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CEPA Calculations on Open-Shell Molecules. III. Potential Curves for the Six Lowest Excited States of He_2 in the Vicinity of Their Equilibrium Distances

Jan Wasilewski

Institute of Physics, Nicholas Copernicus University, Torun, Poland

Volker Staemmler and Ralph Jaquet

Ruhr-Universität Bochum, Abteilung für Chemie, 4630 Bochum 1, Federal Republic of Germany

CEPA-PNO and PNO-CI calculations have been performed for the potential energy curves of the He_2^+ ground state and the six lowest excited states of He_2 in the range of $1.4\ a_0 \leq R \leq 3.5\ a_0$. The calculated equilibrium distances as well as the spectroscopic constants are in very good agreement with molecular constants as derived experimentally from the rotation–vibration spectrum of He_2 by Ginter, except for the $c\ ^3\Sigma_g^+$ state. This latter discrepancy is probably due to an "obligatory" hump in the $c\ ^3\Sigma_g^+$ state occurring at $3.5\ a_0$ which cannot be properly treated in our calculation. The relative energetic positions of the six lowest states and their ionization energies are reproduced by our calculations with an accuracy of $0–400\ cm^{-1}$. Extrapolation of our results to infinite basis sets leads to estimates of the dissociation energies of He_2 excited states which cannot be measured spectroscopically because of the humps in all these states.

Key words: CEPA – Excited states of He_2.

1. Introduction

The excited states of He_2 show some unusual properties which have attracted the early interest both of experimentalists and theoreticians. While the ground state of He_2 is purely repulsive, exhibiting only a very shallow van-der-Waals

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minimum of 10.57°K≈0.00091 eV at 2.97 Å [1, 2], several of the excited states are chemically bound with binding energies up to 2.5 eV and equilibrium distances close to 1.0 Å [3]. The occurrence of highly excited (~16 eV) bound states above a repulsive ground state makes He_2 a favoured candidate for the construction of a VUV excimer laser. On the other hand, the existence of humps at about 2–3 Å on nearly all potential curves of bound excited states has caused a great amount of theoretical studies, both in a qualitative and a quantitative way.

The first calculation of excited state potential curves for He_2 has been reported by Buckingham and Dalgarno [4], the fundamental discussion of the origin of "obligatory" humps is due to Mulliken [5]. Subsequently, many *ab initio* calculations were performed, mainly focussed on the problem of obligatory and non-obligatory humps at intermediate distances. A satisfying explanation for the existence of these humps was given by Guberman and Goddard [6] in their analysis of the nature of He_2 excited states. (Concerning a compilation of previous *ab initio* results the reader is referred to Ref. [6].) The long-range part of the singlet potentials and the hump heights and positions as calculated by Guberman and Goddard have recently been confirmed experimentally by the low-energy high-resolution differential cross section measurements of Brutschy and Haberland [7].

In this paper we focus our attention on the six lowest excited states of He_2, namely the $a\ ^3\Sigma_u^+$, $A\ ^1\Sigma_u^+$, $b\ ^3\Pi_g$, $B\ ^1\Pi_g$, $c\ ^3\Sigma_g^+$, $C\ ^1\Sigma_g^+$ states and in particular on the region near the potential minima of these states. Detailed experimental information about this part of the potential curves is available from the rotation-vibration analysis of electronic transitions between these states as performed by Ginter in a series of papers [8–10] in 1965. From these experiments RKR-potential curves can be deduced in the vicinity of the minima. Such experimental potential curves are presented in [11]. Above these six states about 20 and more higher excited Rydberg states have been identified and analyzed by Ginter and coworkers in later papers [12–15], but they will not be treated in this paper.

