

Long- and Intermediate-Range Interaction in Three Lowest Sigma States of the HeH^+ Ion

W. KOŁOS

*Max Planck Institute for Physics and Astrophysics, D-8 Munich 40,
Federal Republic of Germany*

and

*Quantum Chemistry Group, University of Warsaw, PL-02-093 Warsaw, Poland**

Abstracts

Accurate variational energies have been calculated for three lowest sigma states of the HeH^+ ion. This includes the ground state ($5 \leq R \leq 9$ a.u.) which dissociates into $\text{He} + \text{H}^+$, as well as the $A\ ^1\Sigma^+$ state ($4 \leq R \leq 10$) and the $a\ ^3\Sigma^+$ state ($3 \leq R \leq 10$) which both dissociate into $\text{He}^+ + \text{H}$. The variational results are compared with those obtained using a perturbation theory expansion.

Des énergies variationnelles de haute précision ont été calculées pour les états sigma les plus bas de l'ion HeH^+ . Ceci inclue l'état fondamental ($5 \leq R \leq 9$ a.u.) qui dissocie en $\text{He} + \text{H}^+$, ainsi que l'état $A\ ^1\Sigma^+$ ($4 \leq R \leq 10$) et l'état $a\ ^3\Sigma^+$ ($3 \leq R \leq 10$) que dissocient tous les deux en $\text{He}^+ + \text{H}$. Les résultats variationnels sont comparés à ce qu'on obtient par un développement perturbatif.

Genaue Variationsenergien sind für die drei tiefsten Sigma-zustände des Ions HeH^+ berechnet worden. Dies bedeutet dass Berechnungen für die folgende Zustände gemacht worden sind: den Grundzustand ($5 \leq R \leq 9$ at.E.), der in $\text{He} + \text{H}^+$ dissoziiert, die Zustände $A\ ^1\Sigma^+$ ($4 \leq R \leq 10$) und $a\ ^3\Sigma^+$ ($3 \leq R \leq 10$) die beide in $\text{He}^+ + \text{H}$ dissoziieren. Die variationalen Ergebnisse werden mit entsprechenden Resultaten von Störungsentwicklungen verglichen.

1. Introduction

There is considerable interest in accurate theoretical energies for the HeH^+ ion. The ground-state potential energy curve is needed to interpret the observed HeH^+ resonances (e.g., see Refs. [1-3] and references therein). The potential energy curves for excited states are of interest in certain astrophysical problems [4], as well as in the study of the inelastic scattering processes. Theoretical results

*Permanent address.

for the HeH^+ ion are also of importance when considering the β -decay of tritium in the HT molecule [5, 6]. In addition, HeH^+ represents an interesting model system for the study of the long-range interactions. The ion, depending on its electronic state, may dissociate into $\text{He} + \text{H}^+$ or $\text{He}^+ + \text{H}$. In both cases the induction interaction exists at large internuclear separations. In the former case the effect of electron correlation on the induction interaction can be studied, whereas the latter case represents the simplest system in which the induction and dispersion interaction appear simultaneously. Due to the simplicity of the HeH^+ ion, fairly accurate calculations of the interaction energy between its components are feasible and they may give insight into the reliability of various approximations which are common in the theory of intermolecular interactions.

Accurate computation of the ground-state energy of HeH^+ has been carried out by Wolniewicz [6] but only for relatively small internuclear distances ($R \leq 1.8$ a.u.). Using simple wave-functions of the configuration interaction type, Michels [7] has calculated the energies of the ground state and of several excited states of HeH^+ for a wide range of R . In the latter article, complete references to earlier studies of HeH^+ can also be found. Recently a configuration interaction calculation for a large number of singlet sigma states of HeH^+ has been carried out by Green et al. [8]. The authors also give a detailed motivation of the theoretical work on HeH^+ , as well as complete references to recent theoretical papers on this subject.

In the present work, the energy of HeH^+ for relatively large internuclear distances has been determined more accurately than in any previous calculation. Variational method has been used, assuming wave-functions in the form of expansions in elliptic coordinates and depending explicitly on the interelectronic distance. The calculations have been carried out for the ground state which dissociates into $\text{He} + \text{H}^+$, and for the two lowest excited states, $A\ ^1\Sigma^+$ and $a\ ^3\Sigma^+$, which dissociate into $\text{He}^+ + \text{H}$, both in their $1s$ states. The interaction energies in the above three states have also been calculated using simple perturbation theory expansions. The two sets of results are presented in the following sections and the accuracy of the perturbation theory calculations is discussed.

