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Theoretical study of the interaction of ionized transition metals (Cr,Mn,Fe,Co,Ni,Cu) with argon

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Ab initio Hartree-Fock effective-core-potential calculations have been performed to determine the binding-energy trends of the transition-metal–argon diatomic positive ions. The interaction in these systems is mainly governed by charge-induced dipole forces, with the metal carrying the charge. It is found that all the species are bound and that the binding energy is strongly dependent on the electronic state of the transition-metal ion. A configuration-interaction prediction of the binding energy is also presented for the Cu^+Ar system. The importance of the electron correlation in these systems is discussed.

I. INTRODUCTION

The technique of rare-gas matrix isolation has been extensively used to study the spectroscopy of atoms, small aggregates of atoms, and stable as well as highly reactive molecules and radicals.[1] Of particular interest have been spectroscopic studies of matrix-isolated transition-metal atoms.[2] A great of deal of effort, both experimental and theoretical, has been devoted to understanding the interaction between the isolated species and the matrix.[3] In previous studies two of us have extensively applied the multiple-scattering (MS) $X\alpha$ model to the description of the first-row transition-metal atoms and ions isolated in an argon matrix.[4–7] In these studies we used an M-Ar_{12} cluster, M=Mn, Mn^+, Fe, Fe^+, Co, Ni, and Cu, designed to represent the transition metal as a substitutional impurity in a crystalline Ar lattice. This simple model has provided a good description of the main features of the interaction between the isolated neutral-metal and the host matrix atoms, where repulsive effects such as overlap distortion of the outer metal orbitals play a dominant role, yielding reasonable agreement between the calculated hyperfine parameters and those determined from Mössbauer and EPR spectroscopies. However, our estimate indicated a large increase in the van der Waals interaction when a charged species is placed within the rare-gas lattice and that the MS-$X\alpha$ method may be inadequate for studying a charged species in a rare-gas matrix.

Recently we extended this study by performing *ab initio* all-electron self-consistent-field (SCF) calculations on FeAr, Fe^+Ar, ArFeCO, and FeCOAr, and *ab initio* effective-core-potential (ECP) SCF calculations on Fe^+Ar.[8] Although the interaction between Fe^0 and Ar was found to be repulsive at all distances, Fe^+Ar was found to be bound by charge-induced dipole forces. This finding encouraged us to extend our study to include other M^+Ar (M=Cr,Mn,Fe,Co,Ni,Cu) systems to determine whether all the diatomic positive species are bound, and to elucidate the nature of this binding. In addition, there have been recent experimental studies of the M^+-Ar species,[9] as well as other theoretical investigations.[10] The presence of binding predicted in our previous study was subsequently observed experimentally[9] and confirmed theoretically.[10] These later studies determined that the binding is even stronger than that predicted by our SCF study. Nevertheless, it is useful to complete our SCF study because the computational effort is modest compared to more sophisticated treatments enabling the investigation of a sufficient range of systems to make possible the determination of binding trends, if any, in these systems.

Electrostatic and induction forces are, of course, the dominant interactions at long range between a transition-metal ion and neutral Ar. In the overlap region, exchange interactions, which mix the metal and Ar wave functions, become important. The electronic configuration assumed by the transition metal will also influence binding in these systems. In this investigation we use the SCF method to study the interaction of transition metal cations in both the $4s^0 3d^{N-1}$ and $4s^1 3d^{N-2}$ states (N is the number of $4s$ and $3d$ electrons in the neutral atom) with a single Ar atom. In addition, multiconfiguration Hartree-Fock (MCHF) and configuration-interaction (CI) calculations have been carried out for Cu^+Ar to determine the role of electronic correlation in that system.

II. COMPUTATIONAL METHODS

The ECP calculations were carried out with the "core" defined to be the $1s$, $2s$, and $2p$ electrons of both the metal

TABLE I. Dipole polarizability (α) of Ar.

Method	Basis set	α (Å^3)
CPHF	$(4sp)$[a]	0.29
CPHF	$(4sp/2d)$[b]	1.54
CPHF	numeric[c]	1.59
Expt.		1.63

[a] Basis set from Reference 12.

[b] Same as (a) with two added *d* functions.

[c] Reference 14.

