Research paper

Coupled cluster study of spectroscopic constants of ground states of heavy rare gas dimers with spin–orbit interaction

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ABSTRACT

The CCSD(T) approach based on two-component relativistic effective core potential with spin–orbit interaction just included in coupled cluster iteration is adopted to study the spectroscopic constants of ground states of Kr_2, Xe_2 and Rn_2 dimers. The spectroscopic constants have significant basis set dependence. Extrapolation to the complete basis set limit provides the most accurate values. The spin–orbit interaction hardly affects the spectroscopic constants of Kr_2 and Xe_2. However, the equilibrium bond length is shortened about 0.013 Å and the dissociation energy is augmented about $18\,cm^{-1}$ by the spin–orbit interaction for Rn_2 in the complete basis set limit.

1. Introduction

The electronic configuration of heavy rare gas (Rg) atom is $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^2np^6$. The dimers Rg_2 are weakly bonded diatomic molecules with electronic configuration $(\sigma_g)^2(\pi_u)^4(\pi_g)^4(\sigma_u)^2$, using non-relativistic notation. The spectroscopy of Rg_2 (and Rg_3) have been reported in theoretical [1,2] and experimental [3] researches. Theoretically, the highly precise theoretical approaches are necessary to obtain accurate spectroscopic constants of Rg_2.

It is well known that density functional theory (DFT) is a popular and low-cost computational protocol [4]. Unfortunately, the advantage of DFT is describing the molecules containing covalent bond and light element [5] although the van der Waals interaction based on Kohn Sham theory has been considered in some previous papers to improve the performance of DFT [5–8]. Thus DFT cannot provide the benchmark results.

Another very interesting theoretical method, namely range separated DFT, pioneered by Savin (see Ref. [9] and references therein) can be adopted to study the spectroscopy of Rg_2. In this approach, wave function theory (WFT) is employed to treat the long range region (lrWFT) and DFT is used to treat the short range region (srDFT) [10–15]. In one recent paper, [16] based on the eXact 2-Component (X2C) molecular-mean field Hamiltonian, the spec-

troscopic constants of Xe_2, Rn_2 (and $(E118)_2$) obtained from lrCCSD(T)-srLDA approach by Saue et al. are close to their own benchmark results obtained from CCSD(T) approach. Although the lrWFT-srDFT approach can in some extent remedy the deficiency of DFT in the long range region, it is still inappropriate to be used to provide the benchmark results.

The coupled cluster theory at the CCSD(T) level is the 'gold standard' of quantum chemistry for the electronic ground state with a dominant single reference character. Hobza et al. has indicated that CCSD(T) approach combined with extrapolation to the complete basis set (CBS) limit can provide chemical accuracy of 1 kcal/mol for such systems [17] in spite of its high-cost. Furthermore, both scalar relativistic effect (SRE) and spin–orbit interaction (SOI) [18] are important to obtain accurate spectroscopic constants of heavier Rg_2. An efficient method to treat SRE and SOI is adopting the two-component relativistic effective core potential (2c-RECP) [19]. In this approach, the SOI operator is taken from the 2c-RECP and simplified to a one-electron operator. Besides, it has been indicated that considering SOI only in the post Hartree Fock (HF) iteration is an efficient and highly precise treatment for SOI based on 2c-RECP [19]. Firstly, the HF section and the integral transformation is the same as in the nonrelativistic or scalar relativistic calculations. Secondly, both the molecular orbitals (MOs) and the two-electron integrals in the MO representation are real and can be classified according to the irreducible representation of the molecular single point group. The above two issues have been explored and the coupled cluster theory with SOI just included in the coupled cluster iteration (SOI-CC) based on 2c-RECP has been achieved [19]. Moreover, Lee et al. confirmed that such a

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two-step procedure in which SOI is included only in the post HF procedure works better with coupled cluster than configuration interaction since the former is better at describing the orbital relaxation [20]. The authors think that the SOI-CC approach based on 2c-RECP should be widely utilized since its high efficiency and precision. Thus the SOI-CC approach at the CCSD(T) level (SOI-CCSD(T)) based on 2c-RECP is adopted to study the spectroscopic constants of ground states of Kr_2, Xe_2 and Rn_2 in present work.

To authors' best knowledge, the spectroscopic constants of ground state of Rn_2 have no experimental reports yet and only a limited number of theoretical studies have been reported [16,21–24]. Runeberg and Pyykkö have employed CCSD(T) method based on relativistic large core pseudopotentials to study the spectroscopic constants of ground states of Xe_2 and Rn_2 [21]. A similar computational protocol was employed by Nash to obtain the corresponding values for Rn_2 (and $(E118)_2$) [22]. The spectroscopic constants of ground states of He_2-$(E118)_2$ are reported by Kullie and Saue using lrMP2-srDFT approach based on the four-component relativistic Dirac-Coulomb (DC) Hamiltonian [24]. Most recently, as mentioned above, Saue et al. performed the CCSD(T) calculations based on the X2C molecular-mean field Hamiltonian to provide the benchmark results of spectroscopic constants of ground states of Xe_2, Rn_2 (and $(E118)_2$) [16].

It is worthwhile to mention that, for dissociation energy of Rn_2, Runeberg and Pyykkö's value is 222.6 cm^{-1} [21], Nash's value is 129.1 cm^{-1} [22], and Kullie and Saue's value is 323.9 cm^{-1} [24]. Nevertheless, the recent benchmark results by Saue et al. is 282.80/281.41 cm^{-1} [16]. Thus the motivation of present work is to confirm that the SOI-CCSD(T) approach based on 2c-RECP developed by Wang et al. [19] can provide reliable dissociation energy (and equilibrium bond length, harmonic frequency) of ground state of Rn_2 (and Kr_2, Xe_2) compared to the benchmark results [16] (and the available experimental values).

