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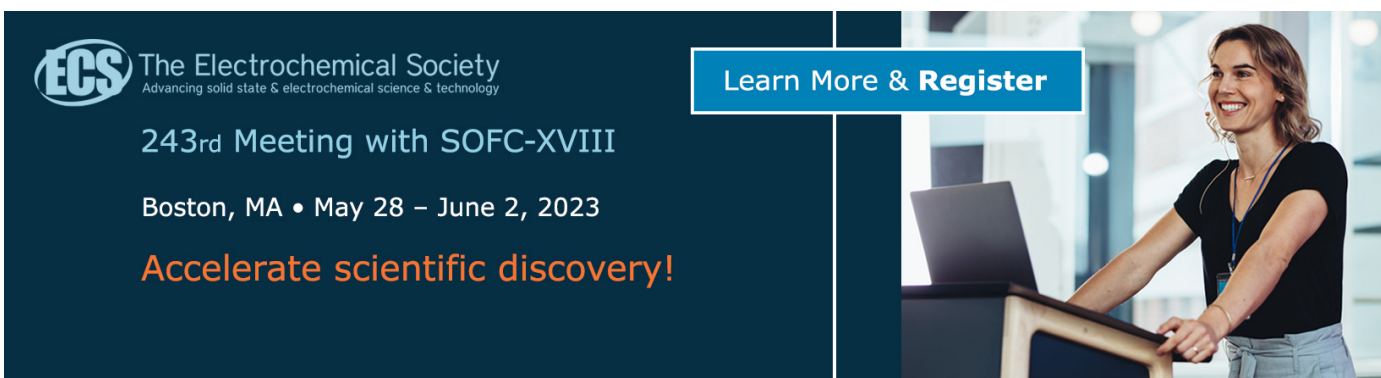
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# Electronic structure of metal-doped aluminum clusters by quantum Monte Carlo method

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**Abstract.** Using the fixed-node diffusion quantum Monte Carlo method (FN-DMC), the density functional theory (DFT), and the Hartree-Fock (HF) approximation, we investigate the valence electron binding energies of atomic clusters. Calculations are applied to the metal-doped anionic aluminum clusters  $XAl_4^-$  ( $X = K, Rb, Ag, \text{ and } Au$ ) and their vertical detachment energies (VDE) are obtained. A comparison between the FN-DMC results and the HF ones allows us to quantify the electron correlation effects and their impact on the stability of the clusters. The analysis reveals that the electron correlation enhances the vertical detachment energies of the atomic clusters significantly.

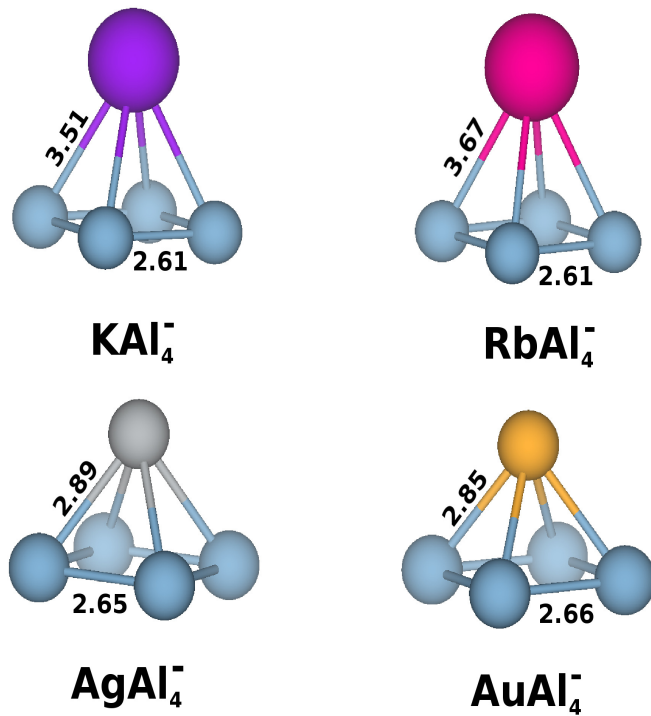
There is nowadays a consensus that the quantum Monte Carlo (QMC) technique has become a competitive tool at the level of high-level quantum chemistry methods such as CI and CCSD(T), but with clear advantages in terms of scale with system size [1, 2]. The power of QMC in overcoming the deficiencies of density functional theory (DFT) has been demonstrated in several applications such as in the structural transition[3, 4], energetics of point defects in silicon[5] and carbon[6, 7], surface reconstruction[8] and its interaction with  $H_2$ [9], and in several studies on clustered materials in which the electron correlation plays a decisive role[10, 11, 12, 13, 14, 15, 16, 17, 18, 19].

