PHYSICAL REVIEW LETTERS

Anions of Xenon Clusters Bound by Long-Range Electron Correlations

Victor G. Bezchastnov,* Victor P. Vysotskiy, and Lorenz S. Cederbaum

Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, INF 229, D-69120 Heidelberg, Germany

In contrast with the single atom, atomic van der Waals clusters can form stable anions where the excess electron is bound due to long-range correlations with the electrons of the cluster. We report on extensive all-electron many-body *ab initio* studies on Xe clusters. Three-dimensional, planar, and linear structures of the clusters are investigated and compared. In particular, we find that the minimal number of Xe atoms in the cluster required to form a stable anion is 5 independently of the dimensionality of the cluster. We provide electron affinities for clusters made of 5, 6, and 7 atoms in all dimensions and find that the planar clusters form the most stable anions. The Dyson orbitals of the excess electrons are computed and analyzed.

Electron attachment to atomic and molecular systems is an important area of research. In the case of clusters of rare-gas atoms, the research is of particular fundamental interest due to the fact that these atoms themselves cannot bind an excess electron. Here, the questions how many rare-gas atoms can bind an extra electron and what are the properties of the resulting cluster anions have challenged many researchers and have stayed in the focus of both theoretical and experimental studies over a long time [1]. Although addressed in a substantial number of studies, the currently available answers to these questions are rather qualitative and imprecise. Both theoretically and experimentally, it is found that clusters comprised of sufficiently many atoms do form stable anions. Examples of the available estimates of the minimal number of atoms needed to stabilize the anions are 7, 14, and 46 for Xe, Kr, and Ar clusters, respectively [1], and ≈ 6000 for Ne [1,2] and $\approx 5 \times 10^5$ for He [3,4] clusters. The critical size of the cluster is larger the larger the polarizability of the constituent atom is, reflecting the role of long-range effects in the binding. However, the reported values of the critical cluster sizes cannot be regarded to be accurate, and, importantly, there is a lack of reliable data on the electron binding energies. Experimental uncertainties relate to the delicate experimental techniques required to measure the electron binding energies in the cluster anions, and the current theoretical predictions are rather imprecise because of the underlying approximations used.

To be more specific, we concentrate here on Xe cluster anions, which have attracted major interest since the Xe atom possesses the largest polarizability among the rare-gas atoms. Experiments performed by Haberland, Kolar, and Reiners [5] have indicated that Xe cluster anions are definitely stable for sizes of 6 atoms and larger and that they are probably stable for sizes down to 2 atoms. The available theoretical results all rely on model descriptions of the interaction of the excess electron with the Xe atoms. To be mentioned are the following estimates for the critical

sizes of stable Xe cluster anions: ≈ 50, ≈ 10, 7, and 6 atoms [1,6–8]. To the best of our knowledge, the only estimated electron affinities are 17 meV for a cluster of 12 and 7 meV for 13 Xe atoms [9]. Clearly, it is demanding to elucidate the issue of how many Xe atoms are actually required to form the smallest stable cluster anion as well as to provide accurate values for the electron affinities. Moreover, we wish to investigate the dependence of the binding on the dimensionality of the clusters, an issue which has been essentially neglected so far.

To achieve these goals without any model assumptions on the electron-atom interactions requires rigorous *ab initio* all-electron quantum calculations, a nontrivial effort indeed. We encounter here the aggravating situation that Hartree-Fock (HF) calculations do not predict a bound anionic state and appropriate calculations including electron correlations can yield such states. The anion is then essentially *correlation-bound* as outlined in Ref. [10]. Standard computational approaches that incorporate correlations on top of the HF solution, e.g., Møller-Plesset perturbation theory or coupled-cluster methods, turn out to be inefficient or even not possible to apply because the HF calculations of the anion do not converge to a bound state. Here, evaluating the electron binding energy as the difference of the ground-state energies of the neutral and anionic systems faces a major problem. In addition, even if one manages to compute an anionic ground-state energy, one can expect the difference of two large total energy values to yield numerically inaccurate results because of the smallness of the electron affinity. We also mention that the excess electron is extended in space, implying that large basis sets are needed for the computations of the correlations, and this fact makes standard approaches very cumbersome to employ. We can circumvent the first mentioned difficulties by employing Green's function methods, often also called propagator methods [11–16], which determine the excess electron binding energy directly, without computing the ground states of the anion

and neutral species separately. The last mentioned difficulty has been solved by the recently developed parallel code [16] particularly adapted to the method used (see below).

