

# Applications of Newly Developed *spds*MCPs for First-Row Transition Metal Atoms

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*Abstract:* We have examined newly developed relativistic model core potentials (MCPs) for the first row transition-metal atoms from Sc to Zn, in which  $3s$  and  $3p$  electrons are treated explicitly together with the  $3d$  and  $4s$  electrons. By adding suitable correlating functions, we demonstrated that the present MCP basis sets show excellent performance in describing the electronic structures of atoms and molecules, bringing about accurate excitation energies for atoms and very good molecular spectroscopic constants.

*Key Words:* model core potential, first transition metal atom, correlation energy, spectroscopic constant, excitation energy

## 1 Introduction

During the past two decades, we have developed non-relativistic and relativistic model core potentials (MCPs) together with valence functions for atoms up to Rn [2], while Seijo and co-workers developed ab initio model potentials (AIMPs) [2]. Both the MCP and AIMP methods are based on the theory originally proposed by Huzinaga and co-workers [3]; the MCP and AIMP methods are unique among various effective core potential (ECP) methods in that they are naturally capable of producing valence orbitals with a nodal structure. The nodeless pseudo-orbitals in ECP approaches may yield overly large exchange integrals, resulting in exaggerated correlation energies and overly large singlet-triplet splittings [4]. Thus, the MCP and AIMP methods are well suited to accurately describe the correlation effects of valence electrons due to the accurate nodal

structure of the valence orbitals.

For transition metal elements, we have developed two types of MCPs, *ds*MCP and *pds*MCP. In the former type, only  $(n-1)d$  and  $ns$  electrons are explicitly treated, while in the latter,  $(n-1)p$  electrons are also treated as well as  $(n-1)d$  and  $ns$  electrons. Both MCPs have described well the ground state properties of transition-metal complexes [26]. However, the MCPs have a weak point for describing the excited states: for example, the relative energies of the  $3d^{n+1} 4s^1$  state with respect to the  $3d^n 4s^2$  state at the Hartree-Fock level using *pds*MCPs differ largely ( $\sim 0.7$  eV) from those given by the reference numerical Hartree-Fock calculations. Recently, we have developed new *spds*MCPs for first transition metal atoms in which  $3s$  electrons as well as  $3p$ ,  $3d$  and  $4s$  electrons are treated explicitly. The *spds*MCPs reproduce the quasi-relativistic Hartree-Fock (QRHF) relative energies within about 0.1 eV as shown in Fig.1 [5].

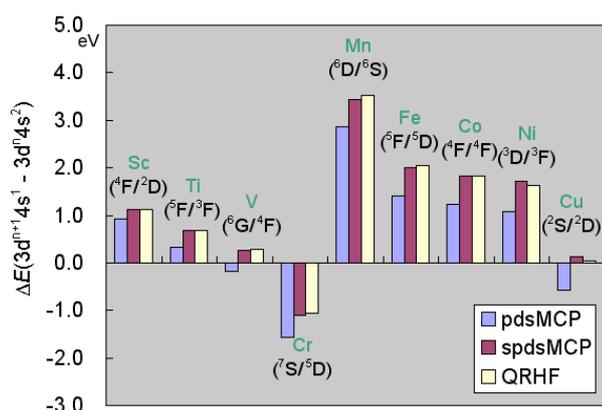


Fig. 1. Relative energies of  $3d^{n+1}4s^1$  to  $3d^n4s^2$  states

In this study, we applied the *spdsMCP*s to atomic and molecular calculations. Atomic applications related to the calculations of the ionization potentials of atoms at correlated levels are performed and compared with all-electron (AE) calculations in section 2, while the molecular applications are discussed in comparison with AE calculations in section 3. All calculations of the atomic and molecular applications were performed using the program packages, ATOMCI [6] and MOLCAS6 [7], respectively.

## 2 Atomic Applications

The quality of the present *spdsMCP* sets was examined through the correlated calculations of the relative energies of the  $3d^{n+1}4s^1$  state with respect to the  $3d^n4s^2$  state for Sc, Mn, and Cu atoms.