In this work, we employ two types of QMC techniques, namely, the variational Monte Carlo (VMC) and the diffusion Monte Carlo (DMC), to study the electronic structures of atomic clusters. In particular, we present in this paper a case study of the quantum Monte Carlo simulations on the electron correlation effects in the valence electron binding energies of atomic clusters. We choose for the study the following anionic clusters:  $XAl_4^-$  ( $X = K, Rb, Ag, \text{ and } Au$ ). The protocol of the calculations involves the use of a combination of the QMC methods and DFT, as well as the Hartree-Fock (HF) approximation to access with accuracy the electronic correlation effects. From the numerical results of the QMC and HF calculations, we analyze the impact of electron correlation in the vertical detachment energies (VDE) of these clusters. The vertical detachment energy is a fundamental quantity that is experimentally accessible for small clusters. It carries specific information about size-dependent stability and may also provide thermochemical values that are important for understanding the nature of the cluster formation.

In the VMC, an optimized fermionic trial wavefunction is constructed as a product of the Slater determinant of single-electron orbitals and the Jastrow correlation factor. Since the



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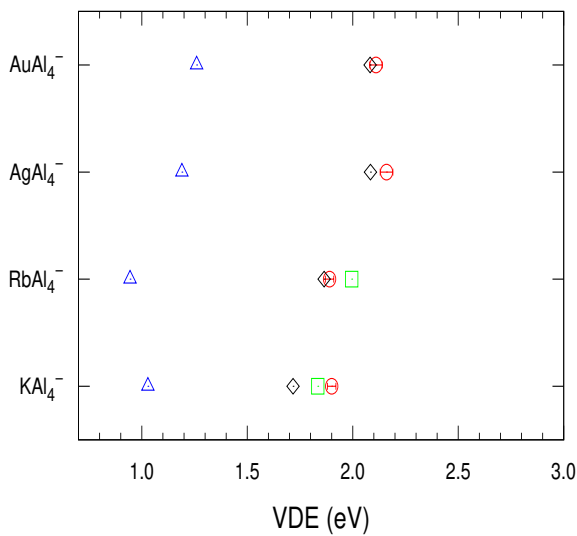
**Figure 1.** The lowest energy structures of the anionic metal-doped aluminum clusters  $XAl_4^-$  ( $X = K, Rb, Ag, \text{ and } Au$ ) obtained in Ref. [11].

VMC is not usually accurate enough, the VMC optimized trial wavefunction is then used in DMC[20, 21]. The DMC calculations have been performed with the Casino code[22] using fermionic trial wavefunctions of the Slater-Jastrow type

$$\Psi_T(R) = D_\uparrow(\phi_i)D_\downarrow(\phi_i)J(R). \quad (1)$$

Here  $R$  is the electronic configuration,  $D_\uparrow(\phi_i)$  and  $D_\downarrow(\phi_i)$  are determinants of up- and down-spin orbitals,  $\phi$ 's are the single-particle orbitals from all-electron DFT calculations using SVWN semi-local  $xc$  functional, and 6-311+G(3df) basis set as implemented in the Gaussian03 program[23]. The Jastrow factor  $J(R) = e^U$ , and  $U$  is an explicit sum of electron-nucleus, electron-electron, and electron-electron-nucleus distances, including variational parameters that are varied to minimize the local energy  $E_L(R) = \frac{\hat{H}\Psi_T(R)}{\Psi_T(R)}$ , with  $\hat{H}$  being the many-electron Hamiltonian. The stochastic evolution in imaginary time using both the short time and fixed-node approximations[24] yields the DMC energy being an upper bound of the exact ground-state energy. For all-electron DMC calculations, the fixed-node error is the only uncontrollable source of error. However, calculations using pseudopotential can also suffer from inaccuracy due to the nonlocality characteristic of the angular-momentum dependent pseudopotentials[25]. We have checked time steps varying from 0.005 to 0.001 a.u., and find that with a time step of 0.002 a.u. total energy converges within the statistical error. For the production, we use a time step of 0.001 a.u., which yields calculations with an acceptance ratio of 99.9% in an ensemble of 10000 walkers.

Fig. 2 shows the vertical detachment energy (VDE) of the clusters under study obtained from the HF and DMC calculations, together with the results of DFT/PBE and CCSD(T). The VDE is the total energy difference between the anionic and neutral clusters with the neutral



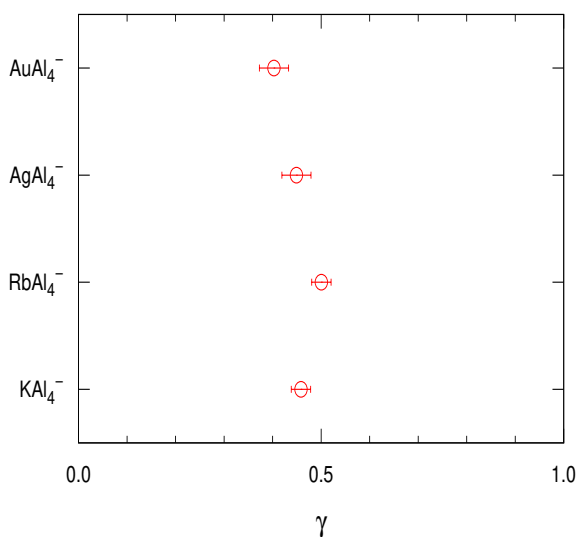
**Figure 2.** The vertical detachment energy (VDE) of the metal-doped anionic aluminum clusters. The theoretical results are indicated by the blue open-triangles (HF), the black diamond (DFT/PBE), the green open-square (CCSD(T))[11], and the red open-circles with error bars (FN-DMC).

