

1P140

Theoretical study of first-row transition metal dimers using newly developed spdsMCP

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1. INTRODUCTION

Heavy metal clusters are difficult to calculate because of the following reasons: many electrons, relativistic effect, and electron correlation. Normal all-electrons treatment is faced with these problems and we must treat many electrons including inactive core electrons in heavy elements. Furthermore, we must consider relativistic effects at the same time, resulting in high-cost calculations. However, we can overcome these problems by using so-called effective core potential (ECP) or model core potential (MCP). In usual ECP methods, valence orbitals do not have naturally correct nodal structure. It is well known that the nodeless pseudo-orbitals in the usual ECP approaches may produce a large exchange integral and thus overestimate the correlation energies. The MCP method is one of ECP methods, and the MCP Hamiltonian has a shift operator. Due to the shift operator, the MCP method is able to represent the correct nodal structures of valence orbitals. Thus MCP method is suitable to accurately describe the correlation effects of valence electrons.

We have recently developed new relativistic model core potentials, spdsMCP, in which 3s, 3p, 3d and 4s electrons explicitly, for the first-row transition-metal atoms [1], where we demonstrated that the spdsMCP basis sets have excellent performance in describing the electronic structures of atoms and molecules, bring about accurate excitation energies for atoms and very good spectroscopic constants for some molecules. In this study, we performed application of the newly developed relativistic spdsMCPs for the first-row transition metal dimers from Sc₂ to Zn₂.

2. METHODS OF CALCULATION

We used three-types of basis set: BS1 [4s2p4d1f], BS2 [5s4p4d2f1g], and BS3 [5s5p4d3f2g]. Using the basis sets complete active space self-consistent field (CASSCF) with twelve active orbitals and second-order multiconfiguration quasidegenerate perturbation (MCQDPT2) theory given by Nakano [2] were performed for the first-low transition metal dimers. In MCQDPT2, all 3s, 3p, 3d and 4s electrons were correlated.

3. RESULTS AND DISCUSSION

The first-low transition metal dimers are difficult to calculate in spite of their simple structures, because the dimers have different characteristic electron configurations for each ground state. Among these transition metal dimers, Mn₂ is one of the least understood systems from both experimental and theoretical points of view. The binding between the Mn atoms seems to be very weak and a type of van der Waals molecule. Moreover, it is indispensable to consider both static and dynamic correlation energies to investigate the electronic structures of

the dimer. Thus, we first examined the Mn₂ dimer to demonstrate the performance of spdsMCPs. Results of spectroscopic constants for three low-lying electronic states of Mn₂ given by using BS3 are listed in Table 1 with experimental and recent all-electron (AE) theoretical data [3]. Calculated spectroscopic constants are very similar to results of AE calculations and experimental values, indicating the spdsMCP works well for Mn₂, which requires a highly correlated calculation.

We also calculated the other first-low transition metal dimers. The results of our calculations for Sc₂, Ni₂, Cu₂ and Zn₂ given by using BS2 are summarized in Table 2 with existing theoretical and experimental data. The present results are comparable with the existing data.

Table1. Spectroscopic constants of Mn₂ given by MCQDPT2 with BS3.

State		$R_e / \text{\AA}$	$\omega_e / \text{cm}^{-1}$	D_e / eV
$^1\Sigma_g^+$	spdsMCP	3.13	55.2	0.17
	AE/ nonrel. [3]	3.29	53.5	0.14
	AE/ rel. [3]	3.18	59.2	0.16
	Exp.	3.4	68.1	0.1
$^{11}\Sigma_u$	spdsMCP	3.47	65.0	0.15
	AE/ nonrel. [3]	3.42	62.6	0.13
$^{11}\Pi_u$	spdsMCP	2.55	240.3	1.34
	AE/ nonrel. [3]	2.53	240.5	1.21

Table2. Spectroscopic constants by MCQDPT2 with BS2 for Sc₂, Ni₂, Cu₂ and Zn₂.

	State		$R_e / \text{\AA}$	$\omega_e / \text{cm}^{-1}$	D_e / eV
Sc ₂	$^5\Sigma_u^-$	spdsMCP	2.66	272	0.89
		AE/ MRSDCI [4]	2.74	---	0.59
		Exptl.	---	238	1.04
Ni ₂	$^3\Sigma_g^-$	spdsMCP	2.07	288	2.26
		AE/ CASPT2 [4]	2.228	---	1.78
		Exptl.	2.155	259.2	2.04
Cu ₂	$^1\Sigma_g^+$	spdsMCP	2.206	288	1.90
		AE/ nonrel. [4]	2.215	---	1.97
		Exp.	2.219	266.46	2.01
Zn ₂	$^1\Sigma_g^+$	spdsMCP	3.378	35.92	0.05
		Exptl.	2.35, 4.19	80, 25.9	0.06, 0.03

References

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