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The polarisability of Hg and the ground–state interaction potential of Hg_2*

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Summary. The Hg atom electric polarisability at MP3, MP4, QCISD or QCISD(T) level using a 20 valence-electron pseudopotential and a (9*s*8*p*7*d*2*f*)/[7*s*6*p*4*d*2*f*] basis set converges and agrees with experiment. The calculated Hg_2 $X^1\Sigma$ $V(R)$ at the same level is roughly half of experiment at R_e but twice as large as the experimental C_6 at large R.

Key words: Mercury atom polarisability – Mercury dimer – Relativistic effects – Pseudopotential – MP*n* – QCISD – QCISD(T)

1 Introduction

The attractive interactions between metal atoms or ions with closed electron shells are of great current interest [1]. Perhaps the most striking example is the strong "aurophilic" Au(I)... Au(I) attraction (see Ref. [2]). While these, formally $5d^{10}$ systems contain ligands, we now consider the ligand-free, bare $6s^2 \ldots 6s^2$ case to see what level of theory would be required to eventually reproduce the Hg...Hg attraction in this simple case. As an even simpler, related test we calculate the electric polarisability, α, of Hg. We thus use Hg_2 as a simplified model for $(ClAuPH_3)_2$, for instance, and α(Hg) as a test on the Hg monomer.

Actually the Hg_2 $X^1\Sigma$ potential–energy curve $V(R)$ is a classic problem of interest in its own right, see Morse [3]. The experimental spectroscopic parameters, since those published by Franck and Grotian in 1922 [4] have varied greatly converging only recently to those in Table 1. The earlier calculations are also summarised there.

The early Gordon–Kim D_e calculated by Pyper, Grant and Gerber [7] is actually near experiment, but the R_e is 48 pm too large. The density functional

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* Dedicated to Inga Fischer–Hjalmars whose wit and charm made Quantum Chemistry a better place

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Table 1. Earlier results for Hg_2 $X^1\Sigma$. Non-relativistic values in parentheses

Method	R_e/pm	D_e/eV	$\omega_e/\mathrm{cm}^{-1}$	$\omega_e x_e/\mathrm{cm}^{-1}$	Ref.
Exp.[a]	325(20)	0.068–0.134	49	–	[3]
Exp.[b]	363(4)	0.0434(25)	18.5(5)	0.27	[5]
Exp.[b]		0.0434(25)	19(2)	0.25	[6]
Gordon–Kim	411	0.0349	–	–	[7]
	(410)	(0.0763)	–	–	
PP-LDF[c]	299	0.23	71	–	[8]
PP-DFT					
LM[d]	324	0.05	32.1	–	[9]
BP[e]	363	0.01	13.4	–	[9]
PP-CAS-RCI[f]	384	–	–	–	[10]

[a] Gas-phase viscosity, Knudsen cell effusion, ...

[b] UV spectroscopy of jet-cooled Hg vapor

[c] Pseudopotential, local density functional

[d,e] Pseudopotential density functional theory with non-local corrections by Langreth and Mehl ("LM") or by Becke and Perdew ("BP"), see Ref. [9]

[f] Pseudopotential complete active space relativistic configuration interaction

theory (DFT) results [8, 9] are very model-sensitive. Balasubramanian et al. [10] obtain an R_e, 21 pm larger than experiment but report no D_e or ω_e. They have no corrections for the basis-set superposition error (BSSE). Celestino and Ermler [11] also were mainly interested in calculating electronic excitation energies, rather than in a very precise ground-state $V(R)$.

2 Method

The 20-valence electron (20-VE) (quasi)-relativistic (R) or non-relativistic (NR) pseudopotentials (PP) and (8*s*8*p*7*d*) valence basis sets of Ref. [12] were used. An additional diffuse *s*-function ($\alpha_s = 0.05$) and two *f*-functions ($\alpha_f = 0.5$ and 1.5) were added and the final basis sets is (9*s*8*p*7*d*2*f*).