We performed the first restricted Hartree-Fock (RHF) calculations followed by a configuration interaction single and double (CISD) and its Davidson correction (+Q), in order to include the electron correlation effects among the 3s, 3p, 3d, and 4s electrons. The correlating functions  $[2p2f1g]$  from Ref.[8] were utilized with our valence orbitals in the *spdsMCP* sets ( $6s4p5d$ ), which were decontracted to (33111/31/311). One more diffuse *d*-type GTF was augmented (0.0376626 for Sc, 0.0761019 for Mn, and 0.0969874 for Cu). Thus, the resulting basis set was  $[5s4p4d2f1g]$ . A smaller set  $[4s3p4d1f]$  with correlating functions  $[1p1f]$  [8], contraction (4411/31/311), and diffuse *d*-function, was also examined. For comparison, we performed

all-electron (AE) calculations with very large basis sets that were formed from Huzinaga's well-tempered sets [9],  $[26s17p13d]$  for Sc and Mn, and  $[26s17p14d]$  for Cu, augmented by *p*-type and *d*-type diffuse functions with the same exponents of *s*-type diffuse functions. The *f*-type and *g*-type GTFs having the same exponents as the *d*-type GTFs were also considered. Thus, the uncontracted GTFs in the AE calculations were  $[26s20p15d15f15g]$  for Sc and Mn, and  $[26s21p16d16f16g]$  for Cu. Using these basis functions we performed CISD calculations for each atom, followed by CISD calculations with a  $[7s5p4d2f1g]$  basis set composed of occupied  $[4s2p1d]$  Hartree-Fock orbitals and correlating  $[3s3p3d2f1g]$  atomic natural orbitals (ANO) for the sake of comparison. The AE  $[7s5p4d2f1g]$  basis set has the same number of correlating orbitals as the *MCP*/ $[5s4p4d2f1g]$  basis set. A small AE  $[6s4p4d1f]$  basis set with the occupied orbitals and correlating  $[2s2p3d1f]$  orbitals was also used for the comparison with the *MCP*/ $[4s3p4d1f]$  basis set. The relativistic effects were taken into account in the AE calculations through the third-order Douglas-Kroll (DK3) approximation [10].

The resulting relative energies are listed in Table 1 together with the observed values (for the sake of saving space we give only the results of Cu). Correlation effects on the relative energies are also given in parentheses in the last column. The *spdsMCP* calculations reasonably well reproduce the relative energies given by the AE calculations with the same size of the ANO sets. The HF relative energies given in AE almost exactly coincide with those achieved by the QRHF. The deviations of HF relative energies by *spdsMCP* from those by AE are somewhat larger than the deviations of *spdsMCP* HF from QRHF shown in Table 1. This deterioration of HF energies in *spdsMCP* is caused by the contraction of the basis sets. It is notable that the correlation effects on the relative energies in *MCP* calculations are the almost the same as those in AE calculations: the differences between the correlation effects by *MCP*  $[5s4p4d2f1g]$  and AE  $[7s5p4d2f1g]$  calculations are within 0.1 eV and those by *MCP*  $[4s3p4d1f]$  and AE  $[6s4p4d1f]$  are within 0.13 eV.

Table 1. Energy of the lowest  $LS$  state with  $3d^{n+1}4s^1$  relative to that with  $3d^n4s^2$  for Cu at the HF and correlated calculations.

Method/ Basis set	Calculation Level	Relative energy (eV) <sup>a)</sup>
spdsMCP/		
[5s4p4d2f1g]	HF	-0.060
	CISD	-1.301 (-1.241)
	CISD+Q	-1.348 (-1.288)
[4s3p4d1f]	HF	-0.104
	CISD	-1.253 (-1.149)
	CISD+Q	-1.273 (-1.169)
AE/		
[7s5p4d2f1g]	HF	0.059
	CISD	-1.161 (-1.220)
	CISD+Q	-1.180 (-1.239)
[6s4p4d1f]	CISD	-1.161 (-1.220)
	CISD+Q	-1.166 (-1.225)
Exptl. <sup>b)</sup>		-1.490

a) Values in parentheses are correlation effects on the relative energy.

b) J.E. Sansonetti, W.C. Martin, S.L. Young, Handbook of Basic Atomic Spectroscopic Data, available at <http://physics.nist.gov/Handbook>.

