

On the localization of electrons and holes in Hg_n and rare-gas clusters

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Abstract. We have used a microscopic theory to study the size dependence of the degree of localization of the valence electrons and holes in neutral and ionized rare-gas and Hg_n clusters. We discuss under which circumstances localization of the electrons and holes is favoured. We have calculated the ionization potential of Xe_n , Kr_n and small Hg_n clusters. Good agreement with experiments is obtained. We have also determined the dependence of the ionization potential on cluster structure.

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The size evolution of the electronic structure of Hg_n clusters is one of the most interesting problems in cluster physics. From the point of view of the electronic structure in the atom (closed shell), small Hg_n clusters should be expected to be van der Waals bonded. However, since the bulk band widths, and consequently the hopping elements, are large, one cannot exclude the possibility of covalent bonding even in the very small clusters. It has been shown [1, 2], that a correct theoretical description of the electronic properties of small Hg_n clusters is only possible if one takes into account both the van der Waals and covalent bonding, and their interplay, on the same electronic level. Thus, a microscopic theory has been developed [1] which takes into account both bonding mechanisms. By using this theory one obtains that small Hg_n clusters with $n \lesssim 10$ are mainly van der Waals bonded, whereas in Hg_n with $n \geq 20$ the bond character is mainly covalent [1]. Furthermore, there is a clear interdependence between the degree of localization of the valence electrons and the bond character. In small Hg_n clusters ($n \lesssim 10$), and in rare-gas clusters, electrons are almost

completely localized around the atoms, whereas in larger Hg_n clusters with $n \geq 20$ a delocalization of the electrons takes place together with the transition to covalent bonding. Concerning the changes in the electronic structure of van der Waals clusters like rare-gas clusters or small Hg_n clusters upon ionization, many important questions need be answered. For instance, the dependence of the ionization potential on cluster size and cluster structure, and its dependence on the degree of delocalization of the hole produced in the ionization process. In this paper we use a microscopic theory to shed light on this problem.

The essential changes in the ionized van der Waals clusters with respect to the neutral ones can briefly illustrated as follows. Neutral rare-gas and small Hg_n clusters are characterized by having local charge neutrality and no net dipole moments. Only dipole fluctuations are present, which give rise to the van der Waals interactions. In the ionized clusters, there is a hole which can polarize its environment, inducing dipole moments on the neighbouring neutral atoms. The physics mentioned below is contained in the following many-body model Hamiltonian [2, 3]

$$H = H_{\text{vdW}} + H_{\text{cov}} + H_{Q-P} + H_{P-P}. \quad (1)$$

In (1), H_{vdW} describes the van der Waals interactions, arising from the coupling between local sp electronic excitations [1]. H_{cov} refers to the covalent interactions, represented by a two-band Hubbard Hamiltonian containing s and p on-site energies, hopping elements and Coulomb repulsion. H_{Q-P} and H_{P-P} refer to the charge-dipole and dipole-dipole interactions, respectively. The first two terms are the most important ones in the neutral clusters, whereas for the ionized clusters all four terms have important contributions. The ionization potential of a cluster with n atoms is calculated as [3]

$$I_p(n) = I_p(1) + |D_n^0| - |D_n^+|, \quad (2)$$

where $|D_n^0|$ and $|D_n^+|$ are the binding energies of the neutral and ionized clusters, respectively, and $I_p(1)$ is the atomic ionization potential.

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We calculate the binding energy of the neutral clusters by using the slave boson method in the saddle-point approximation, as described in [1]. The calculation of D_n^+ is more complicated, due to the presence of many interactions at the same time. However, the electronic structure is basically determined by the competition between the kinetic energy of the hole and the polarization energy of the neutral atoms surrounding it. Delocalization of the hole lowers the kinetic energy, while polarization energy is maximal when the hole is completely localized. In order to take into account this competition, we use the *ionic core model*, proposed by Haberland [4] and already used by many authors to calculate properties of charged rare-gas clusters [5]. This model is based on the assumption that the hole delocalizes only within a subcluster of m atoms (ionic core), while the rest of the cluster remains neutral. This physical picture can be applied to the Hamiltonian of (1). We write the dipole and charge operators as [3]