[d] Reference 17.

ions and Ar. The compact effective potentials and basis sets of Stevens and Krauss were used for the transition metals[11] and for Ar.[12] For Ar an additional pair of *d* functions, with exponents 0.4 and 0.12, were added. The SCF calculations were carried out using the spin-unrestricted Hartree-Fock (UHF) formalism for the open-shell species. For all calculations we have used the HONDO program.[13]

III. RESULTS AND DISCUSSION

The rare-gas–metal-ion interaction may be divided into three regions: an attractive van der Waals interaction at long range, a repulsive interaction at short distances, and a molecular-orbital overlap effect at intermediate separations. At long range, the M^+Ar molecule can be viewed as a nearly unperturbed M^+ ion bound to Ar by simple charge-induced dipole forces. The form of the classical attractive interaction between the ionized transition metal and the Ar electron cloud is given by $-\frac{1}{2}\alpha q^2/r^4$, where the metal is considered a point charge ($q=1$) and α is the Ar polarizability. Thus an accurate description of the attractive interaction must include an adequate description of the Ar dipole polarizability. In Table I, we compare the experimental polarizability of Ar with the coupled-perturbed Hartree-Fock (CPHF) value obtained with the Stevens-Krauss basis set[12] (used in our previous study[8]), the same basis set augmented by two *d* functions optimized for the polarizability (exponents 0.40 and 0.12), and the numerical basis-set CPHF values of McEachran, Ryman, and Stauffer.[14] We note that the basis set used in our previous study was inadequate for the Ar polarizability, and anticipate improved results with our present extended basis set.

At intermediate distances, the overlap of the molecular orbitals between the two species has two effects: a distortion effect which shrinks both the metal and rare-gas orbitals of the same spin to reduce the repulsive interaction, and a partial electron transfer from Ar to the metal ion. Both of these effects depend strongly on the particular metal ion and its electronic state. In Table II we compare the total ECP energies for the $4s^03d^{N-1}$ and $4s^13d^{N-2}$ states of singly ionized transition-metal atoms (except for Cr, which is taken to be $3d^5$). Experimentally, the ground states are known to be[15] $4s^03d^{N-1}$ for the Cr, Co, Ni, and Cu cations and $4s^13d^{N-2}$ for the Mn and Fe cations. UHF theory does not accurately predict the ground states of Co$^+$ and Ni$^+$ due to the well-known bias of the Hartree-Fock approximation, which lowers the energy of high-spin states relative to the lower-spin states. Nevertheless, we note that the calculated T_e values for Mn$^+$, Fe$^+$, Co$^+$, and Ni$^+$, are consistently too large by ~ 1.7 eV. Thus we do not expect the overall *trends* observed here to change significantly at higher levels of theory—an expectation borne out by recent theoretical work.[10]

In Table III we give the electronic configuration, equilibrium dissociation energy (D_e), equilibrium bond length (R_e), equilibrium zero-point harmonic frequency (ω_e), and transferred charge (δ) for each of the M^+Ar systems, and in Figs. 1 and 2 we present the interaction potentials for each state. The classical polarization potential is also plotted in Figs. 1 and 2, and shows good agreement with our SCF results at long range. The fact that the more strongly bound curves lie below the classical curve indicates that exchange forces play a role in binding these systems.

From Table III and Figs. 1 and 2, we see the unsurprising result that for a given electronic configuration the

TABLE II. Atomic SCF-ECP total energies (E) and transition energies (T_e) of M^+ systems.

			T_e (eV)	
M	State	E (hartree)	This work	Expt.[a]
Cr	$s^0d^5(^6S)$	$-85.678\,602$		
Mn	$s^1d^5(^7S)$	$-102.972\,704$	0	0
	$s^0d^6(^5D)$	$-102.840\,929$	3.59	1.78
Fe	$s^1d^6(^6D)$	$-122.292\,928$	0	0
	$s^0d^7(^4F)$	$-122.220\,670$	1.97	0.232
Co	$s^1d^7(^5F)$	$-144.004\,666$	0	0.415
	$s^0d^8(^3F)$	$-143.953\,109$	1.40	0
Ni	$s^1d^8(^4F)$	$-168.203\,647$	0	1.041
	$s^0d^9(^2D)$	$-168.170\,535$	0.901	0
Cu	$s^0d^{10}(^1S)$	$-195.775\,802$		
	$s^1d^9(^3D)$	$-195.007\,773$		

[a] Reference 15.

