Correlations beyond CCSD(T) for accurate study of Hg₂ and Cp₂

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Abstract

Contributions from high-order (non-perturbative triple and quadruple) cluster amplitudes to the dissociation energies, equilibrium distances, and vibrational constants for the ground states of van der Waals dimers Hg₂ and Cp₂ are evaluated. The incorporation of these contributions into the results of large-scale CCSD(T) calculations leads to non-negligible corrections of the computed molecular constants for Hg₂ (6% for the dissociation energy), and enables one to attain perfect agreement with the experimental values.
I. INTRODUCTION

The Hg dimer was the subject of a series of ab initio calculations (see Table I). It is well understood from these studies that only highly-correlated relativistic calculations can give reliable results for such systems as the Hg$_2$ molecule in its ground state. The widely used DFT method with the popular B88P86 and PW91 exchange-correlation functionals cannot ensure an acceptable accuracy of the description of the Hg–Hg bonding. In turn, within the wavefunction-based approaches, the basis set superposition error (BSSE) can seriously deteriorate the results for such weakly bound molecules even for rather extensive basis sets. To suppress the BSSE, large basis sets and counterpoise-like corrections should be employed. Fully relativistic calculations appear to be computationally too demanding for highly-correlated treatments and can be performed only with unacceptable restrictions for the basis sets. The calculated spectroscopic properties of Hg$_2$ reported in the papers are in a pretty good agreement with the experimental data. In Ref., the scalar relativistic coupled cluster method with single, double and non-iterative triple cluster amplitudes (CCSD(T)) and the (9s,8p,7d,3f)/[7s,6p,4d,3f] basis set were used to correlate the outermost 24 electrons (5d and 6s shells). Then the effects of correlations with the 5s and 5p shells and the basis set extension to higher angular momentum functions were estimated at the MP2 level of theory. Spin-orbit interactions were neglected at that stage. In Ref., 24-electron CCSD(T) calculations with an uncontracted (9s,9p,8d,4f,2g) basis set were performed. The correlation contributions from the 5s and 5p shells were estimated at the MP4 level of theory. Then the spin-orbit contribution was taken into account using MP2 calculations. CCSD(T) calculations in Ref. with the larger basis set (11s,10p,9d,4f,3g,2h) correlating 40 electrons (5s, 5p, 5d, and 6s shells) and with the spin-orbit correction taken from Ref. are in a worse agreement with the experimental data. As has been noted in Ref., the good agreement of the calculated spectroscopic properties in papers with the experimental data is a result of the fortunate cancellation of errors. Our CCSD(T) calculations with the generalized correlation (14s,12p,9d,5f,3g,2h)/[10s,9p,7d,5f,3g,2h] basis set and spin-orbit contributions from the density-functional theory give results comparable with those in the work. We believe that the visible difference between our results and those obtained in Ref. can be attributed to different relativistic effective core potential models used in the calculations.

Recently long-lived isotopes of the heavier homologue of mercury, Copernicium (Cn or
element 112), have been synthesized (see 8 and reference therein). At present, the experiments on Cn are limited only by the thermochromatography adsorption on the gold surface 8; several quantum chemical calculations on its compounds and, in particular, Cn$_2$ were performed to investigate the chemical properties of the new element (including inertness and van der Waals radius). The available theoretical data for the Cn dimer (see Table III) are rather contradictory. The difficulties in the calculations on Cn$_2$ are similar to those for Hg$_2$, except for the dramatic increase of the relativistic effects (which, in turn, also affects the electron correlations because of the contraction of the $s$ and $p_{1/2}$ shells). Since there are no experimental data on the spectroscopic constants of Cn$_2$, it was important to use the valid method tested in calculations on the Hg$_2$ dimer.