Apart from the spectroscopic investigations there is a number of recent *ab initio* calculations on the equilibrium properties of the He_2 excited states. But contrary to calculations on the long-range part of the potentials the agreement between experiment (i.e. spectroscopic information) and most of the previous calculations is rather poor as far as equilibrium distances, force constants etc. are concerned. The early work of Matsen and coworkers, as reviewed in [16, 17], yields rather poor equilibrium properties; similarly the R_e values for the A and C states reported in [6] are by 0.06 Å too large. Only the CI calculations of Mukamel and Kaldor on the $A\ ^1\Sigma_u^+$ state are comparable in accuracy to our calculations [18].

Since the bound excited states of He_2 are Rydberg states with potential minima closely resembling the potential minimum of the He_2^+ ion we have also included calculations on the ground state ($X\ ^2\Sigma_u^+$) of He_2^+. For this system two excellent *ab initio* calculations exist, one of them [19] for $2.0\ a_0 \leq R \leq 2.125\ a_0$, i.e. in the vicinity of the minimum, the other one [20] yielding a full potential curve between $R = 1.30\ a_0$ and ∞.

2. Method of Calculation and Basis Set

All calculations are performed using the CEPA-PNO program developed by us and described in the first part of this series [21, 22]. We always use canonical occupied SCF orbitals and correlate all four electrons.

Since our CEPA program in the present status of development requires a one-configuration reference wavefunction it was impossible to obtain the correct asymptotic behaviour for the potential curves. As Mulliken has shown [5] the correct dissociation of $a\ {}^3\Sigma_u^+$, say, requires a wavefunction of the kind

$$c_1|1\sigma_g\overline{1\sigma_g}1\sigma_u2\sigma_g|+c_2|1\sigma_g1\sigma_u\overline{1\sigma_u}2\sigma_u|$$

i.e. a superposition of two terms, the first of which consists of the "A-core" of He_2^+ $(1\sigma_g^21\sigma_u)$ with an $2\sigma_g$ Rydberg electron attached to it, the second is the "B-core" of He_2^+ $(1\sigma_u^21\sigma_g)$ with a $2\sigma_u$ Rydberg electron. For $R\rightarrow\infty$, dissociation into neutral atoms, i.e. $He(1s^2)+He(1s2s)$, enforces $|c_1|=|c_2|$ whereas at the minimum the strongly bound A-core dominates, i.e. $|c_1|\gg|c_2|$. Any treatment based on the A-core reference configuration only may yield acceptable results near the minimum but dissociates into a mixture of covalent and ionic states. The same argument holds for the other states. We have limited our treatment to $1.40\ a_0\leq R\leq 3.5\ a_0$. Inspection of the qualitative potential curves given in [16, 17] shows that the humps in all but the $c\ {}^3\Sigma_g^+$ states occur at much larger values of R and that the A-core can be expected to dominate in that region. For the $c\ {}^3\Sigma_g^+$ state, however, the position of the obligatory hump (=avoided crossing) is close to $3.5\ a_0$ such that we cannot hope our CEPA treatment to be as reliable for this state as it is for the other ones.

The orbital basis used in our calculations consisted of Gaussian lobe functions. p- and d-type basis functions are constructed from lobes as described elsewhere in detail [23, 24]. We started from a $6s$ Huzinaga basis [25] for each helium atom, augmented by three flat s-functions, four sets of p-functions and one set of d-functions (only $d\sigma$ and $d\pi$) with suitably chosen exponents. This basis consisting of 44 groups (Σ-basis) proved a satisfactory compromise between accuracy and computer time. It had to be augmented by two additional diffuse π-functions in order to describe the $1\pi_u$ Rydberg orbital in the two Π states (Π-basis, 52 groups). The total basis is given in Table 1.

In Table 2 the results of our SCF and CEPA calculations on the lowest states of He are collected. The S states are calculated with the Σ-basis (but only 22 groups), the P states analogously with the Π-basis. It can be seen that our CEPA excitation energies are too low by about $0.1\ eV\approx 800\ cm^{-1}$. This is caused by the fact that our basis accounts for only about 90% of the correlation energy of the He ground state (0.03776 a.u. instead of 0.04204 a.u. [27]). Since there is no correlation energy for He^+ and only a very small one ($\approx$0.001 a.u.) for the excited states this error of 0.116 eV should influence all excitation energies in the same way and cancel if energy differences between excited states are calculated. Typical errors for them are in the order of 0.01–0.02 eV.

