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Theoretical investigation of the spectroscopic constants for the ground-state diatomic species Cu_2, Ag_2, and Au_2

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ABSTRACT

Within the framework of two-component pseudo-potentials, the coupled-cluster theory with spin-orbit interaction and the equation-of-motion coupled-cluster theory with spin-orbit interaction for ionized states are employed to obtain the spectroscopic constants of the ground-state Cu_2, Ag_2, and Au_2 in this work. The spin-orbit interaction is only calculated iteratively in the post-Hartree-Fock, i.e. the coupled-cluster procedure. It is shown that the CCSD(T) approach with spin-orbit interaction is capable of providing the rather accurate equilibrium distances and harmonic frequencies. Furthermore, the equation-of-motion coupled-cluster approach with spin-orbit interaction for ionized states is able to reasonably estimate the spin-orbit contribution to the binding energy. Hence, the accurate binding energies are obtained by the scalar-relativistic CCSD(T) calculations with the correction of spin-orbit contribution. In addition, the spectroscopic constants have a weak basis set dependence for all the title species.

1. Introduction

Cu, Ag, and Au are open-shell atoms with electronic configuration being $(n\text{-}1)s^2p^6d^{10}ns^1$. Their homonuclear diatomic Cu_2, Ag_2, and Au_2 are bound by a single-covalent bond. The experimental determinations of the spectroscopic constants for them have been collected in Ref. [1]. Furthermore, the ultraviolet laser excited fluorescence spectra of the jet-cooled Cu_2 have been investigated [2]. The spectroscopic constants including the equilibrium distance, the harmonic frequency and the binding energy of the ground-state Cu_2 were re-determined. The spectroscopy of Ag_2 in a supersonic jet has also been studied [3], with the equilibrium distance re-determined. The resonant two-photon ionization spectroscopic method was used to investigate the electronic spectra of the jet-cooled Au_2 [4], and its dissociation energy was re-determined.

Alternatively, the computational investigation plays an important role in systematically studying the spectroscopic constants for the ground-state Cu_2, Ag_2, and Au_2. It is worthwhile to point out the following previous reports. Peterson and Puzzarini used the coupled-cluster theory at the CCSD(T) level based on the pseudo-potentials (PPs) with the correction of spin-orbit interaction (SOI) to determine the spectroscopic constants of the ground-state for these three dimers. The all-electron Douglas-Kroll-Hess calculations at the CCSD(T) level were also performed for comparison [5]. The four-component relativistic density functional calculations (including LDA and BP86 functionals) were reported by Wang and Liu [6]. Kullie et al. carried out the Dirac-Fock-Slater (DFS) density functional calculations by using the two-spinor minimax finite-element method (FEM) [7]. Besides, based on three models containing the Slater's X_α approximation, the non-relativistic and the relativistic local-density approximations, Kullie et al. performed the two-spinor minimax FEM calculations [8]. Zeng and Klobukowski developed the model core potentials (MCPs) for Au element, DK3-MCPs, to calculate the spectroscopic constants of Au_2 within the framework of CASSCF and CASPT2 computational protocols [9]. However, only some of the calculated values mentioned above agree well with the available experiments. Taking Au_2 as an example, the discrepancy of the equilibrium distance obtained by Wang and Liu compared to the experimental value was close to 0.03 Å, which presumably originate from the suboptimal performance of density functional theory applied to such dimers [6]. However, the discrepancies of the equilibrium distances obtained by Peterson and Puzzarini [5], and Zeng and Klobukowski [9] compared to the experimental value were both less than 0.01 Å. A high-level ab initio method is therefore capable of improving the accuracy regardless of the higher computational cost.

In the relativistic quantum chemical calculation, the electronic correlation (including dynamic and static), the scalar-relativistic (SR) effect and the SOI (including spin-same orbit and spin-other

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orbit) [10] should be considered to obtain the precise results. The calculated accuracy is simultaneously determined by the relativistic Hamiltonian, the computational protocol and the basis set. The relativistic effect can be treated with two approaches, all-electron Hamiltonian and PPs. The latter has less computational efforts in the practical calculations since the inner-core electrons are treated implicitly. Both the SR effect and the SOI can be described within the framework of two-component PPs (2c-PPs). The coupled-cluster theory at the level of CCSD(T), the gold standard in quantum chemistry, is able to capture nearly all the electronic correlation energy. In addition, the coupled-cluster theory is size-consistent and better at describing the orbital relaxation than the other quantum chemical methods due to its nature of exponential expansion. Once the relativistic Hamiltonian and the computational protocol are determined, a high-level basis set is necessary to guarantee the accuracy. In practice, the extrapolation is usually used to obtain the results in the complete basis set (CBS) limit. For more details related to the relativistic quantum chemistry, some comprehensive reviews are recommended [10–16].

The SOI operator can be simplified to a one-electron operator when the 2c-PPs are adopted. If the SOI is only calculated in the post-Hartree-Fock, the Hartree-Fock section is the same as in the non-relativistic calculation. The molecular orbitals and the two-electron integrals, which can be classified according to the irreducible representation of the molecular single point group, are both real. The computational efforts are then reduced significantly in this case. Within the framework of 2c-PPs, Wang et al. have developed the closed-shell coupled-cluster theory with SOI (SOI-CC), in which the SOI is only calculated iteratively in the coupled-cluster procedure [17,18]. Although the SOI is neglected when calculating the molecular orbitals in the SOI-CC method, it has been shown that the calculated results of E117H [17] and monohydrides of 6p-block elements [19] agree well with those obtained from the Kramer-Restricted coupled-cluster method, in which the SOI is considered in Hartree-Fock section. As for some open-shell systems, within the framework of 2c-PPs, Wang et al. have developed the equation-of-motion coupled-cluster method for ionized states (EOMIP-CC) [20] and electron attach states (EOMEA-CC) [21] with the SOI only calculated iteratively in the coupled-cluster procedure, both of which use the closed-shell state as reference, so that the spin-contamination can be avoided. Furthermore, the SOI-CC method based on 2c-PPs has been extended to the open-shell systems by Wang et al. most recently [22]. However, the computational cost is rather high since the time-reversal symmetry and the spatial symmetry are both broken.

