

# Accurate potential energy curves for the group 12 dimers $Zn_2$ , $Cd_2$ , and $Hg_2$

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**Abstract** Potential energy curves of the electronic ground states of the group 12 dimers  $Zn_2$  and  $Cd_2$  were computed at the CCSD(T) level of theory, including full triple corrections  $\Delta T$  in the coupled-cluster procedure, and spin-orbit (SO) contributions from four-component coupled-cluster calculations, extrapolated to the complete basis set (CBS) limit. For  $Hg_2$ , the potential energy curve published recently (Pahl et al. in *J Chem Phys* 132:114301, 2010] is complemented in this work by non-relativistic calculations to quantify and discuss relativistic effects. We obtain very accurate fits of our CBS/CCSD(T) and CBS/CCSD(T)+ $\Delta T$  data points to an analytically simple and computationally efficient extended Lennard Jones form. For the CBS/CCSD(T)+ $\Delta T$ +SO curves, we obtain dissociation energies of  $D_e = 226 \text{ cm}^{-1}$  and  $D_e = 319 \text{ cm}^{-1}$  for  $Zn_2$  and  $Cd_2$  respectively, in very good agreement with recent theoretical calculations and experimental data. We also present equilibrium distances and rotational and

vibrational spectroscopic constants to compare with available theoretical and experimental data. The results obtained for non-relativistically treated  $Hg_2$  continue nicely the trends with increasing atom number preset by  $Zn_2$  and  $Cd_2$ , confirming that indeed, relativistic effects account for the known peculiarities for the mercury dimer.

**Keywords** Potential energy curves · Zn dimer · Cd dimer · Hg dimer · Relativistic effects

## 1 Introduction

Despite considerable improvements in the treatment of both electron correlation and relativity for molecules over the past two decades [1–5], reaching now “chemical accuracy” of 1 kcal/mol or better for thermochemical data such as enthalpies of formation, ionization potentials, or electron and proton affinities for atoms and small molecules [6], it remains a formidable task to accurately produce potential energy curves for weakly interacting systems yielding spectroscopic constants close to experimental accuracy [7–12]. This is specially the case for the heavier group 2 and 12 dimers like  $Ba_2$  [13] or  $Hg_2$  [14], where not only scalar relativistic but also spin-orbit effects need to be considered within the electron correlation procedure.

The group 12 dimers have been investigated extensively in the past, both theoretically [8, 14–24] and experimentally [25–35]. However, within the many different approaches used, the spectroscopic constants obtained vary widely, on the theoretical side mainly because of the insufficient treatment of electron correlation, limited basis sets used and approximations in the relativistic procedure. On the experimental side, it is a non-trivial task to obtain

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Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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vibration–rotational spectra and other properties to gain information about the potential energy curve from the short to the long range in interatomic distances. Considerable improvement comes with the use of correlation-consistent basis sets to reduce both basis set superposition and incompleteness errors by extrapolation to the complete basis set (CBS) limit. For example, for Hg<sub>2</sub>, recent calculations by Peterson already gave a much improved dissociation energy of 376 cm<sup>-1</sup> [24]. This result was further improved on very recently in our research group by including non-iterative triples in the correlation procedure and both scalar relativistic and spin-orbit effects, resulting in a dissociation energy of 405 cm<sup>-1</sup> now in excellent agreement with the experimentally estimated value of 407 cm<sup>-1</sup> of Greif and Hensel [20, 31], and spectroscopic constants of similar high accuracy [14]. For Zn<sub>2</sub> and Cd<sub>2</sub>, theoretical work is scarce [19, 22, 36–39] with most accurate results from Peterson and Puzzarini [22] or from Yu and Dolg [37] using coupled cluster within a relativistic pseudopotential approach including spin-orbit coupling. Yu and Dolg showed that the dissociation energy is increasing down the group 12 dimers, but the bond distance for Hg<sub>2</sub> is smallest in that group. They also analyzed the covalent bonding contributions in addition to pure van der Waals interactions [37].

