VAN DER WAALS MINIMA IN EXCITED STATES
BY MØLLER–PLESSET PERTURBATION THEORY:
THE a $^3\Sigma_u^+$ STATE OF He₂ AND THE $^3\Pi$ STATE OF MgHe

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The species which exhibit van der Waals minima in excited states, He₂ in the a $^3\Sigma_u^+$ state and MgHe in the $^3\Pi$ state, were studied by means of Møller–Plesset perturbation theory. Good agreement of R_e and D_e is obtained with a semi-empirical extrapolation in the former case and with the best theoretical estimates in the latter case.

1. Introduction

It has recently been shown that Møller–Plesset perturbation theory (MPPT) can provide a reliable and often accurate description of very weak intermolecular complexes which are bound by dispersion forces [1–5]. Among the many post-Hartree–Fock (HF) theories, MPPT is particularly attractive since this theory may be straightforwardly applied without introducing additional arbitrary choices or approximations and is size consistent. Moreover, it may be viewed as a well defined approximation to the more general coupled-cluster (CC) theory. If applied to calculate interaction energies within the supermolecular approach it may be related to the perturbation theory of intermolecular forces [6]. As pointed out by Chałasiński et al. [2], application of MPPT to "dispersion-bound" complexes requires using (a) a basis set optimized for the intersystem correlation effects (i.e. dispersion), and (b) the full counterpoise (CP) correction [7] to remove the basis set superposition error (BSSE). In earlier work this

strategy was successfully employed in our study of the Mg and Ar dimers [2].

Thus far only the ground states of such van der Waals complexes have been studied by means of the MPPT supermolecular approach. In this Letter we demonstrate the efficiency of this method also in the treatment of very weak van der Waals systems in excited states. To this end we have chosen two very challenging cases: (a) the van der Waals minimum which occurs in the long-range part of the potential of the a $^3\Sigma_u^+$ state of He₂, and (b) the van der Waals well in the $^3\Pi$ state of MgHe. Both these states are the lowest triplet states of these species, a fact which facilitates treatment by means of the unrestricted Hartree–Fock (UHF) MPPT.

The van der Waals well in the a $^3\Sigma_u^+$ state of He₂ belongs to the shallowest minima known and hence it is extremely difficult to investigate. The semi-empirical estimate of D_e by Jordan et al. [8] amounts to 0.982 cm^{-1} at $R_e \approx 6.75$ Å. This finding has been questioned by Konowalow and Lengsfield [9], who obtained a D_e of 3.82 cm^{-1} at $R_e = 6.14$ Å by using the multiconfiguration self-consistent (MC SCF) method with an extended basis set. Resolution of this

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disagreement is desirable since the van der Waals well in this state is of interest to those who discovered that high-energy electron bombardment of liquid helium leads to atomic "bubbles" of radius ≈ 6 Å which contain $2\,^3S$ excited atoms within the liquid [10].

The potential energy curve of the $^3\Pi$ state of MgHe has been calculated by means of the interacting correlated fragments–configuration interaction (ICF–CI) method by Pouilly et al. [11] in their study of the interaction between the ^3P state of Mg and the ground state of He. The interactions between ^3P states of alkaline earth atoms with ^1S states of rare gas atoms are interesting in the context of fine-structure-changing collisions [12]. The $Mg(^3P)\ldots He(^1S)$ interaction serves as the simplest prototype system which is likely to be amenable to experimental determination. According to Pouilly et al. [11], the $^3\Pi$ state is characterized by $R_e = 7.9\ a_0$ and $D_e = 16\ cm^{-1}$. The $^3\Pi$ state is the lowest triplet state out to an internuclear distance R of $14\ a_0$, where it crosses the $^3\Sigma$ state related to the same separated-atom limit.

