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Theoretical study of low-lying electronic states of Mn_2 using a newly developed relativistic model core potential

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ABSTRACT

We investigated the electronic structure of low-lying electronic states of Mn_2 using a newly developed relativistic model core potential (spdsMCP). Calculations were performed at complete active space self-consistent field (CASSCF) and second-order multiconfiguration quasidegenerate perturbation theory (MCQDPT2) levels. The MCQDPT2 calculations reveal that the $1\Sigma g^+$ state is the ground state. Calculated spectroscopic constants are very similar to the results of recent all-electron calculations and experimental values, indicating that the spdsMCP works well for Mn_2, which requires a highly correlated calculation. The wave functions of low-lying states are also analyzed at the CASSCF level.

1. Introduction

Recent progress in quantum chemical techniques has provided solutions for many chemical problems, even those involving complicated biological systems. However, to make calculations for such large systems including heavy elements is still difficult for two reasons: electron correlation and relativistic effects. In usual all-electron (AE) theory, one must treat many electrons including inactive core electrons in heavy elements. One must also consider relativistic effects at the same time, resulting in high-cost calculations. To overcome these problems, it is necessary to separate inactive core electrons from the explicitly treated electrons without degradation of accuracy. The nodeless pseudo-orbitals in effective core potential (ECP) approaches may yield too large exchange integrals, resulting in exaggerated correlation energies and too large singlet–triplet splitting [1,2]. Among numerous ECP methods, the model core potential (MCP) method is unique because it enables natural production of valence orbitals with nodal structure. The MCP method has been confirmed, after applications for a variety of molecular calculations, the method can yield consistently reliable results for molecular calculations [3–15]. We have developed new relativistic model core potentials, spdsMCPs (MCPs with 3s, 3p, 3d and 4s GTF basis sets), for the first-row transition-metal atoms [16]. Using relativistic spdsMCPs, we can treat only valence electrons and solve molecules with heavy elements with low-cost calculations. In a previous Letter [16], we demonstrated that the present spdsMCP basis sets have excellent performance in describing the electronic structures of atoms and molecules, bringing about accurate excitation energies for atoms and reliable spectroscopic constants for some molecules.

There have been many experimental [17–20] and theoretical [21–34] studies for the electronic structure of the manganese dimer. The manganese dimer has been found by Kirkwood et al. to have a singlet ground state from resonance Raman spectra of rare-gas matrices [17,18], which determined also the bond length to be 3.4 Å. An electron spin resonance (ESR) experiment [19] supported the singlet ground state. Kant et al. [20] found that the dissociation energy is ~0.1 eV, indicating Mn_2 is a van der Waals molecule.

A number of studies [21–31] based on density functional theory (DFT) calculations were conducted for Mn_2 and provided different conclusions. For example, Nayak and Jena [23] found bond distances of 1.62, 2.50, and 3.55 Å using functionals of LSDA, BPW91, and B3LYP, respectively. Yanagisawa et al. [27] concluded that Mn_2 is unbound and Gutsev and Bauschlicher [29] found $^{11}\Pi_u$ is the ground state. There have also been many ab initio calculations other than DFT. Single-referenced MP2 calculations [27] and complete active space self-consistent-field (CASSCF) calculations [32] predicted that Mn_2 is unbound. It is therefore implied that both static and dynamic electron correlations are indispensable for describing the electronic structure of Mn_2. Wang and Chen obtained a singlet ground state with a bond length of 3.6 Å for complete active space second-order perturbation theory (CASPT2) calculations [33] using Dolg's relativistic effective core potential [35].

Recently, multi-referenced correlated calculations with a very large all-electron basis set were performed by Yamamoto et al.

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[34], and it was predicted that the ground state of Mn_2 is $^1\Sigma_g{}^+$ with a binding energy of 0.14 eV and a bond length of 3.3 Å, which agreed well with experiments. The experimental values by Kirkwood et al. [18] for the bond length, dissociation energy, and vibrational frequency are 3.4 Å, ~0.1 eV, and 68.1 cm^{-1}, respectively. As mentioned above, almost all experimental results predicted that Mn_2 is a van der Waals molecule with a weak binding energy and has the singlet ground state.

In this study, we performed a theoretical calculation for the three low-lying electronic states of Mn_2 using the newly developed spdsMCP. We performed CASSCF calculations and then second-order multiconfiguration quasidegenerate perturbation theory (MCQDPT2) calculations. Calculated results agreed reasonably well with experimental results and theoretical results given by Yamamoto et al., indicating the spdsMCPs can reasonably describe both static and dynamic correlations in transition-metal compounds as well as be used in all-electron approaches with high-quality basis sets. Computational details are explained in Section 2. Section 3 summarizes the calculated results for the low-lying states in considering relative energy and spectroscopic constants and the discussion of these results. Concluding remarks are given in Section 4.

2. Computation details

We used the spdsMCP of Mn to describe low-lying electronic states of Mn_2. In the spdsMCP, fifteen electrons in 3s, 3p, 3d and 4s orbitals were explicitly treated. 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 $3d^n$ $4s^2$ state and it was shown the spdsMCP with a large basis set [5s4p4d2f1g] gave an experimental relative energy for Mn within 0.04 eV of deviation, although all-electron calculations gave a relative energy ~0.2 eV larger than the experimental value [16]. The p, f, and g-type polarization functions of the basis set were taken from a work by Noro et al. [36]. Three basis sets were used in this study for Mn:

BS1: (4411/42/3111/2) / [4s2p4d1f],
BS2: (33111/3111/3111/31/2) / [5s4p4d2f1g],
BS3: (33111/31111/3111/211/11) / [5s4p4d3f2g].