It was already pointed out that relativistic effects in Hg<sub>2</sub> decrease the equilibrium distance by about 0.25 Å, but barely change the dissociation energy [15]. Relativistic effects in Hg<sub>2</sub> have been analyzed in detail in the past [15], and most recently for the group 12 dimers by Bučinský and Biskupič [40]. In short, the relativistic 6s contraction causes a contraction in the Hg<sub>2</sub> bond distance despite the fact that the polarizability of Hg decreases substantially due to relativistic effects [15, 20, 41]. This comes from the fact that in the dispersion term the relativistic 6s contraction enters the  $R^{-6}$  term. Thus, in spite of being chemically rather inert, Hg<sub>2</sub> (and even more though for the Copernicium dimer, Cn<sub>2</sub>, the next element down in the periodic table) undergoes a rather significant relativistic bond contraction. This contraction effect is observable for clusters throughout to the solid state of mercury [42].

In order to obtain accurate potential energy curves for the group 12 dimers, and the corresponding spectroscopic constants, we carried out relativistic coupled-cluster calculations for Zn<sub>2</sub> and Cd<sub>2</sub>, extrapolated to the CBS limit, similar to our previous study for Hg<sub>2</sub> [14]. It is currently not clear how relativistic effects influence the dissociation energy of Hg<sub>2</sub>, as all previous results were rather limited in accuracy at the non-relativistic level of theory. We therefore decided to carry out non-relativistic CBS limit calculations for Hg<sub>2</sub> as well to discuss relativistic effects.

## 2 Computational details

The potential energy curves for the Zn<sub>2</sub>, Cd<sub>2</sub> and Hg<sub>2</sub> were calculated on a grid with 35 points from 1.75–20 Å (about 3–40 a.u.), with a spacing of 0.25 Å in the well region, 0.1 Å around the minima, 1 Å in the medium range, and finally, 5 Å in the very long-range part. The non-relativistic calculations for Hg<sub>2</sub> were carried out using a non-relativistic pseudopotential (the Hg dimer potential including relativistic effects has already been described recently [14] and will be included here only for the sake of comparison). For the computations, we used coupled cluster with single and double substitutions including perturbative triples, CCSD(T), as contained in the MOLPRO program package [43]. We employed scalar-relativistic energy-consistent small-core pseudopotentials for Zn, Cd, and Hg (ECP10MDF, ECP28MDF [44], and the non-relativistic ECP60MHF [45]), describing the 10, 28, and 60 innermost electrons, respectively. Thus, we only correlate the remaining 20 valence electrons in each atom. We chose corresponding correlation-consistent aug-cc-pwCV $n$ Z-PP basis sets with  $n = D, T, Q, 5$  for Zn, Cd, and Hg [22]. The basis set for the non-relativistic treatment of Hg was optimized for our purpose, and details can be found on the Stuttgart website for pseudopotentials and basis sets [46]. These basis sets were used to estimate the complete basis set limit (CBS) by extrapolation of the correlation energies  $E_n^{\text{corr}}$  with cardinal number  $n$ . Here, we followed the extrapolation procedure of Ref. [22] to derive the CBS limit  $E_{\text{CBS}}^{\text{corr}}$  for the correlation energy,

$$E_n^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + An^{-3}. \quad (1)$$

The Hartree–Fock limit was taken from the aug-cc-pwCV5Z basis set.

For Zn and Cd, the spin-orbit (SO) contribution was obtained from Dirac–Fock calculations using the basis sets by Faegri [47], a (20s16p10d3f2g) basis for Zn<sub>2</sub> and a (21s18p12d5f3g) basis for Cd<sub>2</sub>, using the DIRAC08 computational package [48]. By comparing the 4-component results with spin-free results, we obtained the spin-orbit energies that were then added to the  $E_{\text{CBS}}$  energies. For selected points in the short-range, minimum, and long-range part of the potential, the contribution of the SO coupling obtained on Dirac–Fock level was in excellent agreement with that obtained using the 4-component CCSD(T) approach.

Finally, the variational triple contributions (CCSDT) were computed employing the MRCC code within MOLPRO [49]. In these calculations, only the outermost  $d$  and  $s$  electrons were correlated, and the aug-cc-pVTZ basis set was used. The difference between the variational and the perturbative treatments of the triples yielded the full triple correction  $\Delta T$ . All coupled-cluster energies were

counterpoise corrected in the standard manner as outlined by Boys and Bernardi [50].