$$\mathbf{P}_k = \langle \mathbf{P}_k \rangle + \delta \mathbf{P}_k, \quad (3)$$

$$Q_l = \langle Q_l \rangle + \delta Q_l,$$

i.e., as the expectation values plus fluctuations around them. The charge-dipole fluctuations can be neglected in van der Waals clusters. Moreover, the dipole-dipole fluctuations contribute to the van der Waals interactions in the ionized clusters. Assuming that the strength of the van der Waals interactions is approximately the same in the neutral and in the ionized cluster, the ionization potential is then roughly independent of the van der Waals energy, since it involves a difference of binding energies. Thus, rewriting the Hamiltonian of (1) by using (3) one obtains a decoupling of the different charge operators in the ionized core, and the dipole operators in the neutral rest of the cluster. The ionization potentials depends on the expectation values $\langle Q_l \rangle$ ($l \in$ ionic core) and $\langle \mathbf{P}_k \rangle$ ($k \in$ rest of the cluster), which have to be calculated self-consistently. The physics underlying the calculation can be understood as follows. A given charge distribution $\{\langle Q_l \rangle\}$ in the ionic core induces a dipole distribution $\{\langle \mathbf{P}_k \rangle\}$ in the rest of the cluster. The potential due to this dipole distribution affects the wave function of the hole and consequently produces a rearrangement of the charge distribution and so on. We have calculated vertical ionization potentials for Xe_n , Kr_n and Hg_n clusters for different sizes m and shapes of the ionic core. We use compact cluster structures, which maximize the total coordination number, and thus are expected to be the most stable in van der Waals clusters. For Xe_n and Kr_n clusters, best agreement is obtained with the experimental results [6, 7] by assuming a compact ionic core of four atoms, as is shown in Fig. 1. Note, that the agreement with experiment is better for Xe_n clusters than for Kr_n clusters. Furthermore, it is remarkable that for Xe_n clusters both the experimental and our calculated $I_p(n)$ show a change in the size dependence at $n = 13$ (indicated with an arrow in Fig. 1a). By analyzing the charge distribution of Xe_n^+ clusters as a function of n , we observe that the hole tends to localize more and more for increasing cluster size. For $n = 10$ almost 80% of the positive charge lies at the atom

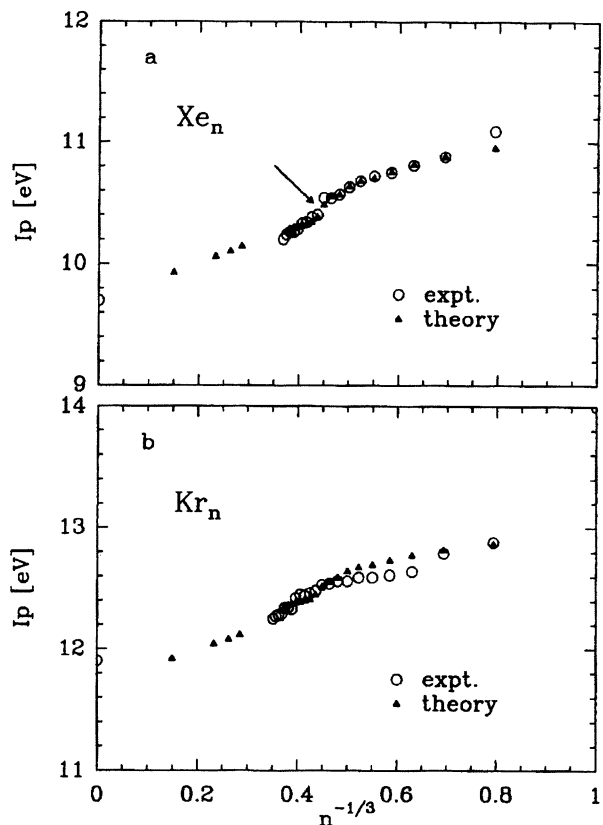


Fig. 1. Results for the size dependence of the ionization potential of a Xe_n , and b Kr_n clusters, obtained by assuming a compact ionized subcluster of size $m=4$. The corresponding experimental results of [7] are also given for sake of comparison. In a the arrow indicates a change in the size dependence of the calculated and measured ionization potentials of Xe_n clusters (see text)

with highest coordination, and the rest of the charge is distributed within the other 3 atoms belonging to the ionic core. The compact structure of $n=13$ has one atom at the center of the cluster and 12 surface atoms surrounding it. The first coordination shell is complete. Thus, for $10 \leq n \leq 13$ the decrease of the ionization potential is essentially governed by the increase of the polarization energy of the atoms surrounding a localized hole. For clusters larger than 13 atoms, neutral atoms occupy the second coordination shell around the central (positively charged) atom. Then, the gain in polarization energy for $n > 13$ is much smaller than for $n \leq 13$ because the central charge is screened by the first coordination shell. Thus, we can explain the change in the size dependence of the ionization potential of Xe_n clusters as arising from a saturation of the polarization energy due to the completion of the first coordination shell. This effect is more evident in Xe_n clusters due to the fact that Xe has a larger atomic polarizability [8] α ($\alpha(\text{Xe}) = 4.04 \text{ \AA}^3$, $\alpha(\text{Kr}) = 2.484 \text{ \AA}^3$). If our physical picture is correct, this effect should be also observable in the ionization potential of Hg_n clusters, since the atomic polarizability of Hg is also large [8] ($\alpha(\text{Hg}) = 5.7 \text{ \AA}^3$). Experimental results for $I_p(n)$ of Hg_n clusters, obtained by Haberland et al. [9] by electron impact ionization, do exhibit such a behaviour, as is shown in Fig. 2. We present also calculations by assuming

