Electron Binding Energies of Anionic Magnesium Clusters and the Nonmetal-to-Metal Transition

Paulo H. Acioli* and Julius Jellinek

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439
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The binding energies of the two most external electrons in Mg_n^-, $n = 2$–22, clusters are computed using the gradient-corrected density functional theory and a new scheme for converting the Kohn-Sham eigenenergies into electron removal energies. The computations are performed for the anionic clusters considered in the most stable configurations of both Mg_n^- and Mg_n. The results are compared with photoelectron spectroscopy data [O.C. Thomas *et al.*, following Letter, Phys. Rev. Lett. **89**, 213403 (2002)], and their implications for the finite-size analog of the nonmetal-to-metal transition are analyzed.

Magnesium, similar to beryllium and mercury, is an element that exhibits a transition from weak van der Waals bonding in the diatomic molecule to metallic bonding in the bulk. Studies of magnesium clusters can, therefore, shed light on the size-induced transition from an insulating to a metallic state. Among the central questions is which property or properties are the most adequate for characterization of this transition. The choice should clearly be such that in the limit of a large number of atoms one recovers the traditional signature of the bulk insulator-to-metal transition, which is the closure of the gap between the valence and conduction bands.

The structural and electronic properties of magnesium clusters have been the subject of a number of theoretical studies [1–11]. Most of these considered neutral clusters and utilized different implementations of the density functional theory (DFT). The issue of transition from nonmetallic to metallic behavior as a function of cluster size was considered in terms of the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the degree of p character of the valence electronic charge, the distribution of the electron charge density, the changes in the nearest-neighbor bond lengths [3,6,11], the similarity with the jellium model picture [4], the electronic density of states [6], and the excitation energies [10]. The common element in the findings of the different studies is that Mg_n clusters exhibit size-dependent features which can be viewed as evidence of a size-induced nonmetal-to-metal-type transition. However, the precise meaning and the understanding of the finite-size analog of what is an insulator-to-metal transition in the bulk remain vague, and the subject certainly warrants further exploration.

Two recent experimental studies provide fresh impetus for theoretical investigations. Diederich *et al.* [12] measured the mass spectrum of Mg_n, $n \le 80$. Through analysis of the intensities in terms of the electron shell model these authors suggested that delocalization of the electrons is complete at about 20 atoms. Thomas *et al.* [13] generated photoelectron spectra (PES) of Mg_n^-, $n = 3$–35, anions, from which they deduced the gap in the binding energies of the two most external electrons. This gap shows an overall tendency to decrease, and even to close, as the cluster size increases, but the decrease is not monotonic and the gap reopens at certain cluster sizes.

In this Letter we present results of a theoretical study, which, on the one hand, are of direct relevance to the measured PES data [13] and, on the other, furnish new insight into the meaning and implications of these data in the context of the size-induced nonmetal-to-metal transition. The quantities computed and analyzed are the binding energies of the two most external electrons in negatively charged Mg_n, $n = 2$–22, clusters and the degree of p character of the charge distribution in the neutral and anionic clusters.

For each n, the electron binding energies were computed by considering the negatively charged cluster in the most stable configuration of Mg_n^- and that of Mg_n. The search for the equilibrium structures of the neutral and anionic species was performed within DFT with the Becke exchange [14] and Perdew [15] correlation functionals (BP'86) as implemented within the GAUSSIAN-98 package. The Ne core of the Mg atoms was represented by the Wadt-Hay pseudopotential with a $(21 \mid 21)$ basis set for the description of the valence electrons [16]. This selection of the functionals and pseudopotential/basis set emerged as the optimal in extensive tests that involved a variety of alternative choices and comparisons with available measured and computed (*ab initio* and/or all-electron) data on Mg_n, $n = 1$–5 (the details will be given elsewhere). The equilibrium structures of the clusters were obtained through extensive searches utilizing unconstrained gradient-driven relaxations from different guess configurations. The latter included structures obtained in earlier studies as well as new ones. Normal mode analysis was used to identify globally or locally stable isomeric conformations.

Since our emphasis here is not on the structural properties (they will be discussed in detail elsewhere), in Table I we present only a list of the most stable isomers of the neutral and anionic clusters. The central, for our present discussion, point is that for $n = 6, 7, 8, 11, 12, 18$, and 21 the most stable configuration of the neutral cluster is different from that of its anionic counterpart, as judged by the atomic packing.