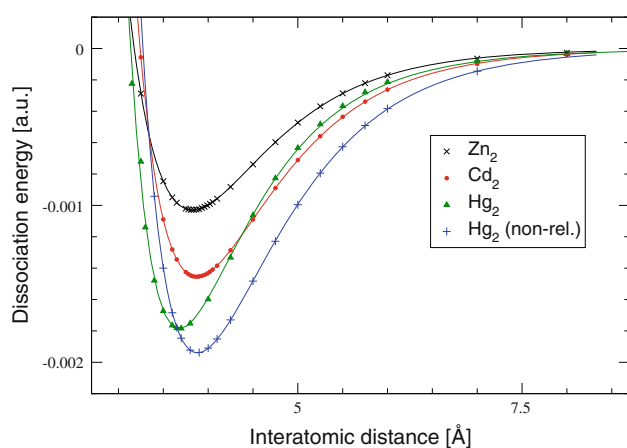
### 3 Results and discussion

#### 3.1 Dimer potentials

The calculated *ab initio* potential curves for  $\text{Zn}_2$ ,  $\text{Cd}_2$ , and  $\text{Hg}_2$  at the CBS/CCSD(T)+ $\Delta$ T level of theory are presented in Fig. 1. The data were fitted to an extended Lennard Jones (ELJ) form, which is computationally efficient and has been shown to be very useful for melting simulations of rare gas solids [51, 52]. The analytical expression for presenting the potential energy curves  $V(r)$  of the electronic ground states of the group 12 dimers as a function of the internuclear distance is given by

$$V_{\text{ELJ}}^{(2)}(r) = \sum_{k=6}^{k=14} a_k r^{-k}. \quad (2)$$

The optimal fit coefficients  $a_k$  are listed in Tables 1, 2, and 3 for  $\text{Zn}_2$ ,  $\text{Cd}_2$ , and non-relativistic  $\text{Hg}_2$ , respectively, at the CBS/CCSD(T)+ $\Delta$ T level of theory. For Zn and Cd spin-orbit interactions SO are included, although they turned out to be very small and almost negligible. The rms error in our fitting procedure is smaller than  $1 \times 10^{-4}$  eV for all data presented here, thus in the same order of magnitude as the rms error for our previous relativistic fit for Hg [14], and errors typically obtained in more sophisticated potentials like the Tang-Toennies [53] or the Silvera-Goldman [54] fits used for Hg. As clearly seen in



**Fig. 1** Potential energy curves of  $\text{Zn}_2$ ,  $\text{Cd}_2$ , and  $\text{Hg}_2$  (with and without relativistic effects for the latter) at the CBS/CCSDT level of theory and corresponding fits to the ELJ potential. Except for the non-relativistic calculations for  $\text{Hg}_2$ , spin-orbit interactions are included. The data for the relativistic calculations on  $\text{Hg}_2$  are taken from Ref. [14]

**Table 1** Fitted coefficients  $a_k$  for the ELJ potential (see Eq. 2) from CBS/CCSD(T)+SO and CBS/CCSD(T)+SO+ $\Delta$ T data for  $\text{Zn}_2$

	CBS/CCSD(T)+SO	CBS/CCSD(T)+SO+ $\Delta$ T
$a_6$	-513.0	-513.0
$a_8$	$1.11956273372600 \times 10^6$	$1.12094516929225 \times 10^6$
$a_9$	$-4.04300737680194 \times 10^7$	$-4.05664705207570 \times 10^7$
$a_{10}$	$5.97585210620898 \times 10^8$	$6.00462536497241 \times 10^8$
$a_{11}$	$-4.57423072252484 \times 10^9$	$-4.60155447595170 \times 10^9$
$a_{12}$	$1.92280605542069 \times 10^{10}$	$1.93636539982602 \times 10^{10}$
$a_{13}$	$-4.23084867898660 \times 10^{10}$	$-4.26529385358249 \times 10^{10}$
$a_{14}$	$3.82159175238128 \times 10^{10}$	$3.85706203529465 \times 10^{10}$