In this work, the closed-shell SOI-CC method at the CCSD(T) level [17,18] and the SOI-EOMIP-CC method at the CCSD level [20] are combined to investigate the spectroscopic constants of the ground-state Cu_2, Ag_2 and Au_2 dimers based on the 2c-PPs and the high-level basis sets. The objective of this work is to enrich the theoretical studies. This manuscript is organized as follows. The computational details such as the 2c-PPs, the high-level basis sets augmented by diffusion functions, and the extrapolation of electronic correlation energy to the CBS limit are given in Section 2. The calculated spectroscopic constants containing the equilibrium distances, the harmonic frequencies and the binding energies are presented and discussed in Section 3. Section 4 is the conclusions of this work.

2. Computational details

The fundamental theories of the closed-shell SOI-CC and the SOI-EOMIP-CC based on the 2c-PPs have been reported in Refs. [17,20], respectively, and unnecessary to be restated here. The small core energy-consistent 2c-PPs are applied in this work, namely 2c-ECP10MDF for Cu, 2c-ECP28MDF for Ag, and 2c-ECP60MDF for Au, respectively [23]. Hence, the atomic orbitals $(n-1)s(n-1)p(n-1)dns$ are correlated. The PPs-based correlation consistent basis sets augmented by diffusion functions, aug-cc-pwCVXZ-PP (X = D, T, Q, 5), are used for Cu, Ag, and Au [5].

As for the removal of basis set superposition error (BSSE), Yang and Wang used a similar theoretical method to study the spectroscopic constants of the ground-state Ca_2, Sr_2, and Ba_2 with counterpoise correction (CP) [24]. The investigations showed that the CP correction in the finite basis sets always increases the equilibrium distance and decreases the binding energy but hardly affects when the basis set is extrapolated towards the CBS limit as expected. In the case of finite basis sets, the CP corrected results often deviates further than the uncorrected ones compared to the results in the CBS limit. A Similar conclusion was also drawn by Dunning [25] and Alvarez-Idaboy and Galano [26]. It is suggested that the best way of removing BSSE is increasing the basis sets rather than performing the CP corrections. Thus, only the uncorrected results are calculated in this work.

All of the ab initio calculations in this work are performed with CFOUR program package [27] (a local version of Professor Fan Wang's group). The computational protocols of the restricted SR-CCSD and SR-CCSD(T), and the closed-shell SOI-CCSD(T) based on the 2c-PPs are used to calculate the nine single-point energies around equilibrium distances of the ground-state closed-shell Cu_2, Ag_2, and Au_2 dimers. The interval between two adjacent point is 0.03 Å. The energies of the separated open-shell Cu, Ag, and Au atoms are needed to calculate the binding energy of the ground-state Cu_2, Ag_2, and Au_2. The unrestricted SR-CCSD and SR-CCSD(T) approaches are used to calculate the atomic energies at the SR level. Since the open-shell SOI-CC approach [22] is rather expensive as mentioned above, the approach of the closed-shell SOI-CCSD(T) combined with the SOI-EOMIP-CCSD is used to calculate the atomic energies at the spin-orbit level. Here, the SOI-CCSD(T) is used to calculate the energies of the closed-shell Cu^-, Ag^-, and Au^- anions, while the SOI-EOMIP-CCSD is used to calculate the ionization energy of Cu^-, Ag^-, and Au^- anion. Therefore, the energies of the open-shell Cu, Ag, and Au atoms at the spin-orbit level can be obtained as

$$E^{XZ}(Cu/Ag/Au) = E^{XZ}(Cu^-/Ag^-/Au^-) + IP^{XZ}(Cu^-/Ag^-/Au^-). \quad (1)$$

In Eq. (1), XZ represents the aug-cc-pwCVXZ-PP basis sets as mentioned above. Eq. (1) can also be applied into the SR case and the spin-orbit contributions to the binding energies are therefore estimated.

In order to obtain the spectroscopic constants in the CBS limit, the electronic correlation energies of the nine single-points around the equilibrium distances and the separated open-shell atoms are all extrapolated according to the following formula [24]

$$\Delta E_{corr}^{CBS} = \Delta E_{corr}^{X} - \frac{c}{X^3}. \quad (2)$$

In Eq. (2), X denotes the cardinal number which is the same as X in the aug-cc-pwCVXZ-PP basis sets. ΔE_{corr}^{CBS} and ΔE_{corr}^{X} are the electronic correlation energies in the CBS limit and the finite basis sets, respectively. ΔE_{corr}^{X} is directly obtained by the quantum chemical calculations. ΔE_{corr}^{CBS} (and parameter c) are indirectly obtained by solving the equation sets. In addition, the Hartree-Fock limit is taken from the aug-cc-pwCV5Z-PP basis set. Hence, the coupled-cluster energy in the CBS limit is the sum of the Hartree-Fock limit and ΔE_{corr}^{CBS}.

Finally, by fitting the coupled-cluster energies of the nine single-point against the fifth-order polynomial, the equilibrium distances and the harmonic frequencies of each species can be determined. The corresponding fitting formulas are available in Ref. [24] and references therein. Moreover, the binding energy is