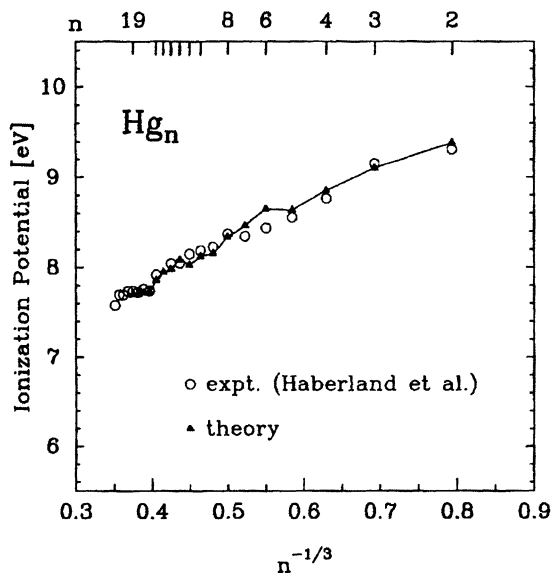


Fig. 2. Calculated size dependence of the ionization potential of Hg_n clusters, obtained by using a ionized trimer core ($m=3$, triangular shape). Results are compared with those obtained experimentally by electron impact ionization (see [7])

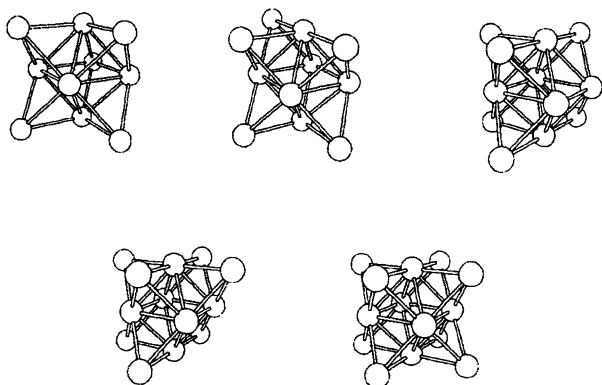


Fig. 3. Illustration of the cluster structures for which the calculated $I_p(n)$ of Hg_n clusters yield best agreement with experiment for $10 \leq n \leq 15$. Since the n atoms are at the surface, the ionization cross section might be large than in the case of compact structures

a compact ionic core of three atoms. It is remarkable that $I_p(n)$ shows a 'plateau' for $16 \leq n \leq 20$. It is a goal of our theory to describe this. However, for Hg_n clusters the saturation of the polarization energy seems to occur only at $n=16$ and not at $n=13$ as it would be if compact structures were assumed. This means other cluster structures, different from the compact ones may be important for the ionization potential of Hg_n clusters with $10 \leq n \leq 15$. In Fig. 3 the structures are shown, which yield best agreement with experiment for $10 \leq n \leq 15$. Note, that these structures have a total coordination number which is smaller than that of the (*fcc* or icosahedral) compact structures, and are therefore less stable. However, they seem to have a much larger ionization cross section than the compact ones. Note, that in the structures shown in Fig. 3, the n atoms of the cluster belong to the surface. The difference between the total coordination numbers of these structures and the compact ones increases with the cluster size. This means that for in-

creasing cluster size the compact structures must begin to dominate. At $n=16$, the saturation in the polarization energy has been reached, indicating that the compact structures govern the dependence of the $I_p(n)$ from this size on. For clusters larger than 20 atoms, the ionic core model fails to describe the further size dependence of $I_p(n)$ for Hg_n clusters. This is due to the transition from van der Waals to covalent bonding. Larger clusters are covalent, and therefore the assumption that the atoms surrounding a charge remain neutral is no longer valid. In the weak covalently bonded Hg_n clusters, i.e., near the transition, a small interatomic charge transfer must be more favourable than local polarization. Itinerancy of the electrons must become more important. However, as long as the covalent bonding is weak, the polarization energy must still dominate the behaviour of $I_p(n)$. Therefore, we expect that the hole remains still localized and that the covalent bonds surrounding this partially localized hole become polarized through interatomic charge transfer. In this way the system can gain polarization energy. Since the polarizability of a dimer is expected to be larger than that of an atom, the gain in polarization energy should be larger than in the van der Waals region. This could explain the relative abrupt decrease of $I_p(n)$ of the covalent clusters. For further increase of the cluster size, the screening of the charge fluctuations must increase, the covalent bonds become stronger, and finally a transition to metallic bonding occurs when the *sp* gap vanishes. Thus, $I_p(n)$ must converge to the behaviour predicted by the classical spherical droplet model [10]. In order to describe the change from atomic polarization to bond polarization and later to metallic behaviour, our theory for Hg_n^+ clusters should be extended in order to describe the change of the bond character, as it has been done for the neutral clusters [1], where one obtains an abrupt change in the binding energy when covalency occurs.

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