The coefficient  $a_6$  is set to the van der Waals coefficient  $C_6$  (see text),  $a_7$  is chosen to be zero, the additional  $a_k$ ,  $k = 8-14$ , were optimized numerically to reproduce the *ab initio* data. Atomic units are used throughout

**Table 2** Fitted coefficients  $a_k$  for the ELJ potential (see Eq. 2) from CBS/CCSD(T)+SO and CBS/CCSD(T)+SO+ $\Delta$ T data for  $\text{Cd}_2$

	CBS/CCSD(T)+SO	CBS/CCSD(T)+SO+ $\Delta$ T
$a_6$	-840.0	-840.0
$a_8$	$2.01777662116438 \times 10^6$	$1.97508960438597 \times 10^6$
$a_9$	$-7.49247654824576 \times 10^7$	$-7.29732825105466 \times 10^7$
$a_{10}$	$1.14336017048802 \times 10^9$	$1.11087439115603 \times 10^9$
$a_{11}$	$-9.07532571280482 \times 10^9$	$-8.80408466052397 \times 10^9$
$a_{12}$	$3.96945377726455 \times 10^{10}$	$3.84641669689086 \times 10^{10}$
$a_{13}$	$-9.10917721544408 \times 10^{10}$	$-8.81819061494874 \times 10^{10}$
$a_{14}$	$8.59321430557602 \times 10^{10}$	$8.31114531899489 \times 10^{10}$

The coefficient  $a_6$  is set to the van der Waals coefficient  $C_6$  (see text),  $a_7$  is chosen to be zero, the additional  $a_k$ ,  $k = 8-14$ , were optimized numerically to reproduce the *ab initio* data. Atomic units are used throughout

**Table 3** Fitted coefficients  $a_k$  for the ELJ potential (see Eq. 2) from CBS/CCSD(T) and CBS/CCSD(T)+ $\Delta$ T data for non-relativistic  $\text{Hg}_2$

	CBS/CCSD(T)	CBS/CCSD(T)+ $\Delta$ T
$a_6$	-1100.0	-1100.0
$a_8$	$2.92102750728655 \times 10^6$	$2.84929740833278 \times 10^6$
$a_9$	$-1.16458795954757 \times 10^8$	$-1.12994132711712 \times 10^8$
$a_{10}$	$1.89852175386730 \times 10^9$	$1.83829671167834 \times 10^9$
$a_{11}$	$-1.60982258650904 \times 10^{10}$	$-1.55761653814320 \times 10^{10}$
$a_{12}$	$7.53288054059401 \times 10^{10}$	$7.28793822049390 \times 10^{10}$
$a_{13}$	$-1.85234701024690 \times 10^{11}$	$-1.79257761981000 \times 10^{11}$
$a_{14}$	$1.87520228505199 \times 10^{11}$	$1.81551451996687 \times 10^{11}$

The coefficient  $a_6$  is set to the van der Waals coefficient  $C_6$  of non-relativistic Hg (see text),  $a_7$  is chosen to be zero, the additional  $a_k$ ,  $k = 8-14$ , were optimized numerically to reproduce the *ab initio* data. Atomic units are used throughout

Fig. 1, the ELJ potentials agree very well with the *ab initio* results over the whole range of data points. The largest errors stem from the repulsive potential region. For all potentials, only seven coefficients,  $a_8$  to  $a_{14}$ , were determined by the fitting procedure, with the first coefficient  $a_6$  set to the value of the van der Waals coefficient  $C_6$  in order to describe the long-range part of the potential curve more correctly, and  $a_7$  was set to zero. For Hg, the relativistic value of  $a_6^{\text{Hg}^{\text{rel}}} = C_6^{\text{Hg}^{\text{rel}}} = -392.0$  a.u. was taken from recent calculations by Tang and Toennies [34], whereas for Zn, Cd, and non-relativistically treated Hg, we could not find reliable data in the literature (see e. g. Ref. [9]). Therefore, we used the approximate relation between  $C_6$  coefficients and the atomic dipole polarizabilities  $\alpha$ ,  $C_6 \propto \alpha^2$ , to obtain

$$C_6^{\text{Zn/Cd/Hg}^{\text{nr}}} = \left( \frac{\alpha^{\text{Zn/Cd/Hg}^{\text{nr}}}}{\alpha^{\text{Hg}^{\text{rel}}}} \right)^2 C_6^{\text{Hg}^{\text{rel}}} \quad (3)$$