### 3 Molecular Applications

The present *spdsMCPs* have also been applied in the calculations of molecular spectroscopic constants in the ground state of CuH and Cu<sub>2</sub> molecules. The basis sets used for Cu were [4s3p4d1f] and [5s4p4d2f1g], and the basis set of hydrogen was a triple-zeta type [3s2p1d] from Ref.[8]. The computational methods employed here were MP2 and CCSD(T). We also performed 3-states averaged CASSCF calculations with 12 electrons in 7 orbitals, which were followed by multi-reference singly and doubly excited configuration interaction (MRCI) calculations. In the correlated calculations, the Cu 3d and 4s and H 1s (twelve and twenty two electrons for CuH and Cu<sub>2</sub>, respectively) electrons were correlated for both basis sets, while the Cu 3s and 3p electrons were also correlated only for the largest set.

Results of the spectroscopic constants for the ground state of CuH and Cu<sub>2</sub> are listed in Table 2 and Table 3, respectively, together with the corresponding experimental values. For CuH,

Table 2. Spectroscopic constants of the ground state  $X^1\Sigma^+$  of CuH.

Calculation level	Spectroscopic constants		
	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ <sup>c)</sup> (eV)
MCP/[4s3p4d1f]			
CASSCF	1.520	1798.7	1.230
MRCI <sup>a)</sup>	1.466	1746.7	2.428
MP2 <sup>a)</sup>	1.451	1972.3	2.560
CCSD(T) <sup>a)</sup>	1.482	1836.4	2.556
MCP/[5s4p4d2f1g]			
CASSCF	1.520	1810.7	1.232
MRCI <sup>a)</sup>	1.465	1768.6	2.424
MP2 <sup>a)</sup>	1.443	2014.7	2.655
CCSD(T) <sup>a)</sup>	1.473	1877.6	2.741
MRCI <sup>b)</sup>	1.453	1794.8	2.465
MP2 <sup>b)</sup>	1.418	1922.0	2.736
CCSD(T) <sup>b)</sup>	1.457	1766.7	2.769
AE <sup>c)</sup>			
CCSD(T) <sup>a)</sup>	1.490	1839.8	2.55
Exptl. <sup>d)</sup>			
	1.463	1941.3	2.85

a) Cu 3d and 4s and H 1s electrons were correlated.

b) Cu 3s and 3p electrons were correlated, as well the Cu 3d and 4s and H 1s electrons.

c) Ref. [12].

d) Ref. [11].

e) Using a contracted basis set from Ref. [8].

CASSCF calculations with the [4s3p4d1f] basis set gave somewhat longer equilibrium distance,  $R_e$ , and too much smaller binding energy,  $D_e$ . These results were significantly improved by considering electron correlations within the twelve (Cu 3d and 4s and H 1s) electrons in all of MRCI, MP2, and CCSD(T). It is notable that MCP CCSD(T) calculations with [4s3p4d1f] give almost the same spectroscopic constants as all-electron CCSD(T) calculations with [8s6p4d1f], where twelve electrons were also correlated [37]. Both expansion of the basis set and inclusion of the correlation of Cu 3s and 3p electrons bring about little change to the calculated spectroscopic constants. The most striking change is 0.19 eV in  $D_e$ , which is brought about by basis set expansion in CCSD(T) calculation.