Table 1. Basis set for He_2

Nr.	Type	η_i	c_i
1	s	192.4388	0.025612
		28.95149	0.191317
		6.633653	0.850953
2	s	1.879204	1
3	s	0.589851	1
4	s	0.193849	1
5	s	0.059	1
6	s	0.018	1
7	s	0.006	1
8–10	p	2.5	1
11–13	p	0.7	1
14–16	p	0.22	1
17–19	p	0.06	1
20–22	$d\sigma, d\pi$	0.28	1
23–24[a]	$p\pi$	0.02	1
25–26[a]	$p\pi$	0.006	1

[a] Excluded for the Σ-states.

Table 2. Results of He-atom calculations

State	SCF a.u.	CEPA a.u.	ΔE(CEPA) eV[a]	ΔE(exp) eV[ab]
He 1^1S	−2.861131	−2.898889	0	0
He 2^3S	−2.173650	−2.174556	19.710	19.820
He 2^1S	−2.123205	−2.145001	20.514	20.616
He 2^3P	−2.130860	−2.132006	20.868	20.964
He 2^1P	−2.121924	−2.122385	20.130	21.218
He^{+} ^2S	−1.999531		24.473	24.588

[a] Energy conversion factors used: 1 a.u. = 27.2116 eV, 1 eV = 8065.465 cm^{-1}.
[b] Ref. [26].

A comment is necessary to the SCF calculation for the 2^1S state with the electronic configuration $1s2s$. It is well known [28] that in this case the SCF approximation is not uniquely defined: Minimizing the energy expectation value of the $^1(1s2s)$ configuration with respect to the rotation $1s \leftrightarrow 2s$ does not yield an upper bound to the true energy of the 2^1S state and is not equivalent to the Brillouin condition $(1s^2|H|^1(1s2s)) = 0$, as long as the orbitals $1s$ and $2s$ are orthogonal. (Compare the respective discussion in Ref. [22].) We have used two alternative procedures: (a) Frozen core SCF, starting from He^+; this yields an energy of −2.154634 a.u., reasonably close to the energy minimum of method (1) as given in [28]; (b) SCF by means of the Brillouin condition, yielding −2.123205 a.u. (compare Table 2, and method (2) of Ref. [28]). The subsequent CEPA-calculations with single excitations included starting from either (a) or

Table 3. CEPA potential curves for the lowest states of He_2 (distances in a_0, energies in a.u.)

R	$a\,^3\Sigma_u^+$	$A\,^1\Sigma_u^+$	$b\,^3\Pi_g$	$B\,^1\Pi_g$	$c\,^3\Sigma_g^+$	$C\,^1\Sigma_g^+$	$He_2^+, X\,^2\Sigma_u^+$
1.40	−5.061223	−5.050165	−5.029011	−5.022053	−4.992203	−4.980768	−4.890755
1.60	−5.114636	−5.104445	−5.086418	−5.080353	−5.053350	−5.042865	−4.950576
1.80	−5.137127	−5.127123	−5.111876	−5.106434	−5.081721	−5.071759	−4.977998
1.984	−5.142062	−5.131928	−5.118854	−5.113818	−5.090931	−5.081160	−4.986551
2.16	−5.138727	−5.128329	−5.117020	−5.112268	−5.090981	−5.081354	−4.986100
2.40	−5.127760	−5.116848	−5.107529	−5.103062	−5.083783	−5.074103	−4.978326
2.70	−5.110553	−5.098846	−5.091395	−5.087140	−5.070221	−5.060316	−4.964134
3.00	−5.094002	−5.081385	−5.075215	−5.071071	−5.056408	−5.046200	−4.949711
3.50	−5.072464	−5.058089	−5.052988	−5.048910	−5.037831	−5.027148	−4.930090

(b) as reference coincide within less than 0.0005 a.u. For the calculation of the potential curve of the $C\ ^1\Sigma_g^+$ state of He_2 consistently method (b) has been chosen.