TABLE III. Spectroscopic parameters for M^+Ar systems. Except where noted, all results are from UHF theory. S^2 is the expectation value of the total spin; R_e, D_e, ω_e, and δ are the equilibrium distance, dissociation energy, zero-point harmonic frequency, and the electronic charge transferred to the metal ion from Ar, respectively.

M	State[a]	S^2	D_e (meV)[b]	R_e (Å)	ω_e (cm^{-1})	δ
Cr	$\sigma^1\pi^2\delta^2(^6\Sigma^+)$	8.751	110	2.962	76	0.029
Mn	$\sigma^1\pi^2\delta^3(^5\Delta)$	6.014	149	2.842	93	0.038
Fe	$\sigma^2\pi^3\delta^2(^4\Pi)$	3.761	151	2.775	96	0.048
Co	$\sigma^1\pi^4\delta^3(^3\Delta)$	2.004	185	2.660	114	0.059
Ni	$\sigma^1\pi^4\delta^4(^2\Sigma^+)$	0.752	231	2.587	129	0.086
Cu	$\sigma^2\pi^4\delta^4(^1\Sigma^+)$	0.000	194	2.622	115	0.082
Cu[c]	$\sigma^2\pi^4\delta^4(^1\Sigma^+)$	0.000	460	2.507	175	0.116
Mn	$s^1\sigma^1\pi^2\delta^2(^7\Sigma^+)$	12.001	45	3.563	39	0.018
Fe	$s^1\sigma^1\pi^2\delta^3(^6\Delta)$	8.753	52	3.417	43	0.022
Co	$s^1\sigma^2\pi^3\delta^2(^5\Pi)$	6.002	55	3.380	43	0.022
Ni	$s^1\sigma^1\pi^4\delta^3(^4\Delta)$	3.752	62	3.222	49	0.029
Cu	$s^1\sigma^1\pi^4\delta^4(^3\Sigma^+)$	2.000	75	3.069	51	0.041

[a] σ^n, π^n, and δ^n identify the metal $3d$ orbitals, s^n labels the metal $4s$ orbital.

[b] Results include BSSE correction.

[c] CISDQ results, see text.

computed results follow a periodic trend (i.e., increasing binding from Cr to Cu). It is important to note, however, that if one only considered the ground-state spin configurations, then the simple periodic trend would be obscured. We also note that the larger binding energies occur for M^+ with no $4s$ electrons. This can be understood as a result of the reduction in the repulsive interaction that arises from the superposition of the diffuse $4s$ metal orbital and the Ar $3p$ orbitals. Depopulation of the $4s$ orbital eliminates the possibility of strong repulsion owing to the Pauli exclusion principle and yields a stronger bond. The Cu$^+$Ar($^1\Sigma^+$) molecule is the one ex-