The calculations were performed using Gaussian 92 [13]. The MPn ($n = 2$–4), QCISD and QCISD(T) [14, 15] approximations were used. In the atomic, $\alpha(0)$, calculations all electrons belonged to the active space. In most dimer calculations the 5*s* and 5*p* shells were kept inactive, except in the case MP2/F in Table 4. The difference between MP2 and MP2/F was used to obtain the final "QCISD(T)/MP2" results, see Table 4. The BSSE correction to $V(R)$ was made using counterpoise method of Boys and Bernardi [16, 17].

A finite-field approach within a coupled HF procedure was used with the electric field, F, equal to 0 and 0.001 a.u. The energy convergence was set at 10^{-10} and 10^{-8} a.u. at SCF and CI level, respectively. The estimated accuracy of α, 0.2 a.u., was verified by calculating the HF and MP2 gradient-derived polarisabilities, as well.

3 The Hg polarisability

The latest experimental result for the static electric polarisability, $\alpha(0)$ of Hg seems to be that of Wüsthoff [18]. Selected earlier *ab initio* calculations are also

Table 2. Earlier results for the Hg ground-state electric dipole polarisability, $\alpha(0)$ (a.u.). Here R stands for fully relativistic and QR for one-component or "quasirelativistic" results

Method	α		Ref.
	NR	R	
Exp.		34(1)[a]	[18, 19]
PP-HF	–	37.0	[20]
PP-MCSCF	–	31.8	[20]
HF[b]	80	43	[21]
HF	–	44.9	[22]
R-PP-HF	–	43	[23]
QR-PP-HF	–	45.7	[23]
R-TD-LDA[c]	–	33.0	[24]
PP[d]	–	35.7	[25]

[a] Wüsthoff [16] reports a dielectric constant $\varepsilon - 1$ of $170 \cdot 10^{-5}$ ($\pm 4\%$) for Hg vapour at 0°C, corresponding to $(r^3)^{1/3}$ of 1.71 Å or $\alpha = 33.7(1.3)$ a.u. Teachout and Pack [19] quote this value as 34 a.u.

[b] Numerical Dirac–Fock values. Only the $6s^2$ shell is polarised

[c] Relativistic time-dependent local-density approximation

[d] Semiempirical PP including core-polarisability terms

Table 3. Electric polarisability α(a.u.) for Hg at various levels of approximation. Δ_C and Δ_R are correlation and relativistic contribution to α, respectively. Note the difference between the $\Delta_C(R)$ and $\Delta_C(NR)$, indicating interplay of relativity and correlation

Method[a]	NR	$-\Delta_C(NR)$	R	$-\Delta_C(R)$	$-\Delta_R$
HF	81.29		44.24		37.05
HF[b]	81.38		44.74		36.34
MP2	46.64	34.65	27.61	16.63	19.03
MP2[b]	47.10	34.28	28.67	16.07	18.43
MP3	56.76	24.53	32.86	11.38	23.90
MP4	56.50	24.79	32.59	11.65	23.91
QCISD	61.60	19.69	34.82	9.42	26.78
QCISD(T)	57.76	23.53	33.44	10.80	24.32

[a] Full active orbital space has been chosen

[b] Extended basis set, i.e. an additional set of ($1s/1p/1d/2f$) set has been added with exponents (s:0.0015/p:0.005/d:0.007/f:4.5;0.15)

summarised in Table 2. For recent literature on the related, ns^2, alkaline earth atoms, see Sadlej et al. [26].

The present results are given in Table 3. A comparison of the HF and the large-basis "HF[b]" results suggests that the basis-set is saturated to 1% level in α. The comparison with the numerical HF results from [21, 22] supports this conclusion. At MP2 level the larger basis (MP2[b]) gives an α nearly 4% larger than the smaller one. The MP2 α value is smaller than experiment. The MP3 and MP4 values appear to converge. The QCISD and the QCISD(T) values are slightly larger, the latter one being 33.44 a.u., compared to the experimental value of 34 a.u. [18].