3. Spectroscopic Constants

Table 3 contains our CEPA results for nine points between 1.4 a_0 and 3.5 a_0 on the potential curves of the six lowest states of He_2 and of the $X\ ^2\Sigma_u^+$ ground state of He_2^+. Though the separation of these points seems to be quite large, in particular near the minima, we found that the calculation of spectroscopic constants from these points is possible without problems. Using two independent and completely different programs for the analysis of the potential curves we obtained results that differed by no more than 0.003 a_0 for R_e and 2 cm^{-1} for the lowest vibrational levels.

A series of different fits to the calculated points was tried in order to evaluate spectroscopic constants and to calculate the rotation-vibration spectrum: Polynomial fits in powers of R; polynomial fits using inverse powers of R and the calculated asymptotic energies; polynomial fits in inverse powers of R allowing for humps at intermediate separations. The results deviate only very slightly from each other.

The Tables 4 and 5 contain the most important spectroscopic properties as well as the dissociation energies for the ground state of He_2^+ and the six lowest states of He_2. The dissociation energy D_e is defined with respect to separated atoms, i.e.

$$D_e = E(\infty) - E(R_e).$$

For states with a hump this has to be distinguished from the "activation energy" for dissociation, $D_a = E(R_{max}) - E(R_e)$, i.e. the difference between the energies at the position of the hump and the equilibrium distance.

Additional information such as Dunham coefficients, rovibrational levels, results of different fitting procedures etc. is available upon request.

4. Discussion of the Results

(a) Contrary to many other examples there is no large difference between CI and CEPA results, therefore Tables 4 and 5 contain only the latter. For a system with only four electrons large "size consistency errors" cannot be expected, not even for the dissociation energy [31]. The CEPA results are slightly better than the CI results for energy differences such as D_e and T_{00}, but this does not hold in general for other properties.

(b) Since all excited states of He_2 are Rydberg states their potential curves closely resemble that of He_2^+, at least in the vicinity of the minima at $R \approx 2.0$ a_0. The extra Rydberg electron has a rather small but significant influence on equilibrium properties: If it is bonding ($2\sigma_g$ in the a, A states and to a smaller extent $1\pi_u$ in the b, B states) R_e is smaller and ω_e larger than for He_2^+, and vice versa if it is antibonding ($2\sigma_u$ in the c, C states). These effects are fairly well

Table 4. Spectroscopic constants of the lowest excited states of He_2 and of He_2^+[a]

State		$a\,{}^3\Sigma_u^+$	$A\,{}^1\Sigma_u^+$	$b\,{}^3\Pi_g$	$B\,{}^1\Pi_g$	$c\,{}^3\Sigma_g^+$	$C\,{}^1\Sigma_g^+$	$X\,{}^2\Sigma_u^+$ (He_2^+)
$R_e[a_0]$	exp[b]	1.975	1.965	2.009	2.014	2.072	2.063	2.042
	CEPA	+0.006	+0.011	+0.011	+0.013	+0.003	+0.010	+0.013
	SCF	−0.036	−0.026	−0.037	−0.035	−0.063	−0.024	−0.032
$\omega_e[cm^{-1}]$	exp[b]	1810	1861	1769	1766	1584[c]	1653	1698
	CEPA	+6	−15	−13	−21	+61	−1	−27
	SCF	+135	+102	+125	+115	+232	+121	+95
$\omega_e x_e[cm^{-1}]$	exp[b]	38.8	35.0	35.0	34.4	52.7[c]	41.0	35.3
	CEPA	−4.3	−1.5	−1.9	−1.8	−17.7	−12.3	−2.4
	SCF	−4.0	−0.4	−1.0	−0.4	−17.4	−6.1	−0.1

[a] The theoretical values are given relative to the experimental ones.