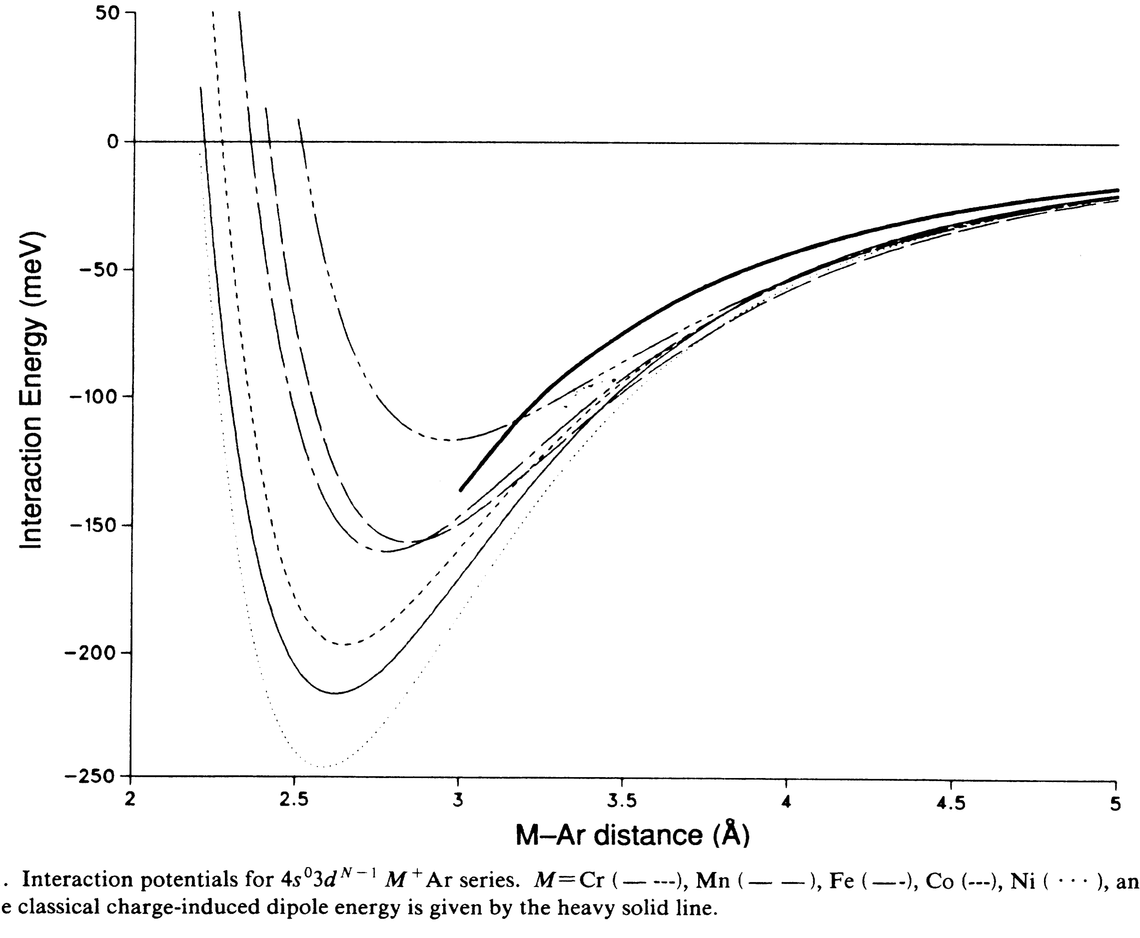

FIG. 1. Interaction potentials for $4s^0 3d^{N-1}$ M^+Ar series. M=Cr (— ---), Mn (— —), Fe (—-), Co (---), Ni (· · ·), and Cu (solid line). The classical charge-induced dipole energy is given by the heavy solid line.