As mentioned, for each size n both structures listed in Table I were used as fixed (nuclear) configurations of the negatively charged cluster, and the binding energies of the two most external electrons were computed for both. Since the Kohn-Sham (KS) one-particle eigenenergies correspond to quasiparticles, rather than to electrons, correction terms are needed to convert these eigenenergies into electron binding energies:

$$BE_i(N) = -\varepsilon_i(N) + \Delta_i(N), \qquad (1)$$

where $BE_i(N)$ is the binding energy of an arbitrary ith electron in an N-electron system, $\varepsilon_i(N)$ is the eigenenergy of the ith KS orbital of that system, and $\Delta_i(N)$ is the correction term. Our prescription for computing $\Delta_i(N)$ is a linear [in $\alpha_i(N)$] interpolation

$$\Delta_i(N) = \Delta_i(N-1) + [\Delta_{i+1}(N) - \Delta_i(N-1)]\alpha_i(N), \qquad (2)$$

where

$$\alpha_i(N) = \frac{\varepsilon_i(N) - \varepsilon_i(N-1)}{\varepsilon_{i+1}(N) - \varepsilon_i(N-1)}. \qquad (3)$$

The correction terms $\Delta_i(N-1)$ and $\Delta_{i+1}(N)$ in the right-hand side of Eq. (2) are themselves defined by Eqs. (2) and (3), which are used recursively until these terms are reduced to $\Delta_j(j)$, $i \leq j \leq N$. The (HOMO) corrections $\Delta_j(j)$ are computed within a chosen implementation of the DFT exactly,

$$\Delta_j(j) = BE_j(j) + \varepsilon_j(j), \qquad (4)$$

where

$$BE_j(j) = E(j-1) - E(j), \qquad (5)$$

and $E(k)$ is the DFT-computed total energy of the k-electron system. The justification of this scheme, its refinements, and comparative merits will be discussed elsewhere [17]. Here we mention only that it is based solely on ground state properties rigorously defined within the traditional DFT; it can be used with any version of DFT (local or nonlocal); it yields orbital-dependent corrections, which account for changes in the orbital energies caused by addition or removal of electrons; and, as is clear from Eqs. (2) and (3), it gives the same correction term for degenerate KS eigenstates. It has been shown to produce highly accurate binding energies of electrons, including those occupying inner shells, in applications to a variety of atoms and molecules (average relative error within 4%; for the Mg atom around 1%) [17].

Figure 1 displays the difference (gap) in the binding energies of the two most external electrons in the negatively charged magnesium clusters computed, for each

TABLE I. Computed lowest energy structures of Mg_n^- and Mg_n, their binding energies, and symmetries. Since the anion of the Mg atom is not stable, the binding energies of both Mg_n and Mg_n^- are defined with respect to energies of n Mg atoms.

	Mg_n^-		Mg_n	
n	BE (eV/atom)	Structure	BE (eV/atom)	Structure
2	0.182		0.046	
3	0.434	Triangle, D_{3h}	0.140	Triangle, D_{3h}
4	0.565	Tetrahedron, T_d	0.313	Tetrahedron, T_d
5	0.534	Trigonal bipyramid, D_{3h}	0.306	Trigonal bipyramid, D_{3h}
6	0.558	Pentagonal pyramid, C_{5v}	0.316	Fused tetrahedra, C_{2v}
7	0.585	Distorted pyramid $+Mg_2$, C_s	0.367	Pentagonal bipyramid, D_{5h}
8	0.623	Staggered square prism, D_{4d}	0.403	Capped pentagonal bipyramid, C_s
9	0.720	Tricapped trigonal prism, D_{3h}	0.504	Tricapped trigonal prism, D_{3h}
10	0.720	Tetracapped trigonal prism, C_{3v}	0.560	Tetracapped trigonal prism, C_{3v}
11	0.689	$Mg_{10}^- + Mg$, C_s	0.546	Pentacapped trigonal prism, D_{3h}
12	0.702	$Mg_{10}^- + Mg_2$, C_1	0.551	$Mg_{10} + Mg_2$, C_s
13	0.714	$Mg_{10}^- + Mg_3$, C_s	0.569	$Mg_{10} + Mg_3$, C_1
14	0.721	$Mg_{13} + Mg$, C_1	0.574	$Mg_{13} + Mg$, C_1
15	0.756	Fused tricapped trigonal prisms, D_{3h}	0.625	Fused tricapped trigonal prisms, D_{3h}
16	0.759	$Mg_{17}^- - Mg$, C_s	0.622	$Mg_{17} - Mg$, C_s
17	0.802	Octacapped fused relaxed square pyramids, C_{2v}	0.681	Octacapped fused square pyramids, D_{4d}
18	0.820	$Mg_{17} + Mg$, C_{4v}	0.700	$Mg_{17}^- + Mg$, C_{2v}
19	0.842	Relaxed $Mg_{18} + Mg$, C_s	0.723	$Mg_{18} + Mg$, C_{2v}
20	0.841	Distorted $Mg_{19}^- + Mg$, C_1	0.749	Distorted $Mg_{19} + Mg$, C_3
21	0.826	$Mg_{20}^- + Mg$, C_1	0.727	$Mg_{20} + Mg$, C_1
22	0.818	$Mg_{20}^- + Mg_2$, C_1	0.723	$Mg_{20} + Mg_2$, C_1