2. Method

In the present calculations, the UHF MPPT method is implemented within the GAUSSIAN 82 computer codes [13,14]. Interaction energies were evaluated by means of the supermolecular approach, and the counterpoise (CP) method [7] was used to correct for basis set superposition error (BSSE). The adequacy of the CP method has recently been rationalized and analyzed by Gutowski et al. [15–17] (see also refs. [4,18]). The CP-corrected interaction SCF energies and the ith order MPPT energies are denoted by ΔE^{SCF} and $\Delta E^{(i)}$, respectively. The related CP corrections themselves are denoted δ^{SCF} and $\delta^{(i)}$, respectively. The energies through the ith order and the related CP corrections are denoted $\Delta E(i)$ and $\delta(i)$, respectively.

3. The a $^3\Sigma_u^+$ state of He$_2$

3.1. Basis sets

Two Gaussian basis sets were used. The first basis, [10s5p2d/7s4p2d], was used by Sunil et al. [19] in

their study of the two lowest $^3\Sigma$ and the two lowest $^1\Sigma$ states of He$_2$. The second basis, [7s4p2d'1f], is a modification of the above [7s4p2d] basis obtained by (a) replacing the exponent of $1.5\ a_0^{-2}$ within the d-symmetry set by $0.15\ a_0^{-2}$, and (b) adding a set of seven f-symmetry functions with an exponent of 0.05 a_0^{-2}. This basis augmentation was necessary to improve the description of the dispersion effect in the region of the van der Waals minimum. The exponents (0.15 and 0.05 a_0^{-2}) are optimized values obtained by minimizing the second-order MPPT interaction energy, $\Delta E^{(2)}$, at 6.75 Å (the van der Waals minimum region). Such a procedure is justified by the fact that $\Delta E^{(2)}$ is dominated in this case by the uncoupled Hartree–Fock dispersion contribution [6], which may be viewed as a variational quantity [20]. The atomic energies obtained with both basis sets are given in table 1.

3.2. Results and discussion

Although the region of the van der Waals minimum was of primary interest to us we have calculated the interaction energies from 0.95 to 15 Å. The UHF MP3 option of GAUSSIAN 82 was chosen [#1] and the multiplicity set equal to 3 to select the lowest triplet state of He$_2$. The resulting triplet states of both the He atom and the dimer were almost pure triplet states, the spin being different from 1 by less than 0.01%.

The interaction energies are listed in table 2. They are analyzed in more detail in table 3 for the three most interesting distances: (a) the chemical well region (1.05 Å), (b) the barrier region (2.5 Å), and (c) the van der Waals minimum region (6.75 Å).

In the region of the chemical well, the interaction energy calculated through third order $\Delta E(3)$ is somewhat too large and at 1.05 Å differs by a few percent from the MC SCF result of Sunil et al. [19]. The agreement deteriorates with increasing R. In this region, BSSE is relatively small and insignificant. The dominant attractive contribution to the interaction energy resides in the SCF energy. A fairly strong bond

[#1] The restriction to the MP3 level of theory was due to the fact that our version of GAUSSIAN 82 could not handle the fourth-order MPPT in the case of the triplet state of a two-electron system.

Table 1
Atomic energies for the ^1S state of He($1s^2$) and ^3S state of He($1s2s$) obtained with the basis sets used in the calculations of the a $^3\Sigma_u^+$ state of He$_2$. All energies in hartree

Order of MPPT	^1S He($1s^2$)		^3S He($1s2s$)	
	[7s4p2d]	[7s4p2d'1f]	[7s4p2d]	[7s4p2d'1f]
E^{UHF}	−2.861480723	−2.861480723	−2.173705302	−2.173705302
$E^{(2)}$	−0.033712393	−0.031588205	−0.000641523	−0.000640254
$E^{(3)}$	−0.004889433	−0.005312914	−0.000164075	−0.000164049
$E(3)$	−2.900082549	−2.898381842	−2.174510900	−2.174509606
full CI	−2.9011 [a]		−2.1746 [a]	
exact	−2.90372 [b]		−2.17523 [b]	

[a] Ref. [19], basis [7s4p2d]. [b] Ref. [21].

