atom. The polarizability can also be analyzed by looking at the change in the number of electrons occupying an orbital with a certain symmetry. The electronic configuration of the neutral 4-cluster in C_{3v} symmetry is $a_1^{10}a_2^{2}e^{24}$, which is the same as for the ionized 4-cluster. The electronic configuration of the neutral 10-cluster in C_{3v} symmetry is $a_1^{22}a_2^{9\,1/3}e^{58\,2/3}$, so that $1^1/_3$ electron goes from an a_2 MO to an e MO upon ionization. In C_{2v} symmetry the electronic configuration of this cluster is $a_1^{30}a_2^{17\,1/3}b_1^{21\,1/3}b_2^{21\,1/3}$. Hence $^1/_3$ electron goes from an a_2 MO and $^1/_3$ electron from a b_2 MO to a b_1 MO upon ionization of an edge atom.

Alternatively, according to second-order perturbation theory, screening is expected to be proportional to the number of nearest neighbors, which is six for the edge and three for the corner atoms.

Discussion and Conclusions

The results presented in Tables II and III demonstrate again the comparable behavior of small-cluster atoms and surface atoms. As for surfaces, neutral particles with the smaller average number of atom neighbors have the higher d valence electron band occupation.

For charged particles the polarization of the valence electrons screening the charge on one of the atoms results in an increased electron density on the atom from which a core electron has been removed. The larger the particle the larger the polarization and the more the positive charge is screened, explaining the large white line area for small particles compared to large transition-metal particles. The results obtained are consistent with earlier[12,13] work concerned with the X-ray absorption edge structure in molecular clusters. As has been clearly demonstrated, the EXAFS spectrum has to be computed by considering scattering of the electron in the field of the ionized cluster and not that of the ground state.

The implication of our work to catalysis is that the change in white line area as a function of particle size cannot be ascribed to the electron deficiency of metal particles.

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Registry No. Ir_4, 121596-91-6; Ir_{10}, 121596-92-7; Ir_4^+, 121597-10-2; Ir_{10}^+, 121597-11-3.

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