2. Method

The variational wave-function used in the present work was assumed in the form of an expansion

$$\Psi = \sum_i c_i [\Phi_i(1, 2) \pm \Phi_i(2, 1)] \quad (1)$$

where the $+$ and $-$ sign refer to the singlet and triplet states, respectively. The basis functions used in eq. (1) are defined by

$$\Phi_i(1, 2) = (1/4\pi) \exp(-\alpha\xi_1 - \bar{\alpha}\xi_2 + \beta\eta_1 + \bar{\beta}\eta_2) \xi_1^{\epsilon_1} \xi_2^{\epsilon_2} \eta_1^{\epsilon_3} \eta_2^{\epsilon_4} \rho^{\epsilon_5} \quad (2)$$

where ξ and η denote the elliptic coordinates; $\rho = 2r_{12}/R$; r_{12} and R denote the interelectronic and internuclear distances, respectively; α , $\bar{\alpha}$, β , and $\bar{\beta}$, as well as c_i

in eq. (1), are variational parameters; and r_i , \bar{r}_i , s_i , \bar{s}_i , and μ_i are integers. An identical basis set was used by Wolniewicz [6] who, however, imposed restrictions on the nonlinear parameters. Since he was interested in small internuclear distances, he assumed $\alpha = \bar{\alpha}$ and $\beta = \bar{\beta}$ for the ground state and $\beta = -\bar{\beta}$ for the $A \ ^1\Sigma^+$ state. These assumptions considerably simplify the numerical computations, however they are unacceptable for large R . Therefore, in the present work all four nonlinear parameters in eq. (2) have been varied independently.

The method of calculation of the matrix elements resulting from the basis set (2) has been described previously [9]. The maximum values of r , s , and μ in eq. (2) were 5, 5, and 2, respectively.

3. Ground State

The final wave-function (1) used for the ground state was composed of 83 terms of the form of eq. (2). It contained most of the terms used by Wolniewicz [6] and, in addition, those terms which were found to be important for larger internuclear distances. Most of the test runs were made for $R = 6$ a.u.

The nonlinear parameters have been optimized for $R = 4.5$ and 8 a.u. in a 45-term expansion, and the same values have been used in the final 83-term wave-function. For intermediate values of R the exponents were interpolated and for $R = 9$ a.u. they were extrapolated.

In Table I we list for the ground state of HeH^+ the total energy E , the interaction energy E_{int} , and the derivative dE/dR obtained from the virial theorem. The 83-term wave-function in elliptic coordinates has also been employed to calculate the energy of the helium atom by using the present program for HeH^+ and $Z_2 = 0$ rather than the proton charge $Z_2 = 1$ in the input data. The resulting energy, given in the last row in Table I, is by 1.104×10^{-5} a.u. $= 2.42 \text{ cm}^{-1}$ higher than the exact value [10]. Most of the discrepancy can probably be accounted for by terms with $\mu > 2$, which are absent in our basis set. For consistency the computed approximate energy of the helium atom rather than the accurate value has been used to get the interaction energies listed in Table I.

TABLE I. Energies of HeH^+ in the $X \ ^1\Sigma^+$ state calculated with an 83-term wave-function.^a

R	E	E_{int}	dE/dR
5.0	- 2.90503585	- 290.26	0.00122961
5.5	- 2.90457118	- 188.28	0.00069936
6.0	- 2.90430035	- 128.84	0.00042875
6.5	- 2.90413077	- 91.62	0.00027922
7.0	- 2.90401924	- 67.14	0.00018986
7.5	- 2.90394302	- 50.41	0.00013370
8.0	- 2.90388937	- 38.64	0.00009697
9.0	- 2.90382196	- 23.84	0.00005479
∞	- 2.90371332		

^aAll results in atomic units; only E_{int} in cm^{-1} .

At large R the calculated interaction energy should be equal to the induction energy which, in the multipole expansion, can be expressed as

$$E_{\text{ind}} = - \sum_{l=1} \alpha_l / R^{2l+2} \quad (3)$$

where α_l denotes the 2^l -pole polarizability of the helium atom. Broussard and Kestner [11] and Singh [12] have calculated the dipole, quadrupole, and octopole polarizabilities of the helium atom neglecting electron correlation, as well as including this effect by using double perturbation theory. More accurate values of the dipole and quadrupole polarizabilities including electron correlation have been obtained by Davison [13]. Using their results in eq. (3), with $l \leq 3$, one gets the induction energies listed in Table II, where they are compared with the variational values.

TABLE II. He . . . H⁺ interaction energy (in cm⁻¹).

