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Quantum Monte Carlo Study of the Electronic Structure and Spectroscopy of the Al_{13} Superatom

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1. Introduction

Atomic clusters consisting of a few to several tens of atoms often exhibit physical and chemical properties that differ significantly from those of isolated atoms or bulk materials. Among these, certain atomic clusters possess well-defined electronic shell structures resembling those of individual atoms and are therefore referred to as superatoms. [1] Because their electronic properties can be tailored through composition and size, superatoms have attracted considerable interest as fundamental building blocks for next-generation functional materials, catalysts, and nanodevices. [2]

One of the most extensively studied superatoms is the aluminum 13-mer cluster, Al_{13} . The anionic cluster Al_{13}^- is exceptionally stable because its forty valence electrons completely fill the superatomic electronic shells according to the jellium model, giving rise to a closed-shell electronic configuration analogous to that of a noble gas atom. [3] Upon ionization, however, the electronic structure changes dramatically. The Al_{13} neutrals possess open-shell configurations that undergo structural distortions driven by the Jahn–Teller effect.

For more than two decades, the electronic structure of Al_{13} has remained the subject of active investigation. Photoelectron and photoionization spectroscopies have provided valuable information on the electron affinity and ionization energies of the cluster, [4] while first-principles calculations based on density functional theory (DFT) have been widely employed to interpret these measurements. While the electronic properties of Al_{13}^- anions are well established, those of the neutral and cationic Al_{13} remain controversial. In particular, theoretical predictions of the adiabatic and vertical ionization energy vary considerably depending on the level of theory, making quantitative comparison with experiment challenging. [5,6]

Diffusion Monte Carlo (DMC) is one of the most accurate first-principles methods for predicting electronic energies because it explicitly accounts for electron correlation, often achieving near chemical accuracy for systems where conventional approaches become unreliable. In this work, benchmark DMC calculations were performed to investigate the photodetachment of Al_{13}^- anions and photoionization of Al_{13} neutrals. The calculated results provide new insight into the electronic structure of this prototypical superatom and are directly compared with available experimental measurements.

2. Computational Methods

The electronic structures of Al_{13}^- , Al_{13} , and Al_{13}^+

were investigated using a hierarchical first-principles approach. Geometry optimizations and vibrational frequency calculations were first performed using DFT with the hybrid PBE0 exchange-correlation functional and 6-311+G(d,p) basis set. The optimized structures were then used to construct trial wave functions for quantum Monte Carlo (QMC) calculations using QMCPack [7].

The trial wave functions for quantum Monte Carlo are of the Slater-Jastrow type. [8] The Slater determinants were generated with Hartree-Fock (HF) and DFT, as well as multideterminant expansions from complete active space configuration interaction (CASSI). For the multireference calculation of Al_{13}^- anion, an active space of 20 electrons in 15 orbitals was chosen. The variational parameters in the Jastrow factor are linearly optimized using variational Monte Carlo (VMC) to minimize the energy of the system.

The optimized wave functions were subsequently employed in Diffusion Monte Carlo (DMC) calculations to obtain benchmark total energies with explicit treatment of electron correlation. [9] DMC is a stochastic projector method that gives the ground state by propagating the many-body trial wave function in imaginary time at a long time limit.

The adiabatic and vertical electron detachment energies (ADE and VDE) of Al_{13}^- and the adiabatic and vertical ionization energies (AIE and VIE) of Al_{13} were evaluated from the DMC total energies. Franck–Condon simulations were further performed to calculate vibronic spectra for direct comparison with experimental photoelectron spectra.

3. Results and Discussion

3.1 Electronic Structures of Al_{13} Clusters

Figure 1 shows the optimized structures of the Al_{13}^- anion, Al_{13} neutral, and Al_{13}^+ cation. The Al_{13}^- anion adopts an icosahedral structure, while removal of one electron induces a Jahn–Teller distortion to a distorted icosahedral geometry in the neutral cluster. Reoptimization of the previously proposed decahedral structure using an all-electron basis set converged to the distorted icosahedral geometry, confirming that the decahedral structure is an artifact of small-basis effective core potential calculations.

For the cation, the cap-like structure was confirmed as the global minimum. In addition, a low-lying oblate isomer was identified 0.51 eV above the cap structure. Although metastable, this oblate isomer plays a key role in interpreting the experimental ionization process. The frontier molecular orbitals

exhibit symmetry breaking consistent with the superatomic shell model and the Jahn–Teller distortion upon electron removal.