Table 2
The interaction energy in the a $^3\Sigma_u^+$ state of He$_2$. All energies in μhartree

R (Å)	ΔE(3)		MC SCF [a]
	[7s4p2d]	[7s4p2d'1f]	
0.95	−59891		−64328
1.05	−67750		−69758
1.50	−20502		−33436
2.00	4097		−3676
2.50	4825		2714
3.00	2982		2535
4.00	649.2		695
5.00	90.7		110
6.00	4.30		7
6.50	−2.34	−3.74	−
6.75	−3.29	−4.28	−
7.00	−3.53	−4.22	−
7.25	−3.40		−
7.50	−3.10		
8.00	−2.4		
9.00	−1.2		

[a] The MC SCF calculations of Sunil et al. [19] with basis [7s4p2d]. The values obtained from table V of ref. [19] assuming that the result at 12 Å corresponds to the separated-atom limit.

in this region has been attributed to the "core" He($1s$)$^+$...He($1s^2$) interaction [22] with the 2s valence electron surrounding the molecule.

In the region of the barrier [23], $\Delta E(3)$ yields an energy of 3.0 kcal/mol, which is to be compared with the MC SCF result of 1.70 kcal/mol [19] and the experimental value of 1.43 kacl/mol [8]. It is fair to state that the height of the barrier is only approximately reproduced (however, the MPPT method is not expected to be appropriate in the region of the barrier). In this region, the SCF interaction energy is repulsive and dominates over the substantially smaller attractive correlation contributions. The BSSE is relatively small and does not exceed 3% of the barrier's height.

In the region of the van der Waals well, the MP3 calculations with our best basis predict R_e to lie between 6.75 and 7.0 Å and D_e of 0.938 cm^{-1}, in good agreement with the semi-empirical values of 6.75 Å and 0.982 cm^{-1} [8]. It is important to analyze the accuracy of our result. The physical origin of the long-range van der Waals well in the a $^3\Sigma_u^+$ state is similar to that in the ground state of He$_2$ except that one helium atom has a 2s orbital occupied which is much

Table 3
The components of the interaction energy in the a $^3\Sigma$ state of He$_2$ in the regions of the chemical minimum (1.05 Å), the barrier (2.50 Å) and the van der Waals minimum (6.75 Å). All energies in μhartree

R (Å)	ΔE^{SCF}	δ^{SCF}	$\Delta E^{(2)}$	$\delta^{(2)}$	$\Delta E^{(3)}$	$\delta^{(3)}$	$\Delta E(3)$	$\delta(3)$
1.05 [a]	−48979	190	−14887	30	−3887	0	−67753	220
2.50 [a]	5297	110	−387	10	−85	0	4825	110
6.75 [a]	5.29	15.91	−6.78	1.83	−1.80	0.12	−3.29	17.86
b)	5.22	23.31	−7.54	3.11	−1.96	0.04	−4.28	26.5

[a] Basis [7s4p2d]. [b] Basis [7s4p2d'1f].

more diffuse than the 1s orbital. The SCF interaction energy is repulsive and dominated by the $2s_a$–$1s_b$ valence exchange repulsion effect. The attraction is brought about by the dispersion effect arising between the 1s2s electron pair of one atom with the $1s^2$ electron pair of the other. The dominant dispersion contribution, the so-called uncoupled Hartree–Fock (UCHF) dispersion term, is reproduced within the second-order MPPT [6]. The third-order MPPT allows for some intrasystem electron correlation corrections (of the so-called "apparent" type) to the UCHF dispersion [6]. Owing to the presence of the p-, d- and f-symmetry polarization functions in our basis set (one d and one f orbital with exponents optimized in the region of the van der Waals minimum), the dominant portions of the dispersion energy through the R^{-10} terms are expected to be reproduced correctly. This conclusion is supported by the experience gained with basis set effects in perturbation and supermolecular calculations of the ground-state potential of He_2 [17,24]. In particular, a basis set of a similar quality to the one used here (a [4s3p2d1f] basis) provided the interaction energy between ground-state He atoms of (van der Waals minimum region) -4.04, -5.84 and -6.54 cm^{-1} at the MP2, MP3 and MP4 level of theory, respectively, compared with the recent experimental result of -7.61 cm^{-1} [25].