The general formalism of Green's functions provides the link between the *exact* (ground as well as excited) states of the system with $N, N \pm 1, N \pm 2, \ldots$ electrons and the ground state of the corresponding N-electron system. A specific Green's function possesses poles which are at the respective energy differences. Here, we concentrate on computing the Green's function which provides access to the anionic $(N + 1)$-electron system and possesses the electron affinities as poles [15–17]. The underlying formalism is based on the Dyson equation [11,12], which yields the electron binding energy ε as the eigenvalue of the Hamiltonian matrix:

$$H_{pq}(\varepsilon) = \varepsilon_p \delta_{pq} + \Sigma_{pq}(\varepsilon), \tag{1}$$

whereas the corresponding eigenvector describes the Dyson orbital of the attached electron. In Eq. (1), the indices p and q enumerate all the HF orbitals of the ground state of the neutral system, and ε_p are the HF orbital energies. The essence of the above approach is the interaction part Σ_{pq} that itself depends on ε and is called the Dyson self-energy. It can be evaluated systematically by employing the algebraic-diagrammatic construction scheme up to nth order, ADC(n), with respect to the electron-electron interactions [13,18]. Following the successful studies of loosely bound anions [10,17], we will employ Eq. (1) along with the ADC(2) self-energy which coincides with the usual second-order self-energy obtained when using the HF basis [13,15]. For a closed-shell system, the corresponding matrix elements read

$$\Sigma_{pq}(\varepsilon) = \sum_{abi} \frac{V_{piab}(2V_{qiab} - V_{qiba})}{\varepsilon - \varepsilon_a - \varepsilon_b + \varepsilon_i}$$
$$+ \sum_{ija} \frac{V_{paij}(2V_{qaij} - V_{qaji})}{\varepsilon - \varepsilon_i - \varepsilon_j + \varepsilon_a}, \tag{2}$$

where V_{piab} are the common two-electron Coulomb integrals computed with spin-free HF orbitals and the pairs of indices i, j and a, b run over the occupied (hole) and the virtual (particle) orbitals, respectively.

On general grounds, we expect the second-order approximation (2) to yield accurate results for the binding energies of the rare-gas clusters. The binding energies under study are very small even compared to the correlation energies of the ground states of the neutral clusters and thus particularly suitable for perturbation theory. From the physically relevant point of view, the second-order expression (2) already includes the polarization contributions that play the primary role in binding the excess electron. In coordinate representation, the self-energy (2) is known [19] to take on at large distances r of the electron from the neutral system the following local behavior which is identical to the polarization attraction of the excess electron by the system:

$$V_{\text{pol}}(\mathbf{r}) = -\alpha_{\mu\nu} n_\mu n_\nu / (2r^4). \tag{3}$$

In this expression, $\alpha_{\mu\nu}$ is the polarizability tensor of the neutral cluster, n_μ and n_ν are the components of the unit vector in the direction of the electron, and the Einstein summation convention is applied.

Approaches to solve the nonlinear eigenvalue problem for the matrix (1) are well developed [13,20]. One can directly search for the roots ε of the matrix eigenvalue equation. Alternatively, one can cast Eqs. (1) and (2) as an eigenvalue equation of a so-called arrow matrix which does not depend on ε at the price of having dimensions much larger than that of the matrix (1) but which can be solved very efficiently. Since the rare-gas clusters possess high symmetries [21], this can be exploited by partitioning the matrix (1) according to the symmetry groups. We have therefore opted to apply the first approach restricting the matrix (1) to the elements of a symmetry group. This allows one to reduce the dimensionality of the nonlinear eigenvalue problem substantially. In practice, we search for the root ε iteratively by calculating the eigenvalues of H_{pq} in each iteration step. The iterations start with $\varepsilon = 0$, and typically only a few iterations are needed to converge to the final small binding energy in those situations where the bound anion exists.

We would like to stress that there is much experience in computing ionization energies and electron affinities of atoms, molecules, and clusters with Green's functions. However, in the majority of these cases, an HF orbital q is a good approximation for the Dyson orbital. In the case of electron attachment of interest here, this implies that the excess electron will reside in the Dyson orbital, which is similar to a HF orbital. In practice, the consequence is that the Dyson equation becomes essentially diagonal in the HF basis and reduces to $\varepsilon - \varepsilon_q = \Sigma_{qq}(\varepsilon)$, which is much simpler to solve than that with the full matrix (1). In contrast, the situation of electron attachment to rare-gas clusters is much more involved. The excess electron is loosely bound and found to reside in an extended Dyson orbital which will be shown below. This orbital does not resemble any virtual HF orbital. On the contrary, to describe a physically meaningful Dyson orbital of an electron bound by long-range correlations, a large number of virtual HF orbitals are needed. Consequently, one must be able to solve the Dyson equation by using (1) in a large and extended basis set as done here.