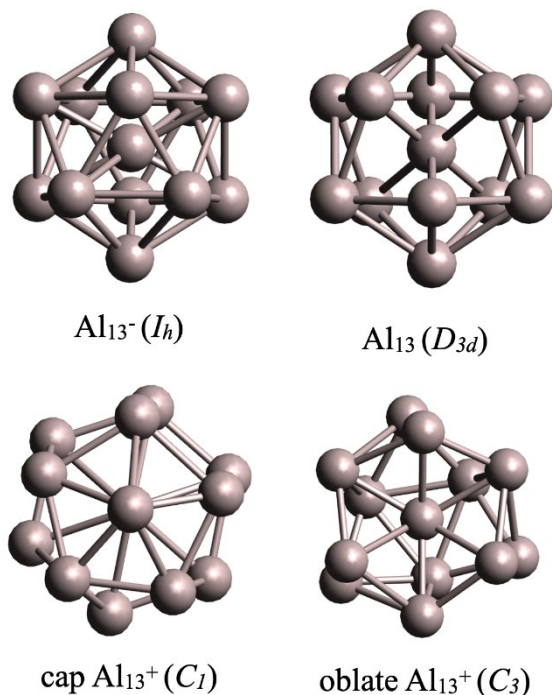


Figure 1: Isomers of Al_{13}^- , Al_{13} , and Al_{13}^+ optimized at the PBE0/6-311+G(d,p) level. The Al_{13}^- anion is icosahedral while the Al_{13} neutral undergoes a Jahn–Teller distortion to a distorted icosahedron. The Al_{13}^+ cation has two low-symmetry isomers: cap and oblate. The ground state cap isomer is 0.51 eV lower in energy than the metastable oblate.

3.2 Diffusion Monte Carlo Benchmark Calculations

Diffusion Monte Carlo calculations were performed using various basis sets and trial wave functions to evaluate their influence on the computed energies. Increasing the basis set from double- ζ to triple- ζ consistently lowered the DMC energies, indicating that basis-set quality remains important even within the fixed-node approximation. In contrast, the choice between Hartree–Fock and DFT trial wave functions had only a modest influence on the results, with DFT orbitals generally producing slightly lower energies. Single-determinant trial wave functions yielded lower DMC energies than the multideterminant CASCI expansions employed in this work and were therefore adopted for the benchmark calculations.

Finally, the use of pseudopotentials (BFD/VTZ) reduces the statistical error bars by a factor of 3–4 relative to all-electron calculations. Because the DMC provides an upper bound to the true ground-state energy within the local minimum defined by the nodal surface, it is appropriate to report the ADE, VDE, AIE, and VIE values using the lowest DMC energy obtained from the single-determinant DFT trial wave functions.

3.3 Photodetachment of Al_{13}^- Anions

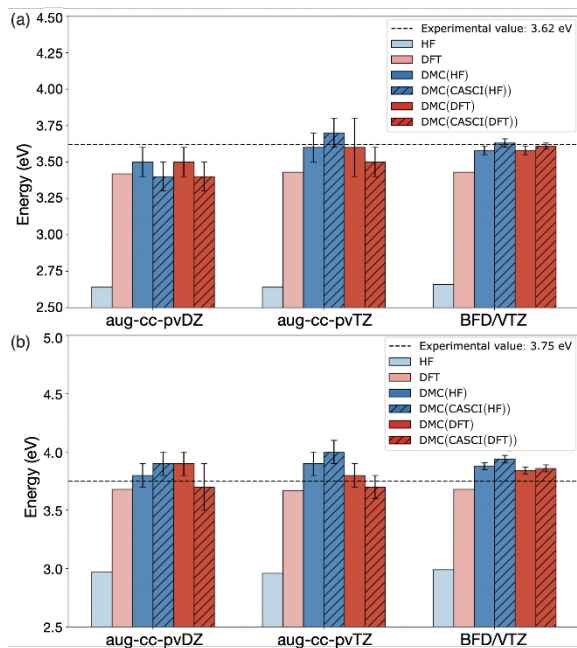


Figure 2: (a) Adiabatic detachment energies (ADE) and (b) vertical detachment energies (VDE) of Al_{13}^- calculated by DMC using different trial wave functions.