Table 3. Spectroscopic constants of the ground states  $X^1\Sigma_g^+$  of  $\text{Cu}_2$ 

Calculation level	Spectroscopic constants		
	$R_e$ (Å)	$\omega_e$ ( $\text{cm}^{-1}$ )	$D_e$ (eV) <sup>c)</sup>
MCP/[4s3p4d1f]			
MP2 <sup>a)</sup>	2.279	265.3	1.513
CCSD(T) <sup>a)</sup>	2.307	243.0	1.536
MCP/[5s4p4d2f1g]			
MP2 <sup>a)</sup>	2.226	279.6	1.852
CCSD(T) <sup>a)</sup>	2.249	259.7	1.830
MP2 <sup>b)</sup>	2.205	295.3	2.012
CCSD(T) <sup>b)</sup>	2.229	272.6	1.930
AE/[5s3p3d1f] <sup>c)</sup>			
CCSD(T) <sup>a)</sup>	2.278	246.8	1.576
Exptl. <sup>d)</sup>	2.220	264.6	2.05

<sup>a)</sup> Cu 3d and 4s and H 1s electrons were correlated.

<sup>b)</sup> Cu 3s and 3p electrons were correlated, as well as the Cu 3d and 4s and H 1s electrons.

<sup>c)</sup> Using a contracted basis set from Ref. [8].

<sup>d)</sup> Ref. [11].

For  $\text{Cu}_2$ , on the other hand, both expansion of the basis set and inclusion of the correlation of Cu 3s and 3p electrons bring about more significant change to the calculated spectroscopic constants. The former improves  $R_e$  by 0.05 ~ 0.06 Å,  $\omega_e$  by 15 ~ 17  $\text{cm}^{-1}$ , and  $D_e$  by 0.3 ~ 0.4 eV. The latter additionally improves  $R_e$  by 0.02 Å,  $\omega_e$  by 13 ~ 14  $\text{cm}^{-1}$ , and  $D_e$  by 0.1 ~ 0.2 eV. As in CuH, MCP CCSD(T) calculations with the [4s3p4d1f] set yield almost the same spectroscopic constants as all electron CCSD(T) calculations with the [5s3p3d1f] set from Ref.[8], indicating that the present MCP set provides sufficiently high performance for description of electronic structures in highly correlated calculations.

The excited state  $A^1\Sigma^+$  of CuH was also studied at the 3-states averaged CASSCF and MRCI calculations. Calculated spectroscopic are listed in Table 4. The CASSCF calculation gave the excitation energy,  $T_e$ , of only a half of the observed value, but inclusion of electron correlation through MRCI improved the  $T_e$  enormously. The spectroscopic constants given by

MRCI with [5s4p4d2f1g] including correlation of Cu 3s and 3p electrons agree well with observed values, again demonstrating the superior capabilities of the present *spds*MCP.

Table 4. Spectroscopic constants of an excited state  $A^1\Sigma^+$  of CuH

Calculation level	Spectroscopic constants		
	$R_e$ (Å)	$\omega_e$ ( $\text{cm}^{-1}$ )	$T_e$ (eV)
[4s3p4d1f]			
CASSCF	1.652	1585.8	1.521
MRCI <sup>a)</sup>	1.623	1548.4	3.006
[5s4p4d2f1g]			
CASSCF	1.645	1600.0	1.555
MRCI <sup>a)</sup>	1.622	1569.8	3.001
MRCI <sup>b)</sup>	1.607	1654.5	2.858
Exptl. <sup>c)</sup>	1.572	1698.4	2.905

<sup>a)</sup> Cu 3d and 4s and H 1s electrons were correlated.

<sup>b)</sup> Cu 3s and 3p electrons were correlated, as well as Cu 3d and 4s and H 1s electrons.

<sup>c)</sup> Ref. [11].

## 4 Conclusions

We examined newly developed model core potentials, *spds*MCPs, for the first row transition-metal atoms from Sc to Zn, in which the (n-1) s and (n-1) p electrons are treated explicitly in addition to the (n-1) d and ns electrons. The *spds*MCP basis sets were tested in the calculation of the energy differences between the  $3d^n4s^2$  and  $3d^{(n-1)}4s^1$  states for Sc, Mn, and Cu atoms and spectroscopic constants of the ground and excited states of the CuH and  $\text{Cu}_2$  molecules. It has been shown that the newly developed MCP basis sets describe well these physical properties. The MCP sets are available in the homepage of Ref.[8].

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