We have applied the above described method to study the electron attachment to clusters made of 4–7 Xe atoms. For each cluster we have considered the lowest energy three-dimensional (3D) topologies reported (see, e.g., Ref. [21]). These comprise the structures of tetrahedron, trigonal bipyramid, octahedron, and pentagonal bipyramid

for the clusters made of 4, 5, 6, and 7 atoms, respectively. In all our calculations we have found that the geometry of the anion and that of the neutral parent cluster are essentially identical. The anions are weakly bound, and the extra electron resides in a rather extended part of space; this kind of weak binding does not have a noteworthy impact on the geometry. It is, therefore, safe to consider the structures lowest in energy of the neutral species. To study the impact of dimensionality, we also computed the binding properties of the respective lowest energy planar (2D) and linear (1D) structures which are planar regular polygons and linear chains (see Fig. 1). Unfortunately, Lennard-Jones interactions between the atoms were used in the reported calculations on the structures, and we found that the resulting values of the internuclear equilibrium distances are not sufficiently precise. We have, therefore, for each neutral cluster structure optimized the equilibrium interatomic distances employing second-order many-body perturbation theory, where all electrons were included in the correlation treatment. The basis set used is reported below (set A). The underlying *ab initio* results were obtained by accounting for scalar relativistic effects according to the Douglas-Kroll method [22,23]. The results are collected in Fig. 1 and are of interest by themselves.

Our *ab initio* affinity calculations were performed for the optimized cluster geometries with the recently developed parallel P-RICDΣ code [16] and utilize two basis sets. The first set comprises the $[9s9p8d4f]$ sets of Gaussian-type orbitals on each of the Xe atoms. This set (denoted set A) was introduced in Ref. [24] and used for accurate all-electron finite-field relativistic calculations of the polarizabilities for the Xe atom and the Xe dimer. We can rely on set A to recover the electron-cluster polarization interaction important for binding the excess electron. However, even more diffuse functions than those included in set A are required to account properly for the delocalization of the attached electron. In order to gain the necessary flexibility as well as to control the accuracy of our calculations, we have extended the basis by sets of *s*-, *p*-, *d*-, and *f*-type uncontracted primitives whose exponents were taken to augment, in even-tempered manner [25], the largest exponents of set A. The resulting second basis set (set B) was placed at the centers of the clusters. In the course of the calculations, we increased the number of primitives in set B until convergence of the electron binding energies was achieved, within the absolute accuracy of ≈ 0.0003 meV. This procedure yielded $[10s5p5d5f]$ for set B of the weakest bound anion which we used throughout. Overall,
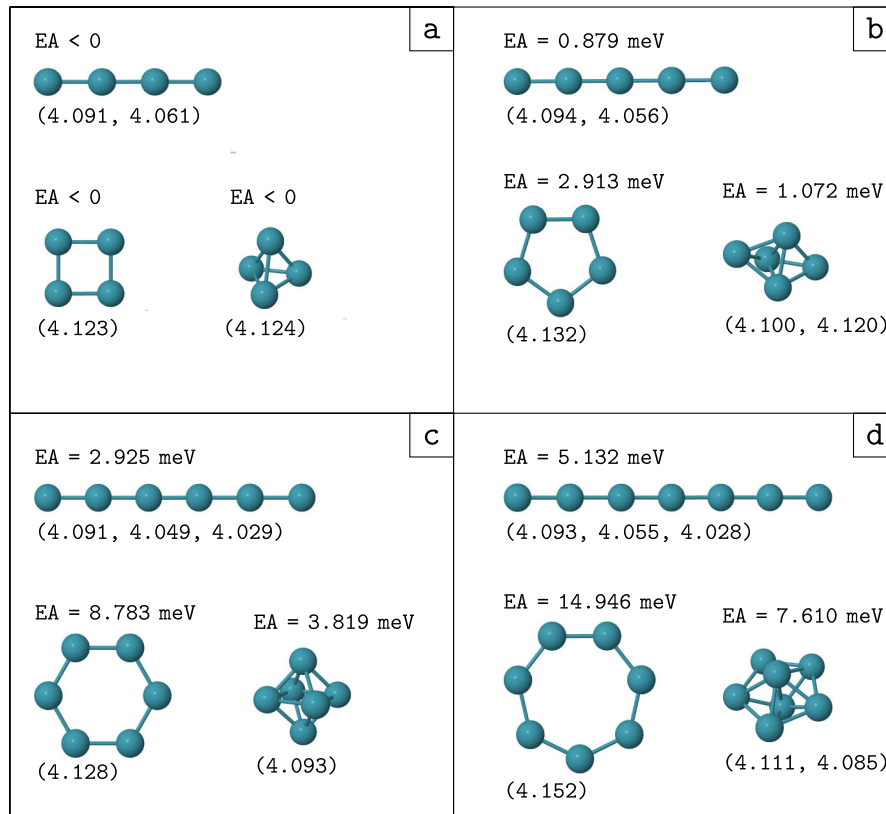