cluster size, in the two different structures specified above, together with the values of that difference deduced from the PES data [13]. The difference between the zero-point energies of the Mg_n^- and Mg_n clusters does not exceed 0.02 eV and was not included in the computation of the electron binding energies. The features to notice in Fig. 1 are the following: (1) The gaps computed in the equilibrium structures of Mg_n^- are, in general, different from those computed in the equilibrium structures of Mg_n. (2) The gaps computed in the structures of Mg_n^- reproduce very well the data deduced from the experiments. (In fact, not only the gaps but also the computed electron binding energies themselves show a very nice correlation with the measured PES spectra [18].) (3) The gaps computed in the structures of Mg_n are, in general, not only quantitatively different from those deduced from the experiments, but they also show locally different trends; cf., e.g., the increase in the gap vs the experimentally observed decrease as the number of atoms in the cluster increases from 10 to 11.

For a fixed n, the reason for the difference in the computed values of the gap is the difference in the equilibrium structures of the Mg_n^- and Mg_n species, be it either due to a "simple" relaxation or the above-mentioned actual change in the isomeric form; the geometric and electronic structures are, of course, coupled and define each other. This change in the equilibrium configuration upon adding an electron to the system is a finite-size effect that cannot, in general, be ignored in the interpretation of the experimental data. A direct implication of the analysis of the results shown in Fig. 1 is that the PES measurements [13] probe the electronic properties of the "native" anionic Mg_n^- clusters which are, in general, different from those of the neutral Mg_n species with an extra electron "added" to them. This conclusion may not be surprising given the fact that the experiments [13] measure the energies of electrons photodetached

from Mg_n^- anions. Its significance, however, becomes clear in view of the following line of reasoning invoked often. It is stipulated that the HOMO-LUMO gap in a finite neutral system, e.g., cluster, is the finite-size analog of the bulk band gap, and the addition of an extra electron to the system populates its LUMO. Therefore, it is argued, the PES experiments on anions probe (neglecting the relaxations of the orbital energies) the desired HOMO-LUMO gap in the corresponding neutrals. Our analysis shows that, in fact, this is not the case, in general.

Does this conclusion reduce the information content on the finite-size analog of the nonmetal-to-metal transition embedded in the anionic PES data? The negative answer to this question comes from the recognition that the possible nontrivial differences in the electronic properties of charged systems and their neutral counterparts are one of the important manifestations of the size dependence, and they should be included in the analysis of the phenomenon of size-induced nonmetal-to-metal transition. In fact, PES data on anions are essential for understanding the role of the charge state as a parameter, which, in general, plays an important role in the small-size regime, and whose role diminishes as the system grows in size (the electronic structure of bulk matter is not affected by addition or withdrawal of electrons). Moreover, the difference in the binding energies of the two most external electrons of a finite-size anion is as legitimate an analog of the bulk band gap as the HOMO-LUMO gap of the corresponding neutral system. The energy difference in an anion and the HOMO-LUMO gap in its neutral counterpart approach each other as the system grows in size, and both converge to the bulk band gap.

Another manifestation of the finite-size differences in the electronic structure is exhibited in Fig. 2, which shows the percentage of the p character in the valence charge distribution in the anionic and neutral magnesium clusters as obtained through the Mulliken population
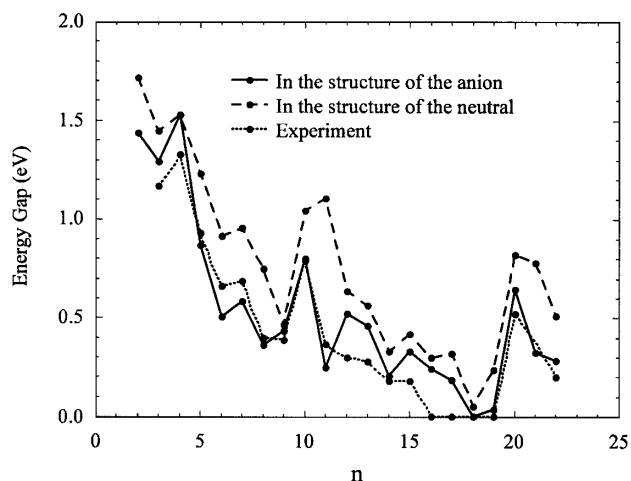