The aim of the present work was to study the role of non-perturbative triple as well as of quadruple cluster amplitudes in the bonding of van der Waals dimers Hg$_2$ and Cn$_2$ for which accurate calculations of spectroscopic constants are required. (By the effect of non-perturbative (or iterative) triples is meant the difference between CCSDT and CCSD(T), whereas by that of quadruples is meant the difference between CCSDTQ and CCSDT.) The letter is of interest, first of all, from the viewpoint of extracting the van der Waals parameters (vdW radius etc.) of the Cn atom.

II. CALCULATIONS AND DISCUSSION

The contribution from the iteration of triple and quadruple cluster amplitudes for the four valence electrons in Hg$_2$ and Cn$_2$ was evaluated as the difference between the total energies obtained in four-electron 4e-FCI and 4e-CCSD(T) calculations 9. The account of similar contributions from the outer-core electrons is extremely expensive, but they are not expected to be noticeable and are not considered here. Scalar relativistic calculations were performed within the generalized relativistic effective core potential (GRECP) model 10–13 using the MOLCAS 14 code. Generalized correlation bases 15,16 comprising the $(14s, 12p, 9d, 3f)/[7s, 7p, 3d, 2f]$ and $(16s, 21p, 16d, 12f, 14g)/[4s, 6p, 3d, 2f, 1g]$ sets were used for Hg$_2$ and Cn$_2$, respectively. These basis sets were chosen as a compromise between the accuracy and computational efforts in FCI calculations. The accuracy was checked by calculating the contribution from non-iterative triple cluster amplitudes for the given and rather large $(14s, 12p, 9d, 5f, 3g, 2h)/[10s, 9p, 7d, 5f, 3g, 2h]$ and
(16s, 21p, 16d, 12f, 14g, 1h)/[11s, 10p, 8d, 5f, 4g, 1h] basis sets used in Ref. 7. These calculations were performed at the point \( R = 7.0 \) a.u. for Hg\(_2\) and \( R = 6.5 \) a.u. for Cn\(_2\) which are close to the equilibrium geometry.

The corresponding contributions from the perturbative (non-iterative) triple cluster amplitudes are \(-90 \text{ cm}^{-1}\) (large basis set) and \(-84 \text{ cm}^{-1}\) (small basis set) for Hg\(_2\), whereas they are \(-51 \text{ cm}^{-1}\) (large basis set) and \(-43 \text{ cm}^{-1}\) (small basis set) for Cn\(_2\). Then the contributions from non-perturbed triples and quadruples for both dimers were evaluated for internuclear distances from 5 to 20 a.u. at a step of 1 a.u. and added to the best potential energy curves obtained in Ref. 7 by the CCSD(T) method with large basis sets taking into account the counterpoise and spin-orbit corrections. The spectroscopic constants derived from these curves are collected in Table I and Table II. One can see in Table II that the agreement with the experimental data is significantly improved. Table III presents the energy differences \( E(7.0 \text{ a.u.}) - E(\infty) \) for Hg\(_2\) and \( E(6.5 \text{ a.u.}) - E(\infty) \) for Cn\(_2\) (the chosen finite distances are close to equilibrium values of the best theoretical level) calculated at the SCF, 4e-CCSD, 4e-CCSD(T), 4e-CCSDT, and 4e-FCI levels of theory using small basis sets. One can deduce from these data that the total contributions from the connected quadruples and from the iteration of triples are \(-23 \text{ cm}^{-1}\) and \(-6 \text{ cm}^{-1}\) for Hg\(_2\) and Cn\(_2\), respectively. Since the contributions from only the iteration of triples are \(-20 \text{ cm}^{-1}\) and \(-5 \text{ cm}^{-1}\), we can conclude that the effect of the iterative accounting for the triple cluster amplitudes is noticeable, whereas the accounting for the quadruples is not. The potential energy curves for the Hg\(_2\) and Cn\(_2\) dimers obtained in SCF calculations are repulsive. They remain repulsive also if only valence s shells are correlated. An interesting feature that can be seen from the data in Table III is that the potential energy curve of the Cn\(_2\) dimer becomes even more repulsive of only the valence 7s shell is correlated. To corroborate the reliability of the DFT-based spin-orbit corrections from Ref. 7 obtained with the generalized-gradient approximations for the exchange-correlation functional, i.e., Perdew-Wang (PW91)\(^7\) and Perdew-Burke-Ernzerhof (PBE)\(^{17}\) models, we performed similar calculations with the meta-GGA TPSS functional\(^{18}\). All three correcting functions were found to be nearly identical.
III. CONCLUSIONS