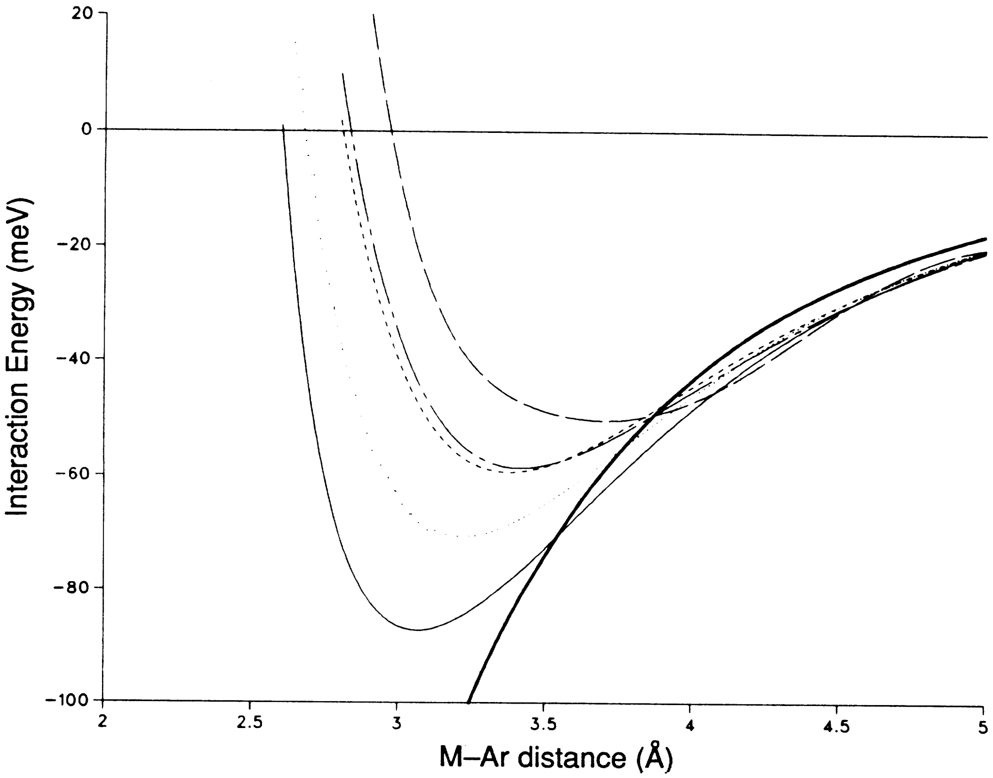

FIG. 2. Interaction potentials for the $4s^1 3d^{N-2}$ M^+Ar series. For labeling, see Fig. 1.

ception to the periodic trend, with a binding energy smaller than that of Ni$^+$Ar($^2\Sigma^+$). This is due to the additional repulsion from the filling of the $3d\sigma$ hole. A similar, but smaller, effect is predicted for Fe$^+$Ar($^4\Pi$) and Co$^+$Ar($^5\Pi$), where $3d\sigma^2$ occupation is our calculated ground state. In Table IV we note that the trends predicted by our simple UHF results are in agreement with those of Ref. 10 obtained by the modified coupled-pair functional treatment. The main difference in these findings is that our binding energies are roughly $\frac{1}{3}$ (for the $4s^1$ systems) to $\frac{1}{2}$ (for the $4s^0$ systems) of the values of Ref. 10; hence we do not attempt to provide quantitative estimates of spectroscopic parameters.

Because of the relatively small binding energies found, and the size of basis sets used in this study, it is important to evaluate the magnitude of the basis-set-superposition error (BSSE).[16] In Table V we have used the counterpoise method to estimate the BSSE for each system. In addition to the BSSE correction to the binding energy, the BSSE has a secondary effect on the predicted bond length because it varies with internuclear separation. To determine the magnitude of this effect we have calculated BSSE-corrected potential curves near the minimum for both singlet and triplet Cu$^+$Ar. For singlet Cu$^+$Ar the resulting bond length is 2.641 Å and the bond energy is 194.0 meV. For triplet Cu$^+$Ar the resulting bond length is 3.094 Å and the bond energy is 75.2 meV. From Tables III and V we conclude that the error in the bond length is only 0.02 and 0.03 Å, respectively, while the error in the binding energy for each is 0.3 meV. Since these errors are much smaller than the expected accuracy of the computational method used here, only the primary BSSE energy shift has been used in Table III, and secondary corrections were not pursued.

TABLE IV. Comparison of theoretical and experimental ground-state dissociation energies, D_0 (meV), for M^+ Ar systems.

	UHF[a]		CISDQ[a]		MPCF[b]		Expt.[c]
M	State	D_0	State	D_0	State	D_0	D_0
Fe	$^6\Delta$	49			$^6\Delta$	140	
Fe	$^4\Pi$	145			$^4\Delta$	297	
Co	$^3\Delta$	178			$^3\Delta$	392	508
Ni	$^2\Sigma^+$	233			$^2\Sigma^+$	450	550
Cu	$^1\Sigma^+$	187	$^1\Sigma^+$	460	$^1\Sigma^+$	405	

[a] This work.
[b] Reference 10.
[c] Reference 9.

TABLE V. Basis-set-superposition errors for M^+Ar systems calculated by the counterpoise method.

M	State[a]	BSSE
Cr	$\sigma^1\pi^2\delta^2(^6\Sigma^+)$	6.7
Mn	$\sigma^1\pi^2\delta^3(^5\Delta)$	7.6
Fe	$\sigma^2\pi^3\delta^2(^4\Pi)$	9.1
Co	$\sigma^1\pi^4\delta^3(^3\Delta)$	12.6
Ni	$\sigma^1\pi^4\delta^4(^2\Sigma^+)$	15.0
Cu	$\sigma^2\pi^4\delta^4(^1\Sigma^+)$	22.5
Mn	$s^1\sigma^1\pi^2\delta^2(^7\Sigma^+)$	4.5
Fe	$s^1\sigma^1\pi^2\delta^{3({}^{6}}\Delta)$	6.7
Co	$s^1\sigma^2\pi^3\delta^2(^5\Pi)$	4.1
Ni	$s^1\sigma^1\pi^4\delta^3(^4\Delta)$	8.3
Cu	$s^1\sigma^1\pi^4\delta^4(^3\Sigma^+)$	12.4

[a] Same as in Table III.