cluster in the geometry of the anionic one. From the difference between the DMC result and that from the HF calculation, we obtain the impact of correlation effect on VDE. Notice that for these metal-doped aluminum clusters, the differences of the vertical detachment energies from the DMC ( $VDE_{\text{DMC}}$ ) and HF calculations ( $VDE_{\text{HF}}$ ) are about 1 eV. The electron correlation contribution is responsible for the enhancement of the electron binding energy of the clusters.

We can quantify the impact of the electron correlation effects on the VDE by the relative contribution of the electron correlation to the VDE, given by the parameter  $\gamma$  defined as

$$\gamma = \frac{VDE_{\text{DMC}} - VDE_{\text{HF}}}{VDE_{\text{DMC}}}. \quad (2)$$

Fig. 3 shows the parameter  $\gamma$ , the impact of the electron correlation on the VDE of the clusters. The contribution of the electron correlation is significant to the VDE of the clusters  $XAl_4^-$  ( $X = \text{K, Rb, Ag, and Au}$ ) being between 40% and 50% of the detachment energies.



**Figure 3.** The impact of electron correlation on the VDE is quantified by the parameter  $\gamma$  for the clusters  $XAl_4^-$  ( $X = \text{K, Rb, Ag, and Au}$ ).

Next, we analyze the stability of the clusters from the electron detachment energy through the decomposition of the VDE into the following three physical components[26],

$$\text{VDE} = \Delta E^{\text{KT}} + \Delta E^{\text{relax}} + \Delta E^{\text{corr}}. \quad (3)$$

The first two terms in the above equation are HF contributions. The energy  $\Delta E^{\text{KT}}$  is calculated using the Koopman's approach[27] taking into account only electrostatic and exchange interactions, and the remaining HF energy, denoted by  $\Delta E^{\text{relax}}$ , is due to orbital relaxation (or the charge redistribution effects). The term  $\Delta E^{\text{corr}}$  is the electron correlation contribution defined as the difference between the exact VDE (approximately given by the DMC result) and the HF one in the complete basis set limit, given by  $\Delta E^{\text{corr}} = \text{VDE}_{\text{DMC}} - \text{VDE}_{\text{HF}}$ . Table 1 shows the decomposition of the VDE in the ground state of these clusters.

**Table 1.** The decomposition of the VDE for  $X\text{Al}_4^-$  ( $X = \text{K}, \text{Rb}, \text{Ag}$  and  $\text{Au}$ ) clusters. The numbers in parenthesis are the estimated statistical error in the last decimal place. The energies are in eV.

Clusters	VDE			
	FN-DMC	$\Delta E^{\text{KT}}$	$\Delta E^{\text{relax}}$	$\Delta E^{\text{corr}}$
$\text{KAl}_4^-$	1.90(2)	1.20	-0.17	0.87(2)
$\text{RbAl}_4^-$	1.89(2)	0.28	0.66	0.95(2)
$\text{AgAl}_4^-$	2.16(3)	0.65	0.54	0.97(3)
$\text{AuAl}_4^-$	2.11(3)	0.68	0.58	0.85(3)

In general, the main factor of stabilization of the attached electron of the studied clusters is due to the correlation effect with its contribution representing about 50% of the total value of VDE. The exception is the K-doped cluster, where the electrostatic and exchange interactions, giving by the Koopmans energy  $\Delta E^{\text{KT}}$  is more significant with 63% (1.20 eV) contribution leading to negative orbital relaxation energy.

In summary, we have performed the quantum Monte Carlo simulations and calculations within the Hartree-Fock approximation to study the electron correlation effects on the electron binding in small atomic clusters. To analyze the binding energy of the valence electron of the clusters, we have calculated the VDE of the metal-doped anionic aluminum clusters  $X\text{Al}_4^-$  ( $X = \text{K}, \text{Rb}, \text{Ag}$ , and  $\text{Au}$ ). We have quantified the impact of the electron correlation in the binding energy by the parameter  $\gamma$ . We have also decomposed the VDE into three physical components: the electrostatic potential and exchange interaction, the orbital relaxation, and the electronic correlation energy. Our numerical calculations show that quantitatively, the electron correlation effects contribute with about 50% to the vertical detachment energies of these clusters.

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