Additional information on the role of the fourth and higher orders is provided by comparison of the C_6 van der Waals coefficient obtained at the MP2 and MP3 levels with the exact coefficient of Victor et al. [26] (see also ref. [27]). The MP2, MP3 and accurate correlated values of C_6 are 19.8, 25.4 and 29.1 a_0^6 hartree respectively. Since the calculation of C_6 for the interaction under consideration requires only p-symmetry polarization functions, our values of C_6 may be regarded as fairly accurate.

On the basis of the above evidence, we expect that our estimate of D_e may be 10–20% to small. Comparison with the semi-empirical estimate suggests an even better accuracy, but one should remember that the semi-empirical result is only an extrapolation based on accurate dispersion coefficients and accurately determined exponential repulsion at long range [8].

It should be stressed that it is unlikely that the cor-

rect well depth is as large as 3.82 cm^{-1} [9]. This high value of D_e, obtained by Konowalow and Lengsfield [9], may be attributed to BSSE. These authors estimated the BSSE of their calculations to be 2.2 cm^{-1} at 12 a_0 but did not correct for it. By using this value as an approximate correction in the CP method one obtains a D_e of 1.6 cm^{-1}, a result much closer to the others.

It is interesting to comment on the BSSE in our calculations. This error is relatively large when compared to the value of the total interaction energy, and, unless removed by the CP method, would provide much too deep a well. It should be stressed that the relative size of BSSE with respect to the interaction energy does not provide any information on the actual error to the latter quantity, in agreement with previous findings [4,15–18].

4. The $^3\Pi$ state of MgHe

4.1. Basis set

For Mg the [13s9p/6s5p] CGTO basis set of McLean and Chandler [28], optimized for the ^3P state of Mg(3s3p), was used. This basis was supplemented with two sets of five d-symmetry orbitals with exponents of 0.26 and 0.086 a_0^{-2}, and one set of seven f-symmetry orbitals with an exponent of 0.14 a_0^{-2}. The exponents of these polarization functions were taken from Diercksen et al. [29] (see also ref. [2]). This basis is hereafter denoted [6s5p2d1f].

For He, a [10s3p2d1f/5s3p2d1f] CGTO basis set was used. The s-symmetry set was taken from van Duijneveldt [30]. The p-symmetry set with expo-

Table 4
Atomic energies of the ^3P state of Mg(3s3p) and the ^1S state of He($1s^2$) obtained with the basis sets used in the calculations of the $^3\Pi$ state of MgHe. All energies in hartree

Order of MPPT	^3P Mg(3s3p)	^1S He($1s^2$)
E^{UHF}	-199.540735379	-2.861672942
$E^{(2)}$	-0.002260952	-0.032334729
$E^{(3)}$	-0.000992374	-0.005096290
$E^{(4)}$	-0.000480381	-0.000908100
$E(4)$	-199.544469086	-2.900012061

nents of 3.0472, 0.7591 and 0.1943 a_0^{-2} is a compromise basis set designed to reproduce simultaneously the intra- and inter-atomic correlation effects in the ground state of He_2 [17,31]. Two sets of five d-symmetry orbitals with exponents of 0.49871 and 0.15293, and one set of seven f-symmetry orbitals with an exponent of 0.1836, were all optimized for the dispersion energy in ground-state He_2 by Gutowski et al. [24]. The atomic energies obtained with these basis sets are given in table 4.

4.2. Results and discussion

The interaction energies between ^3P Mg(3s3p) and ^1S He($1s^2$) were calculated for a wide range of internuclear distances, from 5 to 15 a_0. The UHF MP4 option of GAUSSIAN 82 [14] was chosen and the multiplicity was set equal to 3 to select the lowest triplet state of the MgHe system. The resulting triplet states of both the Mg atom and the MgHe system were almost pure triplet states with the total spin differing from 1 by less than 0.01%. The frozen core approximation was used throughout the calculations with the Mg $1s^2 2s^2 2p^6$ electrons constituting the core.