[b] All experimental values from Ref. [8], except for $b\,{}^3\Pi_g$ [10], $B\,{}^1\Pi_g$ [9], and He_2^+ [13].

[c] Alternative values given in Ref. [8] to fit the observed ΔG values: $\omega_e = 1565\ cm^{-1}$, $\omega_e x_e = 36.7\ cm^{-1}$.

Table 5. Dissociation and excitation energies for the lowest excited states of He_2

	D_e (eV)						T_{00} (cm^{-1})			
	SCF	CEPA	exp	[16]	[18]	[6]	SCF	CEPA	exp	Ref.
$a\,{}^3\Sigma_u^+$	1.031	1.867		1.20			0	0	0	
$A\,{}^1\Sigma_u^+$	2.191	2.396		1.71	2.31	1.883	1728	2238	2344	[11]
$b\,{}^3\Pi_g$	1.569	2.398		2.01			5035	5031	4768	[10]
$B\,{}^1\Pi_g$	1.662	2.524		1.99			6233	6115	5846	[9][c]
$c\,{}^3\Sigma_g^+$	−0.317	0.498		0.2			10 810	10 959	10 889	[8]
$C\,{}^1\Sigma_g^+$	0.673	1.039		0.90		0.644	13 874	13 087	13 290	[8][d]
He_2^+, $X\,{}^2\Sigma_u^+$	1.658	2.414	2.475[a]	2.469 [19][b] 2.459 [20][b]			33 086	33 931	34 302	[11]

[a] Concerning the discussion of the experimental dissociation energy of He_2^+ see Ref. [19, 20, 29, 30]. The best value is probably the estimate of 2.475 eV as given in [20].

[b] At $R = 2.0626\ a_0$.

[c] For A' in Table IV of Ref. [9] a value of 2344 cm^{-1} has been used.

[d] T_{00} for $C\,{}^1\Sigma_g^+ \rightarrow A\,{}^1\Sigma_u^+$ from Ref. [8].

described already in the SCF approximation, therefore the CEPA corrections to properties like R_e, ω_e, $\omega_e x_e$ are nearly the same for the excited states of He_2 (except for the $c\ ^3\Sigma_g^+$ state) as for the ground state of He_2^+.

Typical errors of the calculated properties are (except for $c\ ^3\Sigma_g^+$)

	SCF	CI or CEPA
$R_e(a_0)$	$-0.04 \cdots -0.03$	$+0.01$
$\omega_e(cm^{-1})$	$+120$	± 15
$\omega_e x_e(cm^{-1})$	-2	-2

which is in line with previous CEPA calculations [32, 33]. It should be emphasized that our selection of only 9 points over a rather large range of the potential curves may cause relatively larger errors in R_e, ω_e, $\omega_e x_e$, but should lead to a reasonable description of the higher vibrational levels. Since our values both for ω_e and $\omega_e x_e$ are too small, agreement with experiment becomes much better for the vibrational levels with $v = 2, \ldots, 6$ (which are not documented here, but are available on request).

(c) Similarly, since all states considered here are Rydberg states SCF results for excitation or ionization energies are expected to be rather accurate. The correlation energies of all the He_2 states at their respective equilibrium distances (except for the $C\ ^1\Sigma_g^+$ state for which SCF is treated differently, compare Sect. 2) are only by 0.002 to 0.005 a.u. larger than the one of He_2^+. Thus, correlation enlarges the ionization potentials[1] only by 400–1000 cm^{-1}. (For the higher excited Rydberg states the correlation correction should be even smaller, as we have shown in a similar study on H_2O^* [34].) But this leads to a considerable improvement of the ionization potentials: The SCF results are generally by about 1200–1600 cm^{-1} too low, the CEPA results by only 300–600 cm^{-1}. The remaining errors are primarily due to basis set deficiencies which affect the SCF approximation, but much more the correlation.