The larger basis set "*b*" would raise the calculated α. The HF-level comparison of *jj*-coupled and quasirelativistic (QR) values in Ref. [23] (see Table 2) also suggests that the *jj*-coupled value could be higher. The QR decrease of α in the higher correlated calculations is close to the QCISD(T) Δ_R of -24.3 a.u.

We conclude that the calculated α is quite stable and close to experiment. The theoretical precision may in fact rival the experimental one. Therefore modern measurements would now be needed. Unfortunately no such experiments have apparently been done for nearly two decades [27] and none for Hg since 1936 [18].

4 The Hg...Hg interaction potential

The calculated potential curves at various levels of approximation for the (9*s*8*p*7*d*2*f*) basis set are shown in Fig. 1. A comparison with NR curves is given in Fig. 2. The corresponding spectroscopic parameters are given in Table 4.

The BSSE has a major influence on the $V(R)$, diminishing it by nearly a factor of two. The MP*n* D_e oscillate, the MP4 value of 0.0186 eV is close to the QCISD(T) one of 0.0197 eV. These values have no excitations from 5*s* and 5*p* shells. The latter contribution, estimated at MP2 level, is added in the last column, giving $D_e = 0.0223$ eV. This value is only half of the experimental D_e of 0.0434(25) eV. The BSSE corrections for all methods used are shown as function of R in Fig. 3.

This disappointing result resembles the situation for Be_2 [28] where a 6*s*/4*p*/3*d*/1*f* STO basis, already for a 2nd-row element, and full CI were needed to obtain a D_e of 0.0811 eV compared to the "best" value of 0.0885(91) eV (exp. 0.093–0.099). Similarly, for Mg_2 a (16*s*11*p*2*d*1*f*)/[7*s*4*p*2*d*1*f*] GTO basis proved inadequate and a [7*s*7*p*4*d*3*f*3*g*2*h*] GTO basis and core polarisability corrections were required to obtain a D_e of 0.0571 eV (exp. 0.0533) [29].

The calculated ω_e are about 2/3 of the experiment. A Morse potential:

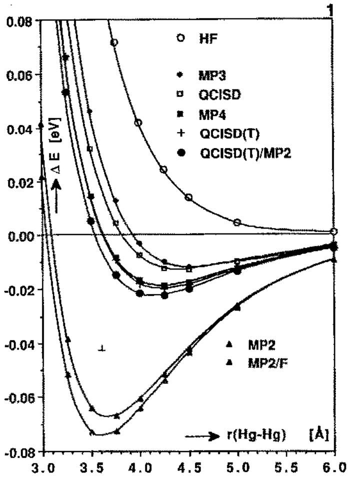
$$V(R) = D_e[1 - \exp(-a(R - R_e)]^2 \qquad (1)$$

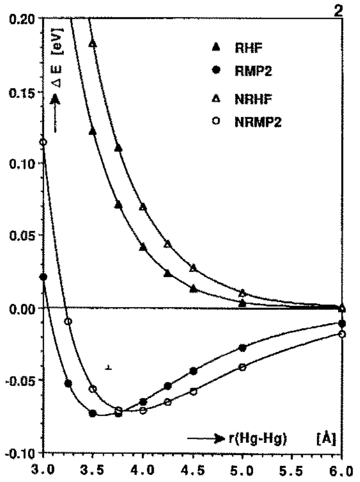
with $D_e = 0.0223$ eV, $k = 1.06\ \mathrm{N\,m^{-1}}$, $R_e = 415$ pm, $a = (k/2D_e)^{-1}$, is able to support 27 vibrational levels.