BS1 and BS2 are the smaller and larger basis sets used in Ref. [16] and BS3 was formed from BS2 by splitting f- and g-type functions, which are composed of 3 and 2 GTFs, respectively, and by adding a diffuse p-type function with an exponent of 0.034965.

Although the molecular symmetry of Mn_2 is $D_{\infty h}$, we used an Abelian D_{2h} symmetry. We calculated three low-lying electronic states, $^1\Sigma_g^+$, $^{11}\Sigma_u^+$, and $^{11}\Pi_u$, of the molecule and solved the $^1\Sigma_g^+$, $^{11}\Sigma_u^+$, and $^{11}\Pi_u$ states as the ^1A_g and $^{11}B_{1u}$ states and an average of the $^{11}B_{2u}$ and $^{11}B_{3u}$ states of D_{2h}, respectively. CASSCF calculations with 14 electrons in 12 orbitals were performed. The 12 molecular orbitals comprising mainly the 4s and 3d atomic orbitals were chosen to construct the CASSCF wave functions. The $^1\Sigma_g^+$ CASSCF wave function is composed of 21 588 configuration state functions (CSFs), and $^{11}\Sigma_u^+$ and $^{11}\Pi_u$ CASSCF wave functions are composed of 12 and 8 CSFs, respectively. In CASSCF for the $^1\Sigma_g^+$ and $^{11}\Sigma_u^+$ states, we performed state-averaged calculations for the lowest three states in the ^1A_g and $^{11}B_{1u}$ symmetries, respectively, in order to obtain smooth potential energy curves against the change of electron configurations in the middle bond length region. After the CASSCF calculations to take the dynamic electron correlation into account, MCQDPT2 calculations [37] were carried out. In the MCQDPT2 calculations, 3s and 3p electrons were also correlated in addition to 3d and 4s electrons. We used the intruder state avoidance (ISA) method [38] with an ISA shift of 0.02. All calculations were done using the GAMESS program [39].

3. Results and discussion

3.1. Potential energy curves and spectroscopic constants

Potential energy curves of the $^1\Sigma_g^+$, $^{11}\Sigma_u^+$, and $^{11}\Pi_u$ states calculated by MCQDPT2 with BS3 are shown in Fig. 1. Among the three low-lying states, we found the lowest energy state is the $^1\Sigma_g^+$ state with $R_e = 3.13$ Å. Detail of the potential energy curves at 2.9–3.6 Å for $1\Sigma g^+$ and $^{11}\Sigma_u^+$ states is shown in Fig. 2. The energy of the $^1\Sigma_g^+$ state is lower than that of the $^{11}\Sigma_u^+$ state with $R_e = 3.47$ Å by 0.01 eV. This observation agrees well with the experimental results [20] and the AE calculations [34] by Yamamoto et al. It is to be noted that the present calculations considered the major relativistic effects but the AE calculations did not. We found that the minimum point for the $^{11}\Pi_u$ state is at $R = 2.55$ Å. The short bond

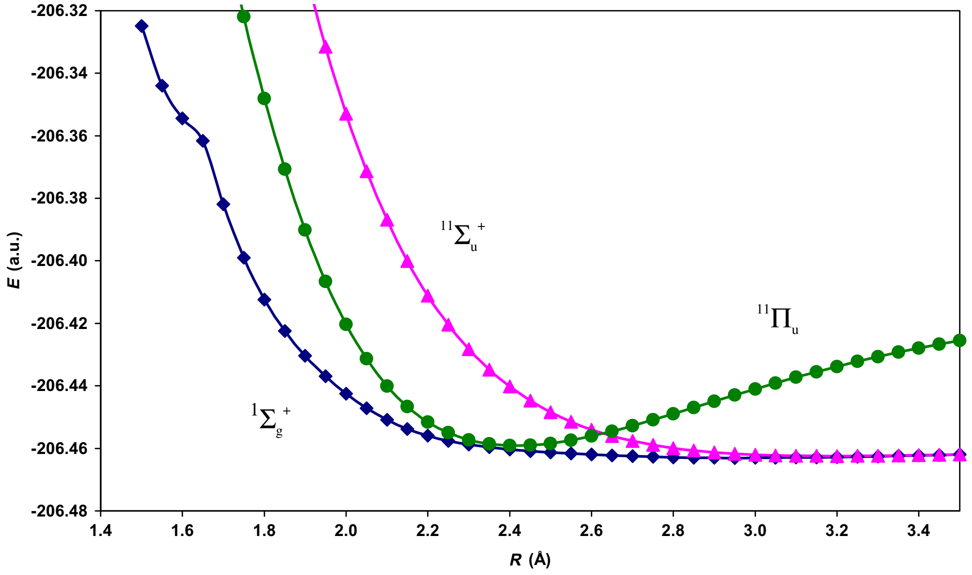

Fig. 1. Potential energy curves of low-lying states of Mn_2 given by MCQDPT2 with spdsMCP/BS3.