FIG. 1.   The computed gap between the binding energies of the two most external electrons in Mg_n^- clusters. The gap obtained from the PES data [13] is also shown.
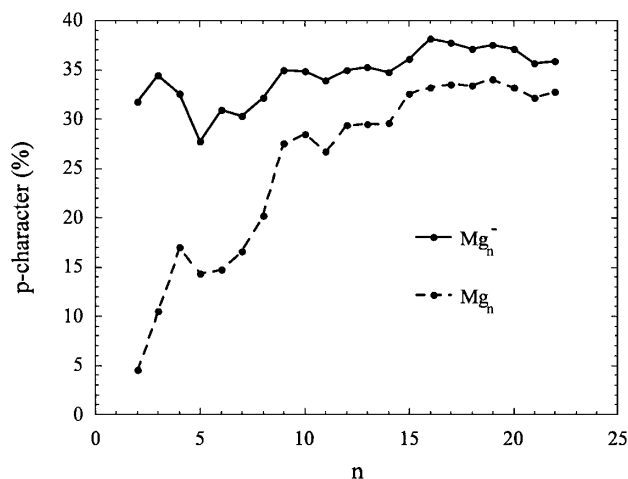

FIG. 2.   The computed degree of p character in the valence charge distribution of Mg_n and Mg_n^- clusters.

analysis. (The displayed degree of the p character is obtained for clusters in their native most stable configurations, but it remains largely unchanged when the structures of the anions are used for the neutrals and vice versa.) The emergence of, or increase in, the p character is often invoked as an indication of the transition to the metallic state. As is clear from Fig. 2, the p character is present in the bonding of even the smallest Mg_n and Mg_n^- clusters, and for Mg_n^- its percentage hardly changes with the cluster size. The features that deserve particular attention are the following: (1) The degree of p character of the charge distribution in the neutrals is, in general, different from that in the anions, (2) The degree of p character in the neutrals approaches that in their anionic counterparts as the size of the clusters increases. It is these features, rather than the degree of the p character in either the neutral or the anionic species alone, that are indicative of the size-induced nonmetal-to-metal transition. (For calibration we note that the degree of p character in the density of states at the Fermi level of bulk magnesium is about 50% [19,20].) Another interesting result is that the 18-atom cluster, for the anion of which the computations give zero gap between the binding energies of the two most external electrons (cf. Fig. 1), is the smallest (and the only, in the size range considered) magnesium cluster with the lowest energy structures of both the neutral and the anion corresponding to higher spin states. The most stable isomer of Mg_{18} is a triplet, rather than a singlet, whereas that of Mg_{18}^- is a quartet, rather than a doublet. We will explore the significance of this finding in future studies.

In summary, we have presented computational evidence that electron photodetachment experiments on anions of clusters (more generally, finite systems) do not, in general, probe the HOMO-LUMO gap of the corresponding neutrals. We pointed out that the difference in the binding energies of the two most external electrons of finite anionic species is as a legitimate finite-size analog of the bulk insulator-to-metal transition as the HOMO-LUMO gap of the neutrals. We draw attention to the fact that the dependence on the charge state is another manifestation of the finite-size effects, and it has to be taken into account in the analysis of the size-induced nonmetal-to-metal transition. In addition to the electron energy gaps, we illustrated this in terms of the degree of p character of the charge distribution in neutral and anionic magnesium clusters. The general observation is that the size-induced transition to metallicity exhibits itself in a variety of complementary ways and only the totality of these can be expected to provide a comprehensive understanding and description of the phenomenon.

The conclusion with regard to the magnesium clusters is that the results of our computations support the interpretation of the PES data [13] as consistent with a gradual, although not monotonic, emergence of metallic features in the clusters as they grow in size. It is also clear that the details of the transition require further attention and an extension of the studies to clusters of larger sizes.

Note added.—Further details of the issues discussed here can be found in Ref. [21].

*Permanent address: Nucleo de Fisica Atomica, Molecular e Fluidos, Instituto de Fisica, Universidade de Brasilia, CP 04455, Brasilia, DF, 70919-970, Brazil.

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