This paper is organized as follows: essential computational details such as the treatment of SOI and extrapolation to the CBS limit of electronic correlation energy are given in Section 2. In Section 3, we present and discuss our calculated values of spectroscopic constants including equilibrium bond length, harmonic frequency and dissociation energy of ground states of Kr_2, Xe_2 and Rn_2 obtained from both SOI-CCSD(T) and CCSD(T) approaches based on 2c-RECP, compared to the available experimental values and other group's theoretical values. The conclusion of present work is given in Section 4.

2. Computational details

The theory of SOI-CCSD(T) approach based on 2c-RECP employed in present work is given in Ref. [19] and references therein, thus it will not be repeated here. However, it is worthwhile to stress the treatment of SOI. In the pseudopotential potential (PP) approximation, the SOI part V_{PP}^{SOI} which has the form of one-electron operator is written as [25,26]

$$V_{PP}^{SOI}(r_i) = \vec{s_i} \cdot \sum_{l=0}^{l_{max}} \left(l + \frac{1}{2}\right)^{-1} \left[V_{PP}^{l,l+1/2}(r_i)\right.$$
$$\left. - V_{PP}^{l,l-1/2}(r_i)\right] \sum_{m'=-l}^{l}\sum_{m=-l}^{l} |lm\rangle_i \langle lm|_i \vec{l_i} |lm'\rangle_i \langle lm'|_i. \quad (1)$$

In Eq. (1), $\vec{s_i}$ and $\vec{l_i}$ are, respectively, spin and orbit angular momentum operator; l and m are, respectively, angular and magnetic quantum number; $V_{PP}^{l,l\pm1/2}(r_i)$ is Gaussian-type function with pseudopotential parameters. V_{PP}^{SOI} is added to the scalar Fock operator (F^{scl}) to obtain the Fock operator with SOI (F^{SOI}), i.e.

$$F^{SOI} = F^{scl} + V_{PP}^{SOI}, \quad (2)$$

to perform the post HF calculation (i.e. coupled cluster iteration in present work). Thus the computational cost is reduced significantly compared to the all-electron relativistic calculations.

The small core energy-consistent 2c-RECPs, namely ECP10MDF for Kr, ECP28MDF for Xe and ECP60MDF for Rn [27], as well as the matching basis sets, namely cc-pwCVXZ-PP(n = Q, 5) [28], are adopted in the coupled cluster calculations. The atomic orbitals $(n-1)s(n-1)p(n-1)dnsnp$ are correlated. As described in Ref. [27], the atomic pseudopotential provided by Peterson et al. contains the two-component extensions (describing the outer core and valence SOI). Furthermore, a perturbative treatment of the Breit interaction was included in the numerical all-electron multi-configuration Dirac HF average-level calculations to fit the pseudopotential parameters. Thus both spin-same and spin-other orbit interactions are contained in the adopted 2c-RECPs. Both CCSD(T) and SOI-CCSD(T) approaches [19,29] based on 2c-RECPs are adopted to assess the magnitude of SOI on equilibrium bond length, harmonic frequency and dissociation energy of ground states of Kr_2, Xe_2 and Rn_2.

With respect to the basis set superposition error (BSSE) [30], Yang and Wang [31] investigated the spectroscopic constants of ground states of Ca_2, Sr_2 and Ba_2 dimers using CCSD(T) approach based on 2c-RECP with counterpoise (CP) correction [32]. Their numerical results showed that the CP correction in the finite basis sets always increases the equilibrium bond length and decreases the dissociation energy but hardly affects the spectroscopic constants in the CBS limit as expected [31]. The CP corrected results in the finite basis sets often deviates even further than the uncorrected ones [31] compared to the results obtained in the CBS limit. Dunning [33] and Alvarez-Idaboy and Galano [34] have also drawn the similar conclusion and the best way of eliminating BSSE is increasing the basis set but not performing the CP corrections. Thus only the uncorrected numerical results are calculated in present work.

All of the coupled cluster calculations are performed with the CFOUR program package [35]. Both CCSD(T) and SOI-CCSD(T) approaches based on 2c-RECP [19,29] are adopted to calculate the electronic energies of ground states of Rg atoms as well as nine single point electronic energies of around equilibrium positions of ground states of Kr_2, Xe_2 and Rn_2. The interval of the nine single points is 0.05 Å. All of the electronic correlation energies of these nine single points and the Rg atoms obtained from coupled-cluster calculations need to be extrapolated to the CBS limit to obtain the values of spectroscopic constants in the CBS limit. The related extrapolated formula is written as [31]

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

In Eq. (3), X is the same as the cardinal number X in the basis set and the value is 4 and 5 in present work; ΔE_{corr}^X and ΔE_{corr}^{CBS} represents the calculated electronic correlation energies in the finite basis set cc-pwCVXZ-PP and CBS limit, respectively; the values of ΔE_{corr}^{CBS} and the constant c are obtained through solving equation sets in the Mathematica software package. The HF limit is taken from the cc-pwCV5Z-PP basis set. Then the coupled cluster energy in the CBS limit is the sum of the energy of Hartree Fock limit and ΔE_{corr}^{CBS}.

Finally, equilibrium bond lengths and harmonic frequencies are obtained by fitting the coupled cluster energies of the nine single points with the 5-order polynomial fitting technique. The coupled cluster energies of Rg atoms are used to obtain the dissociation energies. The related fitting formula can be found in Ref. [31] and references therein.