With the polarizabilities for Zn, Cd, non-relativistic and relativistic Hg  $\alpha^{\text{Zn}} = 5.75 \text{ \AA}^3$ ,  $\alpha^{\text{Cd}} = 7.36 \text{ \AA}^3$ ,  $\alpha^{\text{Hg}^{\text{nr}}} = 8.56 \text{ \AA}^3$ , and  $\alpha^{\text{Hg}^{\text{rel}}} = 5.02 \text{ \AA}^3$  accurately known [55, 56, 41], we arrive at  $a_6^{\text{Zn}} = C_6^{\text{Zn}} = -514$  a.u.,  $a_6^{\text{Cd}} = C_6^{\text{Cd}} = -840$  a.u., and  $a_6^{\text{Hg}^{\text{nr}}} = C_6^{\text{Hg}^{\text{nr}}} = -1100$  a.u. Note that the coefficients  $a_8$  and  $a_{10}$  are determined by the fit procedure having positive values, therefore describing more the repulsive part of the potential curve (together with the coefficients  $a_{12}$  and  $a_{14}$ ). Thus, they do not correspond to the van der Waals coefficients  $C_8$  and  $C_{10}$ . The smoothness and the absence of unwanted zeros in the very short- and very long-range part of the two-body curves was ensured via checking the first and second derivatives of the potential functions.

Figure 1 shows that the curves for Zn, Cd, and non-relativistic Hg change in a systematic manner—while the equilibrium distances increase only marginally, the potential depths increase substantially with increasing atomic number. It is clearly notable that relativistic effects change the picture for Hg, i.e., the equilibrium distance is pronouncedly shorter with a corresponding onset of the repulsive wall at much shorter distances and the potential well becomes less deep. With larger interatomic distances, relativistic effects cause the potential to approach more rapidly the dissociation limit, even crossing the Cd dimer curve. This behavior is in accordance with the strongly decreased polarizability of only  $\alpha = 5.02 \text{ \AA}^3$  of the Hg atom due to relativistic effects, thus making Hg a very hard atom and reducing dispersive type of interactions in the long range [15]. The difference between the non-relativistic and relativistic interactions might be responsible for the fact that mercury is a liquid at room temperature [55]. We note however that many-body effects become non-negligible for

solid mercury, and a simplified picture drawn from two-body interactions only is not applicable for extended systems (and even for the smaller clusters) [57, 58].

### 3.2 Spectroscopic constants

A grid of 100 equally spaced points generated from the ELJ potentials was used to obtain the spectrum of the rovibrational Schrödinger equation within the Numerov–Cooley procedure [59] (we used 8–12 vibrational and 10 rotational levels for a least-squares fit of the spectroscopic constants to the calculated spectrum). The spectroscopic constants are listed in Table 4 for the CBS/CCSD(T) as well as for the CBS/CCSD(T)+ $\Delta T$  level of theory (+SO for the relativistic case).