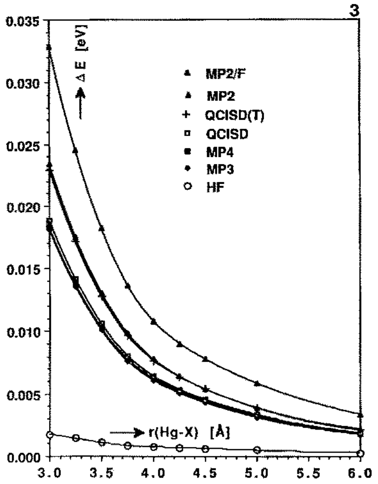
The present "best" calculated R_e of 415 pm is 52 pm larger than experiment. Without BSSE correction, 393 pm would be obtained. Balasubramanian et al. [10] obtained 384 pm, without BSSE correction, with a 12-VE PP, a (4*s*4*p*4*d*) basis set, and no excitations from the $5d^{10}$ shell.

What is the origin of the large BSSE? We studied the Hg_2 correction at $R = 350$ pm at three different levels: a) HF, b) MP2 with $6s^2$ valence correlation only and c) MP2 including the $5s^2 5p^6 5d^{10} 6s^2$ electrons. The results, in meV, became 2.17, 5.59 and 36.34, respectively. Thus the main BSSE contribution consists of correlation from the 5*s*5*p*5*d* core. Therefore it would be interesting, if one could afford to move even deeper core shells into the valence space, in the future.

We are aware of one chemical compound with a weak Hg...Hg interaction, at $R = 322.5(1)$ pm: $[Pt_3Hg(\mu_2\text{-}CO)_3(PPh\text{-}i\text{-}Pr_2)_3]_2$. The Pt–Hg distances, however, are short, from 293 to 308 pm. Even shorter Hg–Hg distances of 287.2(7) pm [31] or 274.4(5) and 282.0(3) pm [32] have just been reported in cluster compounds also containing Pt or Pt and Os. In these compounds (like in the mercurous ion),







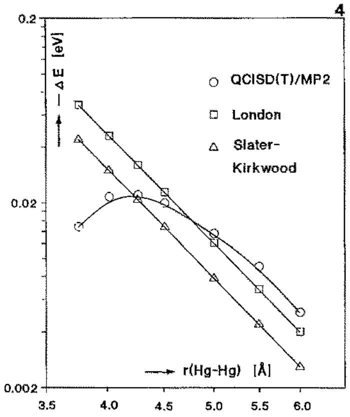


Fig. 1. Relativistic potential energy curves for the Hg...Hg interaction. The experimental (R_e, D_e) is indicated by "⊥". MP4 is "SDQ" only

Fig. 2. Comparison of relativistic and non-relativistic $V(R)$ at HF and MP2 level. The experimental (R_e, D_e) is indicated by "⊥"

Fig. 3. The counterpoise BSSE corrections for Hg_2 as function of R in the relativistic case. MP4 is "SDQ" only

Fig. 4. $V(R)$ at large R compared to London or $(n = 2)$ Slater–Kirkwood formulae

considerable covalent bonding must occur; they are not related to the present dimer.

As the Hg...Hg bond is much longer and weaker (363 pm, 0.0434 eV) than the "aurophilic" Au(I)...Au(I) attraction having typically $R_e = 300$–350 pm and $D_e = 0.28$ eV [2], the present failure to reproduce the Hg_2 $V(R)$ does not imply that the agreement for gold would be a coincidence.

Table 4. Calculated spectroscopic parameters for Hg_2 $X^1\Sigma$. Non-relativistic values in parentheses

Method[a]	R_e/pm	D_e/eV	D_0/eV[e]	ω_e/cm^{-1}	k_e/Nm^{-1}
without correction for BSSE					
MP2/F[b]	344	0.1098	0.1077	33	6.51
	(369)	(0.0980)	(0.0964)	(26)	(3.69)
MP2	356	0.0906	0.0889	27	4.37
MP3	440	0.0208	0.0201	12	0.80
MP4[c]	410	0.0298	0.0288	14	1.10
QCISD	425	0.0228	0.0221	12	0.82
QCISD(T)	407	0.0334	0.0325	14	1.19
QCISD(T)/MP2[d]	393	0.0431	0.0422	14	1.20
with correction for BSSE					
MP2/F[b]	361	0.0745	0.0729	26	3.92
	(387)	(0.0716)	(0.0703)	(21)	(2.59)
MP2	368	0.0673	0.0660	22	2.79
MP3	453	0.0120	0.0114	10	0.62
MP4[c]	422	0.0186	0.0179	12	0.86
QCISD	442	0.0128	0.0122	10	0.64
QCISD(T)	422	0.0197	0.0189	12	0.91
QCISD(T)/MP2[d]	415	0.0223	0.0215	13	1.06