The effects of the non-perturbative treatment of triples and the inclusion of quadruples on the computed Hg–Hg and Cn–Cn van der Waals interaction energies are evaluated. For Hg$_2$, the account of these contributions substantially improves the CCSD(T) results, bringing the computed dissociation energies, equilibrium distances, and vibrational constants into nearly perfect agreement with the experimental values. One can suppose that the non-perturbative treatment of triples can play important role in the accurate description of other van der Waals complexes.

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TABLE I: Calculated equilibrium distance (in Å) and other spectroscopic constants (in cm$^{-1}$) for the ground state of the Hg$_2$ molecule as compared to the experimental and previously calculated data.

| method                  | $R_e$ | $D_e$ | $w_e$ | $w_ex_e$ |
|-------------------------|-------|-------|-------|----------|
| DFT(B88/P86)$^2$        | 3.63  | 73    | 14    |          |
| DFT(PW91)$^2$           | 3.55  | 385   | 24    |          |
| $^a$CCSD(T)$^3$         | 3.60  | 581   |       |          |
| CCSD(T) $+\Delta E_{SO}^5$ | 3.729 | 379   | 19.4  | 0.24     |
| CCSD(T)$^4$             | 3.718 | 379   | 19.4  | 0.24     |
| CCSD(T)$^{10}$          | 3.836 | 315   | 16.3  |          |
| CCSD(T) $+\Delta E_{SO}^6$ | 3.743 | 328   | 18.4  | 0.28     |
| CCSD(T) $+\Delta E_{SO}^7$ | 3.730 | 355   | 18.74 | 0.24     |
| This work               | 3.711 | 377   | 19.32 | 0.24     |
| Experiment$^{20}$       | 3.69 ± 0.01 | 380 ± 25 | 19.6 ± 0.3 | 0.25 ± 0.05 |

$^a$ Total relativistic version of the coupled-cluster method. Small basis set, BSSE is not compensated.

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TABLE II: Calculated equilibrium distance (in Å) and other spectroscopic constants (in cm\(^{-1}\)) for the ground state of the Cn\(_2\) molecule as compared to the previously calculated data.

| method                  | \(R_e\) | \(D_e\) | \(w_e\) | \(w_e x_e\) |
|-------------------------|---------|---------|---------|-------------|
| DFT(B88/P86)\(^2\)     | 3.45    | 315     | 25      | ???         |
| DFT(PW91)\(^2\)        | 3.39    | 649     | 30      | ???         |
| \(^a\)CCSD(T)\(^3\)    | 3.07    | 1508    |         |             |
| CCSD(T) +\(\Delta E_{SO}\)\(^7\) | 3.323  | 768     | 29.83   | 0.3272      |
| This work               | 3.322   | 775     | 29.94   | 0.3266      |

\(^a\) Total relativistic version of the coupled-cluster method. Small basis set, BSSE is not compensated.

TABLE III: Calculated energy differences (in cm\(^{-1}\)) \(E(R = 7.0 \text{ a.u.}) - E(R = 200.0 \text{ a.u.})\) for Hg\(_2\) and \(E(R = 6.5 \text{ a.u.}) - E(R = 200.0 \text{ a.u.})\) for Cn\(_2\)

|         | Hg\(_2\) | Cn\(_2\) |
|---------|----------|----------|
| SCF     | 617.4    | 944.5    |
| 4e-CCSD | 211.9    | 1573.3   |
| 4e-CCSD(T)| 128.2  | 1530.0   |
| 4e-CCSDT| 108.3    | 1524.7   |
| 4e-FCI  | 105.4    | 1523.9   |

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