In general, our calculated spectroscopic constants agree well with previous theoretical and experimental values. For  $\text{Zn}_2$ , we find an equilibrium distance of  $3.826 \text{ \AA}$  slightly smaller than the (so far) most accurate theoretical calculation of Peterson and Puzzarini [22]. In accordance with the improved bond distance, our calculated dissociation energy excluding the vibrational zero-point energy ( $D_e = 226 \text{ cm}^{-1}$ ), and other constants are slightly larger. Moreover, our dissociation energy is in excellent agreement with the value of  $232 \text{ cm}^{-1}$  from Patkowski et al. [9], who performed CCSD(T) calculations, but with a different family of basis sets and a different way of accounting for relativistic effects. They estimated the full triple corrections to be  $3 \text{ cm}^{-1}$  in accordance with our result. It is not to be expected that quadruple or higher excitations in the coupled-cluster procedure will yield a larger correction than that found for the triples. Experimentally, the latest result for the dissociation energy is down from the original  $279 \text{ cm}^{-1}$  [30] to  $242 \text{ cm}^{-1}$  [33], but still larger by  $16 \text{ cm}^{-1}$  compared to our theoretical value. Nevertheless, with  $4.19 \text{ \AA}$ , the experimentally estimated equilibrium distance is much larger than all calculated distances which casts some doubts on these results. One has to be aware that the experimental determination of equilibrium distances from the measured excitation and fluorescence spectra is rather difficult: While potential parameters like the well depth and the fundamental vibrational frequency can be measured more or less precisely, the equilibrium distance cannot be determined directly (only differences between the ground and excited states); thus, an analysis of the rotational spectrum is required using for example different isotopes. The other available “experimental” value for the equilibrium distance of  $4.62 \text{ \AA}$  [32] is even larger as it stems from a fit to viscosity data using the (most probably wrong) experimental dissociation energy of  $279 \text{ cm}^{-1}$ . The equilibrium distance for  $\text{Cd}_2$  given by these authors is also much larger than any other reported value.

**Table 4** Spectroscopic constants for the group 12 dimers obtained at different levels of theory

System		$r_e$	$D_e$	$\omega_e$	$\omega_e x_e$	$\alpha_e$
Zn <sub>2</sub>	Ref. [8]	4.024; 3.944	219; 199	21.3; 21.1	0.52; 0.56	
	Ref. [22]	3.847	226	23.9	0.54	
	CBS/CCSD(T)+SO	3.826	223	23.9	0.59	0.9
	CBS/CCSD(T)+SO+ $\Delta T$	3.826	226	24.0	0.60	0.9
	Experiment	4.19 <sup>a,b</sup> ; 4.62 <sup>c</sup>	242 <sup>a</sup> ; 279 <sup>b</sup>	25.9 <sup>a,b</sup>	0.69 <sup>a</sup> ; 0.60 <sup>b</sup>	
Cd <sub>2</sub>	Ref. [8]	3.953; 3.915	293; 310	19.7; 20.1	0.33; 0.32	
	Ref. [22]	3.894	325	20.2	0.20	
	CBS/CCSD(T)+SO	3.847	340	21.9	0.33	0.3
	CBS/CCSD(T)+SO+ $\Delta T$	3.873	319	21.3	0.33	0.3
	Experiment	3.78 $\pm$ 0.03 <sup>d</sup> ; 4.07 <sup>b</sup> ; 4.33 <sup>c</sup>	328 $\pm$ 3 <sup>d</sup>	21.4 $\pm$ 0.2 <sup>d</sup> ; 23.0 <sup>b</sup>	0.35 $\pm$ 0.02 <sup>d</sup> ; 0.40 <sup>b</sup>	
Hg <sub>2</sub> <sup>nr</sup>	CBS/CCSD(T)	3.856	455	18.9	0.20	0.14
	CBS/CCSD(T)+ $\Delta T$	3.882	426	18.3	0.20	0.14
Hg <sub>2</sub>	CBS/CCSD(T)+SO	3.650	424	21.2	0.28	0.165
	CBS/CCSD(T)+SO+ $\Delta T$	3.679	392	20.4	0.28	0.168
	Experiment	3.605 <sup>e</sup> ; 3.69 <sup>f</sup> ; 3.63 <sup>g</sup>	380 <sup>f</sup> ; 407 <sup>h</sup>	19.9 <sup>f</sup>	0.3 <sup>f</sup>	0.21 <sup>f</sup> ; 0.17 <sup>h</sup>

Bond distances  $r_e$  (in Å), dissociation energies  $D_e$ , harmonic frequencies  $\omega_e$ , anharmonicity constants  $\omega_e x_e$  (all in  $\text{cm}^{-1}$ ), and the vibrational–rotational coupling constant  $\alpha_e$  (in  $10^{-3} \text{ cm}^{-1}$ ), as compared to known experimental data and most recent theoretical calculations [8, 22]. For Hg<sub>2</sub>, non-relativistic results are shown as well in comparison with our recently published relativistic calculations [14]