R	Induction energy		Variational energy
	No. correl. ^a	With correl. ^b	
5	- 280.5	- 262.2	- 290.3
6	- 132.1	- 123.2	- 128.8
7	- 70.4	- 65.5	- 67.1
8	- 40.9	- 38.0	- 38.6
9	- 25.4	- 23.6	- 23.8

^aObtained using $\alpha_1 = 1.4870$, $\alpha_2 = 2.3591$, $\alpha_3 = 10.036$ [12].

^bObtained using $\alpha_1 = 1.3796$, $\alpha_2 = 2.4403$, $\alpha_3 = 10.014$ [12, 13].

It is seen that at $R = 9$ the induction energy obtained from accurate polarizabilities agrees fairly well with the result of variational calculation of the interaction energy. The discrepancy amounts to 0.2 cm⁻¹, i.e. 1%. When the internuclear distance decreases to $R = 5$ the absolute discrepancy increases by two orders of magnitude and the relative discrepancy by one order of magnitude.

There are several possible reasons for the above discrepancy. Part of it may be due to our assumption of $\alpha_l = 0$ for $l > 3$ in expansion (3). This, however, is not likely to introduce a large error in the region under consideration. Most of the discrepancy is probably due to the charge overlap effects and to the inability of the first-order correction to the wave-function, which generates the induction energy (3), to describe properly the electron distribution in the vicinity of the proton. The variational energy obtained with a wave-function which is more flexible and not limited to the first order is seen to be lower than the induction energy at all values of R . At $R \approx 5.5$ the correlation error approximately cancels the error caused by the charge overlap effects, and E_{ind} calculated without taking into account electron correlation becomes fortuitously equal to the correct value.

4. Excited States

For the first excited singlet state of HeH⁺ a new selection of terms has been made, and in a 40-term expansion all 4 exponents have been optimized for $R = 4$,

5, 6, 8, and 10 a.u. For intermediate internuclear distances the exponents have been interpolated. In the final runs a 52-term expansion has been used. The resulting improvement of the energy over the 40-term result, being very small at large R (1 cm^{-1} at $R = 10$), amounted to 15 cm^{-1} at $R = 6$. Since for large R some instability of the energy has been noticed, the final values of the energy listed in Table III may be less accurate than those for the ground state. The equilibrium internuclear distance resulting from the calculated energies is $R_e = 5.53\text{ a.u.}$, which is only by 0.12 cm^{-1} smaller than the value obtained by Michels [7], whereas the total energy in the vicinity of R_e is by about 100 cm^{-1} lower than his result. For large R the recent results of Green et al. [8] agree very well with the present ones. This shows that the azimuthal correlation neglected by these authors is indeed very small for large R .

For the lowest triplet state of HeH^+ the energy has been found to converge faster with the number of terms in expansion (1) than for the singlet states. The nonlinear parameters have been optimized in a 28-term expansion for $R = 3, 4, 5, 6, 8$, and 10 a.u. The final energies listed in Table IV have been obtained with a 40-term wave-function. For $R = 10$ and $R = 6$ they are lower by only 0.03 and 3.4 cm^{-1} , respectively, than the 28-term results. In the vicinity of the equilibrium internuclear distance the total energy is by about 190 cm^{-1} lower than the result

TABLE III. Energies of HeH^+ in the first excited singlet state $A\ ^1\Sigma^+$ calculated with a 52-term wave-function.^a

R	E	E_{int}	dE/dR
4.0	- 2.49404468	1307.0	- 0.01690078
4.2	- 2.49686154	688.8	- 0.01163817
4.4	- 2.49878047	267.7	- 0.00782498
4.6	- 2.50005202	- 11.4	- 0.00509140
4.8	- 2.50086213	- 189.2	- 0.00315666
5.0	- 2.50134788	- 295.8	- 0.00180790
5.2	- 2.50160963	- 353.3	- 0.00088493
5.4	- 2.50171959	- 377.4	- 0.00026938
5.5	- 2.50173454	- 380.7	- 0.00004818
5.6	- 2.50172976	- 379.6	0.00012750
5.8	- 2.50167695	- 368.0	0.00037079
6.0	- 2.50158679	- 348.3	0.00050815
6.2	- 2.50147691	- 324.1	0.00057420
6.4	- 2.50135893	- 298.3	0.00059297
6.6	- 2.50124045	- 272.2	0.00058183
6.8	- 2.50112616	- 247.2	0.00055271
7.0	- 2.50101881	- 223.6	0.00051384
7.5	- 2.50078766	- 172.9	0.00040509
8.0	- 2.50060929	- 133.7	0.00030718
8.5	- 2.50047470	- 104.2	0.00022952
9.0	- 2.50037390	- 82.1	0.00017177
9.5	- 2.50029806	- 65.4	0.00012964
10.0	- 2.50024034	- 52.7	0.00009884

^aAll results in atomic units; only E_{int} in cm^{-1} .

of Michels [7], whereas the value of R_e is practically in agreement with his result, $R_e = 4.47$ a.u.