Figure 2 shows the ADE and VDE calculated by DMC using different trial wave functions. The calculated ADE of Al_{13}^- is 3.58 ± 0.03 eV in excellent agreement with experimental photoelectron spectra. [3] This value is obtained from the DMC energies with single-determinant DFT and using BFD pseudopotential with VTZ basis set. The calculated VDE is 3.84 ± 0.03 eV, which is about 0.1 eV higher than the experimental value. [10]

To better understand this discrepancy, the Franck–Condon factors (FCFs) are calculated. At 0 K, the most intense transition corresponds to the $9_5' + 24_3' \leftarrow 0''$ band. This is a combination-band transition from the vibrational ground state of the electronic ground state anion to a vibrational excited state of the electronic ground state of the neutral. At 260 K, low-frequency modes are thermally populated, enabling hot-band transitions. Although their individual FCFs are smaller than that of the fundamental transitions, the large number of accessible hot-band transitions leads to an overall shift of the spectral envelope toward lower energies. As a result, the simulated spectrum matches well with the experimental photoelectron spectrum produced at 260 K. This vibronic effect shifts the VDE to 3.80 ± 0.03 eV, bringing it into excellent agreement with experiment.

3.4 Photoionization of Al_{13} Neutrals

Unlike the photodetachment spectrum of Al_{13}^- , the photoionization of neutral Al_{13} has remained controversial. Although numerous theoretical studies have attempted to reproduce the experimental ionization energies, [11] the reported adiabatic ionization energies span nearly 1 eV depending on the computational method employed. [12] These

discrepancies highlight an important question on which structure and ionization pathways truly correspond to the observed experimental threshold, and does the measurement reflect an adiabatic or vertical process?

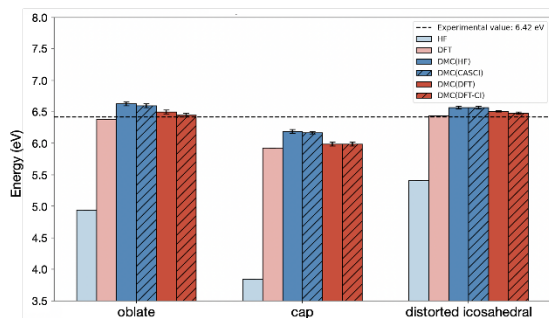


Figure 3: Adiabatic ionization energies for the ionization of Al_{13} neutral to oblate, cap, or distorted icosahedral isomer. The ionization energy leading to an oblate Al_{13}^+ cation matches well with the experiment.

To resolve this issue, photoionization was investigated by considering three possible cationic structures as shown in Figure 3: the cap ground state, the newly identified metastable oblate, and the distorted icosahedral structures. While the cap isomer is the global minimum of Al_{13}^+ , its calculated AIE (5.99 ± 0.03 eV) is significantly lower than the experimental threshold. In contrast, ionization to the metastable oblate isomer gives an adiabatic ionization energy of 6.50 ± 0.03 eV, in excellent agreement with experiment. The distorted icosahedral cation yields a similar energy but was confirmed to be a transition state rather than a stable structure.

These results indicate that the experimentally measured ionization threshold should not be assigned to the cap-like ground-state cation, as has commonly been assumed. Instead, the threshold is attributed to the formation of the metastable oblate Al_{13}^+ isomer, while the cap structure is reached only after subsequent structural relaxation.

This interpretation resolves the long-standing discrepancy between theory and experiment and is further supported by recent laser photoionization mass spectrometry measurements. [13] The calculated vertical ionization energy of 6.95 ± 0.03 eV also provides excellent agreement with the higher-energy ionization feature observed experimentally.

4. Conclusion

In this study, benchmark diffusion Monte Carlo calculations were performed to investigate the electronic structure and spectroscopy of the aluminum superatom Al_{13} . The calculated adiabatic and vertical detachment energies of Al_{13}^- showed excellent agreement with experimental photoelectron spectra, demonstrating the accuracy of the quantum Monte Carlo approach for describing electron correlation in superatomic clusters.

For the photoionization of neutral Al_{13} , the

calculations revealed that the experimentally observed ionization threshold corresponds to the formation of a metastable oblate Al_{13}^+ isomer rather than the cap-like ground-state cation. This finding resolves the long-standing discrepancy between theoretical predictions and experimental measurements and provides a consistent interpretation of the photoionization process.

The present work demonstrates that benchmark quantum Monte Carlo calculations can provide reliable electronic structures and spectroscopic properties for highly correlated systems. As computational resources continue to advance, these approaches will become increasingly valuable for investigating complex superatomic systems and guiding the interpretation of experimental spectroscopy.

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