<sup>a</sup> Ref. [33]; <sup>b</sup> Ref. [30]; <sup>c</sup> Ref. [32]; <sup>d</sup> Ref. [35] and references therein; <sup>e</sup> Ref. [62]; <sup>f</sup> Ref. [27] and [29]; <sup>g</sup> Ref. [26]; <sup>h</sup> Ref. [31]

For Cd<sub>2</sub>, we find excellent agreement with very recent experimental results of Strojceki et al. [35]. The harmonic frequency  $\omega_e$  and the vibrational–rotational coupling constant  $\omega_e x_e$  agree within the experimental errors given; the experimentally determined dissociation energy of  $D_e = 328 \text{ cm}^{-1}$  lies between our CBS/CCSD(T)+SO value of  $340 \text{ cm}^{-1}$  and the one of  $319 \text{ cm}^{-1}$  including triple corrections. In contrast to Zn<sub>2</sub>, the triple corrections for Cd<sub>2</sub> are quite pronounced with  $21 \text{ cm}^{-1}$  and only slightly smaller as found previously for the case of Hg<sub>2</sub> [14]. An estimation for the quadruple contributions and the effects of correlating the 4f electrons explicitly, our result for the dissociation energy of Hg<sub>2</sub> increased by about  $15 \text{ cm}^{-1}$ . If we assume that the same trends will prevail for Cd<sub>2</sub>, an increase of about  $10 \text{ cm}^{-1}$  is to be expected when including quadruple excitation which would bring us very close to the experimental result. Concerning the equilibrium distance, there are some discrepancies to the experimental values, but not as large as found for Zn<sub>2</sub>, i.e., the theoretical and latest experimental values deviate by about  $0.1 \text{ Å}$ .

We only discuss Hg<sub>2</sub> briefly and concentrate on the relativistic effects, more details can be found in Ref. [14]. As pointed out before [15], we see a relativistic contraction of the equilibrium distance, but now we can give a more precise value of  $\Delta_R r_e = -0.203 \text{ Å}$ . The dissociation energy decreases relativistically, i.e.,  $\Delta_R D_e = -34 \text{ cm}^{-1}$ . As the potential energy curve is shifted toward a smaller bond distance, the curvature around the minimum increases, and

therefore, the harmonic frequency increases as well for Hg<sub>2</sub> being now similar to that of Cd<sub>2</sub>. Similar effects are seen for the anharmonicity constant and the vibrational–rotational coupling constant. Much larger effects are predicted for the super-heavy dimer Cn<sub>2</sub> [60, 61].

#### 4 Summary

We presented calculations on the ground state potential energy curves of Zn<sub>2</sub>, Cd<sub>2</sub> and non-relativistic Hg<sub>2</sub> at the CCSD(T) level of theory including full triple corrections as well as spin-orbit interactions for the relativistic case. For all computations, we employed small-core energy-consistent pseudo-potentials, scalar-relativistic ones for Zn and Cd, a non-relativistic one for Hg, leaving only the outermost 20 electrons to be correlated. The corresponding large augmented basis sets aug-cc-pwCVnZ-PP ( $n = \text{D, T, Q, 5}$ ) were used, which allowed for extrapolation of the data to the complete basis set limit.

The obtained *ab initio* data sets were then fitted to an extended Lennard-Jones potential form. These fits are very accurate, describing the short- to long-range part of the potentials extremely well with only one single functional form. This will prove beneficial in future simulations studies, for gas-phase studies as well as for simulations of two-body interactions in the liquid or solid state.

For the spectroscopic constants, we found very good agreement with recent theoretical calculations as well as

with experimental data. The largest discrepancies can be found for the equilibrium distances, which is caused by the difficulties in direct determination of such quantities from experimental measurements.

The work on Hg<sub>2</sub> started almost twenty years ago in collaboration with Prof. Friedrich Hensel (Marburg) resulting in a joint first paper with Prof. Pekka Pyykkö on this subject in the very same journal in 1994. We came a long way since. PS thanks Pekka for many fruitful discussions and collaborations over the last twenty years. PS also thanks the Alexander von Humboldt Foundation for continuous support. This work was supported by the Royal Society of New Zealand (Marsden grant 07-MAU-016), and KP was funded by the visitor's programme of Massey University.

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