FIG. 1 (color online). Properties of the Xe clusters of different dimensionalities with 4 (a), 5 (b), 6 (c), and 7 (d) atoms. The clusters are shown by atomic spheres connected by bonds, with the radii of the spheres being 1.08 Å (half of the van der Waals radius of Xe). Indicated above each cluster are the electron affinities (EA), and the numbers given in brackets below each cluster are the internuclear separations in angstroms.

the number of basis functions required to compute the electron affinities accurately is about 900. Each of the approximately 4×10^5 elements $\Sigma_{pq}(\varepsilon)$ of the self-energy given by Eq. (2) contains about 10^{14} terms.

The results of our extensive calculations are summarized in Fig. 1. Independently of the cluster dimensionality, there is no evidence for binding the excess electron for clusters of four Xe atoms. In contrast, all depicted clusters with 5, 6, and 7 atoms were found to support a correlation-bound state of the anion, i.e., a positive electron affinity. The *minimal number* of Xe atoms required to form a stable cluster anion has therefore been found to be *five* atoms.

In every dimension of the clusters, the affinities increase with an increasing number of cluster atoms which naturally reflects the increase in the long-range polarization attraction of the excess electron by the clusters. The electron affinities, on the other hand, clearly depend on the dimension of the clusters. Interestingly, for each cluster size they are largest for the planar structures and not for the 3D structures as one might *a priori* expect. The binding energies of the excess electron in the planar structures are approximately twice as large as those of the 3D ones for the same number of atoms. The linear chains exhibit the lowest binding energies although their values are surprisingly close to those of the respective 3D structures.

The hierarchy of the values of the electron affinities $2D > 3D > 1D$ found for all clusters of the same number of Xe atoms relates to the decrease of the distance between the center of the cluster and the atoms most close to this center (see Fig. 1). This is due to the interplay of the long-range attraction by the polarization and the short-range repulsion the excess electron experiences in the vicinity of an atom of the cluster. The larger these distances are, the smaller the short-range electron-atom repulsions in the centers of the clusters are, making it easier for the excess electron to penetrate into the inside of the clusters. This is illustrated in Fig. 2 by the electron density plots for the Xe_6^- cluster anions of different dimensionalities. In the figure, the densities of the Dyson orbital of the excess electron are shown along directions selected to pass through the center of the cluster avoiding the cluster atoms. For the 1D, 2D, and 3D Xe_6 clusters, these directions are orthogonal to the linear chain, the planar hexagon, and a facet of the bipyramid, respectively.

The axes along which the electron densities are shown in Fig. 2 have been chosen to be "optimal" for the excess electron to get inside the clusters. Even so, the electron density along these axes exhibits a global maximum in the center of the cluster only for the planar structure. For the 3D cluster, the density in the center does possess a maximum but only a local one which is substantially smaller than the two global maxima which are located right outside the cluster. In contrast to the 2D and 3D clusters, the density of the electron attached to the 1D cluster exhibits a local minimum in the center. While close to the cluster

the electron density is seen to be very different for all three clusters, this density is essentially identical in all cases at large distances from the center of the cluster. The tails of the electron density distributions are determined by the long-range polarization attraction created by the six Xe atoms. The overall extensions of the Dyson orbitals of the attached electron are seen from the figure to be about 40 Å, i.e., about 10 times larger than the internuclear separations of the atoms in the clusters.