(d) The accuracy of the relative excitation energies, i.e. the T_{00} values with respect to the $a\ ^3\Sigma_u^+$ state, is even better: Within the Σ-states our results are good to about 100 cm^{-1}, the two Π-states are about 250 cm^{-1} too high. This indicates that the Π-basis is slightly worse than the Σ-basis.

(e) An estimate for the dissociation energies D_e of the different states can be obtained in the following way: Our basis set is capable of yielding about 90% of the total correlation energy of the He atom ground state. If we assume that the same percentage of the total correlation energy is also covered in the states of He_2 we find for He_2^+: Calculated total correlation energy at the CEPA minimum: 0.0658 a.u.; extrapolated total correlation energy: 0.0729 a.u. (to be compared to Liu's value of 0.0712 a.u. [19] and to the one obtained by Maas et al. of 0.0679 a.u. [20], both at $R = 2.0625\ a_0$); calculated and extrapolated extra molecular correlation energies: 0.0280 and 0.0309 a.u. respectively. The

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[1] The ionization potentials IP_{00} can be obtained from Table 5 as difference between the T_{00} value of the corresponding state and the T_{00} value of He_2^+.

difference of 0.0029 a.u. = 0.079 eV has to be added to the calculated dissociation energy, giving $D_e(\text{extrap.}) = 2.493$ eV which is rather close to the estimate of 2.475 eV of [20].

Using the same argument for the excited states of He_2 we get the following extrapolated D_e values: $a\ {}^3\Sigma_u^+$: 1.954 eV; $A\ {}^1\Sigma_u^+$: 2.476 eV; $b\ {}^3\Pi_g$: 2.476 eV; $B\ {}^1\Pi_g$: 2.611 eV; $c\ {}^3\Sigma_g^+$: 0.581 eV; $C\ {}^1\Sigma_g^+$: 1.134 eV. Assuming that our basis sets cover 85 or 95% of the total correlation we get an error estimate of ±0.04 eV consistently for all states. It is remarkable that the dissociation energies of three states, namely $X\ {}^2\Sigma_u^+$ of He_2^+ and A, b of He_2 nearly coincide; for X of He_2^+ and A of He_2 this has been also observed experimentally [11].

(f) The only severe deviation from experiment occurs for the $c\ {}^3\Sigma_g^+$ state. The vibration frequency in CEPA approximation is still 60–80 cm^{-1} higher than the experimental value [8]. The reason is probably the inadequacy of the present CEPA program to properly account for the "A-core" versus "B-core" interaction which affects the $c\ {}^3\Sigma_g^+$ potential curve already at rather short distances because of its low dissociation energy.

5. Conclusions

Since the excited states of He_2 are very well known spectroscopically the main object of our CEPA-PNO calculations was to investigate how reliable CEPA results are for equilibrium properties of excited states and for excitation energies themselves. The results seem to be encouraging. The values obtained for equilibrium properties (R_e, ω_e, $\omega_e x_e$) are comparable in their accuracy to those of previous CEPA calculations on molecular ground states [32, 33], even for the $C\ {}^1\Sigma_g^+$ state being the first excited state of ${}^1\Sigma_g^+$ symmetry. Typical errors are in the order of 0.01 a_0 for R_e and 20 cm^{-1} for ω_e.

The excitation energies with respect to the repulsive He_2 ground state are by about 1000 cm^{-1} too small. CEPA calculations on He atom excited states show that this discrepancy is due to basis set deficiencies: Our basis describes only 90% of the correlation within the He K-shell; but this defect of about 0.1 eV occurs consistently for all excitation energies of He and He_2. Relative excitation energies, i.e. energy differences between excited states are much more accurate. Typical errors are in the order of 200 cm^{-1}.

For nearly all properties considered here the CEPA method brings a considerable improvement with respect to SCF results. Though He_2 is a rather favourable example (only four electrons; one can afford a rather large basis set; Rydberg states of simple electronic structure in the vicinity of the minima) we are confident that we can get results of similar accuracy also for larger systems.

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