Both states, $A\ ^1\Sigma^+$ and $a\ ^3\Sigma^+$, dissociate into $\text{He}^+ + \text{H}$ in their $^2S(1s)$ states. Thus they are formally analogous to the $X\ ^1\Sigma_g^+$ and $b\ ^3\Sigma_u^+$ states of H_2 , respectively, except for the additional induction energy. However, a simple analysis demonstrates that the states in HeH^+ are quite different from those in H_2 .

In Table V the variational interaction energies of HeH^+ for the two states under consideration are compared with the long-range interaction energies calculated in the polarization approximation E_{pol} and with $E^{(1)} + E_{\text{pol}}$, where the first-order correction $E^{(1)}$ denotes the interaction energy obtained with the Heitler-London type wave-function.

The polarization energy E_{pol} , listed in Table V, has been calculated as

$$E_{\text{pol}} = E_{\text{ind}}(5) + E_{\text{disp}}^{(2)} \quad (4)$$

where $E_{\text{ind}}(5)$ is the induction energy calculated in the polarization approximation through the fifth order of the perturbation theory, including all terms up to the order of R^{-11} . The coefficients of the expansion calculated by Dalgarno and

TABLE IV. Energies of HeH^+ in the lowest triplet state $a\ ^3\Sigma^+$ calculated with a 40-term wave-function.^a

R	E	E_{int}	dE/dR
3.0	- 2.48696295	2861.3	- 0.03835147
3.2	- 2.49332464	1465.1	- 0.02607966
3.4	- 2.49760394	525.9	- 0.01732106
3.6	- 2.50040052	- 87.9	- 0.01110957
3.8	- 2.50214991	- 471.9	- 0.00674747
4.0	- 2.50316836	- 695.4	- 0.00372724
4.2	- 2.50368519	- 808.8	- 0.00167335
4.4	- 2.50386574	- 848.4	- 0.00031674
4.5	- 2.50386832	- 849.0	0.00016497
4.6	- 2.50382824	- 840.2	0.00054350
4.8	- 2.50365631	- 802.5	0.00105598
5.0	- 2.50340810	- 748.0	0.00132868
5.2	- 2.50312311	- 685.4	0.00144261
5.4	- 2.50282758	- 620.6	0.00145171
5.6	- 2.50253818	- 557.1	0.00139537
6.0	- 2.50201321	- 441.8	0.00118951
6.5	- 2.50148856	- 326.7	0.00089581
7.0	- 2.50110194	- 241.8	0.00064898
7.5	- 2.50082421	- 180.9	0.00046480
8.0	- 2.50062554	- 137.3	0.00033398
8.5	- 2.50048238	- 105.9	0.00024244
9.0	- 2.50037788	- 82.9	0.00017859
9.5	- 2.50030037	- 65.9	0.00013368
10.0	- 2.50024195	- 53.1	0.00010164

^aAll results in atomic units; only E_{int} in cm^{-1} .

TABLE V. $\text{He}^+ \dots \text{H}$ interaction energies for the lowest singlet and triplet states (in cm^{-1}).

R	$E_{\text{ind}}(5)$	$E_{\text{disp}}^{(2)}$	E_{pol}	$A \ ^1\Sigma^+$		$a \ ^3\Sigma^+$	
				$E^{(1)} + E_{\text{pol}}$	E_{var}	$E^{(1)} + E_{\text{pol}}$	E_{var}
6	-529.94	-4.18	-534.12	-554.17	-348.26	-512.84	-441.85
7	-250.63	-1.55	-252.17	-255.09	-223.60	-249.10	-241.85
8	-137.27	-0.66	-137.93	-138.35	-133.72	-137.50	-137.29
8.5	-105.40	-0.45	-105.85	-106.01	-104.18	-105.69	-105.87
9	-82.46	-0.31	-82.78	-82.84	-82.06	-82.72	-82.94
9.5	-65.56	-0.22	-65.78	-65.80	-65.42	-65.76	-65.90
10	-52.84	-0.16	-53.00	-53.01	-53.75	-53.00	-53.10

Stewart [14] have been used. $E_{\text{d} \text{isp}}^{(2)}$ in eq. (4) denotes the second-order dispersion energy which has been calculated up to the order of R^{-8} , using the coefficients computed by Davison [13]. Both components of E_{pol} are also given in Table V. No comparison of the results can be made for $R < 6$ since in this region the perturbation theory expansion for E_{ind} diverges. For $R < 9$ the asymptotic expansion of $E_{\text{i} \text{nd}}^{(4)}$ also diverges. Although the latter divergence does not seem to introduce a very serious error, the error is certainly of the order of $E_{\text{d} \text{isp}}^{(2)}$ which, therefore, has little meaning.