This Letter reports rigorous quantum all-electron calculations of the anions formed by attaching an electron to neutral Xe clusters. The binding of the excess electron is due to electron correlations. Both the equilibrium geometries and the electron affinities are computed by methods which take electron correlations into account (second-order many-body perturbation theory and Green's functions). The minimal size of a Xe cluster which forms a stable anion has been unknown and has now been accurately determined to have five atoms. The experimental indications [5] are that the minimal size of Xe cluster anions is between 2 and 6 atoms. Values of the electron binding energies are reported for linear, planar and 3D clusters with 5, 6, and 7 Xe atoms. The binding energies grow with the number of atoms in the cluster and are shown to depend on the dimensionality of the cluster's structure. The electron density of the excess electron is computed as well and sheds much light on the understanding of the binding. This density significantly extends over the size of the clusters and depends on the topology of the clusters.
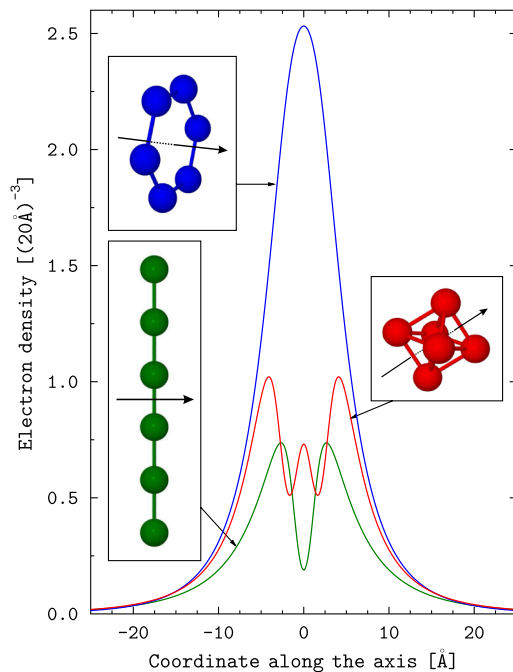

FIG. 2 (color online). Electron density of the Dyson orbital of the attached electron along selected axes for the Xe_6^- clusters of different dimensionalities. The centers of the axes coincide with the centers of the clusters.

We hope that our benchmark calculations and the underlying theory will also help to construct an explicit simple model potential describing the binding of the excess electron.

---

*On leave from Department of Theoretical Astrophysics, Ioffe Institut, 194021 St. Petersburg, Russia.

[1] P. Stampfli, Phys. Rep. **255**, 1 (1995).

[2] M. Rosenblit and J. Jortner, J. Chem. Phys. **101**, 8039 (1994).

[3] M. V. Rama Krishna and K. B. Whaley, Phys. Rev. B **38**, 11 839 (1988).

[4] M. Rosenblit and J. Jortner, J. Chem. Phys. **101**, 9982 (1994).

[5] H. Haberland, T. Kolar, and T. Reiners, Phys. Rev. Lett. **63**, 1219 (1989).

[6] D. Thirumalai, in *Large Finite Systems*, edited by J. Jortner *et al.* (Reidel, Dortrecht, 1987).

[7] P. Stampfli and K. H. Bennemann, Phys. Rev. A **38**, 4431 (1988).

[8] G. J. Martyna and B. B. Berne, J. Chem. Phys. **88**, 4516 (1988); **90**, 3744 (1989).

[9] P. Stampfli and K. H. Beneman, Z. Phys. D **20**, 53 (1991).

[10] T. Sommerfeld *et al.*, J. Chem. Phys. **133**, 114301 (2010).

[11] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Dover, New York, 2003).

[12] P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry* (Academic, New York, 1981).

[13] W. von Niessen, J. Schirmer, and L. S. Cederbaum, Comput. Phys. Rep. **1**, 57 (1984).

[14] L. S. Cederbaum, in *Encyclopedia of Computational Chemistry*, edited by P. V. R. Schleyer *et al.* (Wiley, New York, 1998).

[15] J. V. Ortiz, in *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczynski (World Scientific, Singapore, 1997), Vol. 2.

[16] V. P. Vysotskiy and L. S. Cederbaum, J. Chem. Phys. **132**, 044110 (2010).

[17] S. Feuerbacher *et al.*, J. Chem. Phys. **118**, 6188 (2003).

[18] J. Schirmer, L. S. Cederbaum, and O. Walter, Phys. Rev. A **28**, 1237 (1983).

[19] H.-D. Meyer, J. Phys. B **21**, 3777 (1988).

[20] O. Walter *et al.*, J. Math. Phys. (N.Y.) **25**, 729 (1984).

[21] M. R. Hoare and P. Pal, Nature (London), Phys. Sci. **230**, 5 (1971).

[22] M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974).

[23] B. A. Hess, Phys. Rev. A **32**, 756 (1985); **33**, 3742 (1986).

[24] V. G. Bezchastnov *et al.*, Phys. Rev. A **81**, 062507 (2010).

[25] R. D. Bardo and K. Ruedenberg, J. Chem. Phys. **60**, 918 (1974); **60**, 932 (1974).

[26] bwGRiD, http://www.bw-grid.de, funded by the Bundesministerium für Bildung und Forschung and the Ministerium für Wissenschaft, Forschung und Kunst (Baden-Württemberg).