[a] Hg (5*s*5*p*) core has been kept inactive in the correlation procedures otherwise indicated.
[b] Full active orbital space including the Hg (5*s*5*p*) core.
[c] MP4 without triples (MP4SDQ).
[d] QCISD(T) corrected by substitutions out of the Hg (5*s*5*p*) core (difference between MP2 and MP2/F).
[e] D_0 contains the zero-point vibrational energy correction.

At large R, the $V(R)$ tends to $-C_6/R^6$ and could be related to the monomer properties through the Casimir–Polder formula [33]:

$$C_6 = \frac{3}{\pi}\int_0^\infty \alpha(iE)^2\,dE \tag{2}$$

C_6 being the van der Waals coefficient. Such a calculation of C_6 for Hg_2 using a simple 2 VE-PP was reported by Maeder and Kutzelnigg [34]. In terms of this formula, our $\alpha(0)$ is good but the $\alpha(iE)$, $E > 0$, less good.

We did verify that the calculated Hg_2 $V(R)$ behaves as R^{-6} for larger R, see Fig. 4. The simple London formula:

$$V_L = -(3/4)\alpha^2(IP_1)R^{-6} \tag{3}$$

or the Slater–Kirkwood formula:

$$V_{S-K} = -(3/4)\alpha^{3/2}n^{1/2}R^{-6} \tag{4}$$

give results below the *ab initio* ones. Here n is the number of valence electrons per atom (in Fig. 4, $n = 2$).

Cambi et al. [35] suggest for n in Eq. (4) the formula:

$$n_{eff} = E_{HOMO}\sum_{i=1}^{shells}(n_i/E_i). \tag{5}$$

Using Desclaux's DF data [36] we get for Hg:

$$n_{eff} = 9.668. \tag{6}$$

With this value, the Slater–Kirkwood formula (4) would closely agree with the QCISD(T)/MP2 curve in Fig. 4. (Down to the 5*s* shell, the n_{eff} would reach a slightly smaller value of 8.219). The last point at $R = 6$ Å, would correspond to a C_6 of 399 a.u. The experimental value of Stwalley and Kramer [37] is much smaller, 240 a.u. Maeder and Kutzelnigg [34] obtained, using a simple two-electron pseudopotential, 222 a.u. Thus the conclusion is that in our approach the $V(R)$ at large R becomes too attractive by nearly a factor of 2.

It is interesting to note that the calculated cohesive energy of the metallic bonds of bulk mercury is diminished from 1.21 eV to 0.27 eV by relativistic effects (exp. 0.67 eV) [38]. Pyper *et al.* [7] also found a relativistic decrease of the dimer D_e. Here, at "MP2/F" level, we rather find a very slight increase of D_e from 0.0716 to 0.0745 eV.

5 Conclusion

The calculated α(Hg) at higher levels of correlation (MP3, MP4, QCISD, QCISD(T)) is stable and close to experiment. The weak, attractive potential of the Hg_2 dimer was found to be a much harder problem in the present approach: The D_e at the best affordable level is roughly half of the experimental value while the effective C_6 at large R is roughly twice too large. Future will show whether a larger basis set, core-polarisability corrections, other core effects in the pseudopotential approach, improved BSSE corrections, even higher level of correlation, spin-orbit splitting or, to some extent, the Breit correction are needed to reach agreement with experiment.

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