To investigate the role of electron correlation we have computed R_e, ω_e, D_e, and D_0 values for $\mathrm{Cu}^+(4s^03d^{10})$Ar by single-reference CI with all single, double, and quadrupole (CISDQ) excitations (quadruples by Davidson's correction). The reference determinant is comprised of the natural orbitals from a multiconfiguration Hartree-Fock (MCHF) calculation with single and double excitations from the metal-ion $3d$ orbitals into the $4s$ orbital and a set of unoccupied d orbitals. The orbital space for the CISDQ included excitations from all occupied orbitals (both M^+ and Ar) into 19 unoccupied orbitals. This results in $R_e=2.507$ Å, $\omega_e=175$ cm^{-1}, $D_e=471$ meV, and $D_0=460$ meV. We see that electron correlation greatly enhances the binding, as was reported by Bauschlicher *et al.*,[10] who obtained a bond length of 2.37 Å and a D_0 of 405 meV using the modified coupled-pair functional method. The increased binding can arise from complementary origins: improved description of the atomic wave functions, and accurate description of the correlated motion of the electrons in the overlap region. Comparing our previously reported binding energy[8] for $\mathrm{Fe}^+\mathrm{Ar}(^6\Delta)$, with that obtained with the present improved basis set, shows an increase from 12 to 52 meV. Since the present SCF polarizability is 95% of experiment, it is unlikely that the twofold increase in binding found in the correlated studies could be a result of further improvement of the polarizability. Bauschlicher *et al.*[10] have suggested that the improved first ionization potential of the metal from their correlated calculation increases the contribution of the M^+Ar configuration, which is not properly described at the SCF level. Although it is difficult to quantify how much of the binding is due to this effect, we note that our SCF ionization potential for Cu is 6.62 eV, as opposed to 7.726 eV from experiment,[18] and that the partial charge on Ar increases from 0.082 for the SCF wave function to 0.108 in the CISDQ wave function. Finally, there is the effect of electron correlation in the overlap region. In Table IV we see that SCF recovers about half of the binding of Ref. 10 for the $4s^0$ systems, but only one-third for the $4s^1$ systems, regardless of which configuration is the ground state. This suggests that electron correlation plays a major role in reducing the repulsion between the metal-ion $4s$ electron and Ar.

IV. CONCLUSIONS

We have studied the electronic structure and spectroscopic properties of the M^+Ar (M=Cr, Mn, Fe, Co, Ni, and Cu) systems for both $4s^03d^{N-1}$ and $4s^13d^{N-2}$ atom configurations of the metal ions using the SCF method. All of the studied systems exhibit binding. For the M^+Ar molecular states arising from the $4s^13d^{N-2}$ atomic states of the metal ion, the repulsion of the radially extended M^+ $4s$ electron leads to weak binding. In these cases charge-induced dipole forces are primarily responsible for the binding. On the other hand, the $4s^03d^{N-1}$ metal-ion states lack this repulsion, enabling closer approach and increased binding. Because of this, exchange interactions play a larger role in binding these systems, particularly for the most strongly bound, M=Co, Ni, and Cu.

Within each set of states ($4s^0$ or $4s^1$) the relative magnitude of the binding follows a periodic trend (increasing from Cr to Cu), with the exception of $^1\Sigma^+\mathrm{Cu}^+\mathrm{Ar}$, for which the added repulsion of the filled $3d$ shell weakens the binding significantly. However, if one only considers the experimentally known ground state of the ions, then the binding energies would increase from M=Mn,Fe, Cr, Co, Cu, to Ni.

Electron correlation can play an important role in the binding of these systems. For $\mathrm{Cu}^+\mathrm{Ar}(^1\Sigma^+)$, a CISDQ treatment doubles the calculated binding energy. This is consistent with the results of Bauschlicher *et al.*[10] The present SCF results, however, predict the same electronic configurations and binding energy trends as the more exact methods. Considering the relative expense involved, the findings of the present study imply that SCF calculations can contribute to the understanding of binding in these systems.

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