Our interaction energies at the MP4 level are listed in table 5 along with the values obtained by means of the ICF–CI method by Pouilly et al. [11], who used a fairly large STO basis containing f-symmetry functions. Our results and the results of Pouilly et al. agree very well in the repulsive region (out to 6 a_0). In the region of the minimum, the potential of Pouilly et al. is slightly deeper, the relative difference of 8% with respect to our result at 8.0 a_0 slowly increases

Table 5
Interaction energy between the Mg(^3P) and He(^1S) atoms in the $^3\Pi$ state of MgHe. All energies in µhartree

R (a_0)	$\Delta E(4)$	ICF–CI [a]
5.0	1532.8	1526.2
6.0	237.9	234.7
7.0	−47.7	−53.1
8.0	−66.6	−72.2
9.0	−43.4	−48.2
10.0	−24.7	−28.7
12.0	−8.0	−11.0
15.0	−2.0	−3.4

[a] ICF–CI calculations of Pouilly et al. [11].

with increasing R to reach 13% at 10 a_0 and 26% at 12 a_0. Near 14 a_0, according to Pouilly et al., the curves of the $^3\Pi$ and $^3\Sigma$ states cross, therefore we did not pursue our investigation beyond 12 a_0 by means of MPPT. The difference between the results of Pouilly et al. and ours in the region between the crossing point and the minimum may be attributed to deficiencies in our basis set as well as to the MP4 approximation. It should be noted that the ICF–CI values may not be accurate either. On the one hand, the ICF approach proved capable of providing accurate potential energy curves for several very weakly bound systems [32,33]. On the other hand, the accuracy of this method relies on somewhat arbitrarily balanced treatment of inter- and intra-system correlation effects and may give too deep a well [1,34].

In table 6 the results at three distances representative of three physically different regions are analyzed in more detail: (a) the repulsive part, 6 a_0, (b) the region of the van der Waals minimum, 8 a_0, and (c) the region between R_e and the crossing with the curve of the $^3\Sigma$ state, 12 a_0.

Judging from the relative size of the consecutive perturbation energyes, the convergence of the MPPT is good. The ratios $\Delta E^{(2)}/\Delta E^{(3)}$ and $\Delta E^{(3)}/\Delta E^{(4)}$ are similar at all three distances. To achieve a reasonable accuracy, the fourth-order MPPT is important. For instance, $\Delta E^{(4)}$ amounts to $\approx 10\%$ of the total interaction energy $\Delta E(4)$ at 8 a_0. It is interesting to note that both the single, double and quadruple (SDQ) as well as triple (T) electron excitations provide negative contributions. Moreover, the T terms give rise to half of $\Delta E(4)$.

5. Summary and conclusions

The potential energy curves in the region of the van der Waals minima were calculated for the a $^3\Sigma_u^+$ state of He_2 and the $^3\Pi$ state of MgHe by means of MPPT, through the third and fourth order, respectively. The van der Waals wells under investigation are very shallow. In the case of the van der Waals well in the a $^3\Sigma_u^+$ state of He_2 our calculations yielded values for D_e and R_e equal to 0.938 cm^{-1} and 6.75–7.0 Å, in good agreement with the semi-empirical estimates of 0.982 cm^{-1} and 6.75 Å [8].

In the case of the $^3\Pi$ state of MgHe our calcula-

Table 6
The components of the interaction energy between the $Mg(^3P)$ and $He(^1S)$ atoms in the $^3\Pi$ state of MgHe. All energies in µhartree

$R(a_0)$	ΔE^{SCF}	$\Delta E^{(2)}$	$\Delta E^{(3)}$	$\Delta E^{(4)}$	$\Delta E(4)$	δ^{SCF}	$\delta(4)$
6.0	732.8	−385.6	−80.0	−29.3	+237.9	66.2	89.0
8.0	40.3	−81.9	−18.4	−6.6	−66.6	22.0	27.2
12.0	0.16	−5.94	−1.45	−0.50	−8.05	1.36	1.53

tions yielded D_e and R_e of 8.0 a_0 and 14.6 cm^{-1}, in good agreement with probably the best ab initio values of 7.9 a_0 and 15.8 cm^{-1} [11].

The above results demonstrate that the MPPT method can provide a quantitative description of very weakly bound van der Waals complexes in excited states, provided one can a priori predict and avoid curve crossing and near-degeneracy problems.

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