The results listed in Table V show that $E^{(1)} + E_{\text{pol}}$, in contrast to the interaction of two ground-state hydrogen atoms, represents a very poor approximation to the interaction energy of He^+ and H. We are reluctant to attribute any meaning to these energy differences in Table V which are of the order of a fraction of a cm^{-1} . The results, however, seem to provide conclusive evidence that $E^{(1)} + E_{\text{pol}}$ is not able to represent, even qualitatively, the relative location of the two states. The results shown in Table V strongly suggest that the second-order exchange energy $E_{\text{exch}}^{(2)}$, not included in $E^{(1)} + E_{\text{pol}}$, is very important in both states under consideration and should give a large repulsive contribution to the interaction energy.

5. Conclusions

The results of the present work supplement our previous study [15, 16] of the long-range interaction between simple atoms. It has been found previously [15] that in the case of two ground-state hydrogen atoms the dominant contributions to their long-range interaction energy come from the first-order exchange energy $E_{\text{exch}}^{(1)}$ and the second-order polarization energy $E_{\text{pol}}^{(2)}$. On the other hand, the long-range interaction between a $1s$ and a $2p\sigma$ hydrogen atom [16] is mainly determined by the $E_{\text{pol}}^{(1)}$ and $E_{\text{exch}}^{(2)}$.

The results of the present study of the $\text{He}^+ \dots \text{H}$ interaction show that, in this case, for large internuclear distances the total first-order correction $E^{(1)} = E_{\text{pol}}^{(1)} + E_{\text{exch}}^{(1)}$ is negligible. Here the interaction energy is mainly determined by the second- and higher-order polarization and exchange energies. These results give no basis for extrapolation to larger systems. However, they certainly give a warning

that approximate calculation of intermolecular interaction energies, in which the second-order exchange effects are neglected, may give erroneous results.

On the other hand, the results obtained for the $\text{He} \dots \text{H}^+$ interaction indicate that the effect of electron correlation on the induction energy is not very important. Its magnitude in the region under consideration is roughly of the same order as that of the intraatomic electron correlation on the $\text{He} \dots \text{He}$ interaction [17]. More critical, as in other cases, are the charge overlap effects.

Acknowledgments

It is a great pleasure to acknowledge the very kind hospitality of Dr. G. H. F. Diercksen extended to the author at the Max Planck Institute for Physics and Astrophysics in Munich where most of this work has been done.

This work was also supported, in part, by the Polish Academy of Sciences within the project 06.1.1.

Bibliography

- [1] J. Schopman, P. G. Fournier, and J. Los, *Physica* **63**, 518 (1973).
- [2] J. M. Peek, *Physica* **64**, 93 (1973).
- [3] R. B. Bernstein, *Chem. Phys. Letters* **25**, 1 (1974).
- [4] T. P. Stecher and J. E. Milligan, *Astrophys. J.* **136**, 1 (1962).
- [5] A. H. Snell, F. Pleasonton and H. E. Leming, *J. Inorg. Nucl. Chem.* **5**, 112 (1957).
- [6] L. Wolniewicz, *J. Chem. Phys.* **43**, 1087 (1965).
- [7] H. H. Michels, *J. Chem. Phys.* **44**, 3834 (1966).
- [8] T. A. Green, H. H. Michels, J. C. Browne, and M. M. Madsen, *J. Chem. Phys.*, in publication.
- [9] W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965).
- [10] C. L. Pekeris, *Phys. Rev.* **115**, 1217 (1959).
- [11] J. T. Broussard and N. R. Kestner, *J. Chem. Phys.* **53**, 1507 (1970).
- [12] T. R. Singh, *Chem. Phys. Letters* **11**, 598 (1971).
- [13] W. D. Davison, *Proc. Phys. Soc.* **87**, 133 (1966).
- [14] A. Dalgarno and A. L. Stewart, *Proc. Roy. Soc. (London)* **A238**, 276 (1956).
- [15] W. Kołos, *Int. J. Quantum Chem.* **S8**, 241 (1974).
- [16] W. Kołos, *Int. J. Quantum Chem.* **9**, 133 (1975).
- [17] P. Bertoncini and A. C. Wahl, *J. Chem. Phys.* **58**, 1259 (1973).

Received February 18, 1975.