Theoret. Chim. Acta (Berl.) 52, 163–170 (1979)

THEORETICA CHIMICA ACTA

Original Investigations

Natural Spin Orbital Analysis of Diatomic Molecular Wave Functions in Terms of Generalized Diatomic Orbitals

III. Variable Screening Models for Some Excited States of HeH^+ *

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The original idea of the model applied to HeH^+ excited states is: One electron occupies a diatomic orbital similar to the HeH^{++} ground state $1s\sigma$ function. The other electron occupies an orbital which can be represented by a linear combination of functions similar to H_2^+ excited state functions. One or two screening parameters are variationally optimized to compensate for the smallness of the one-electron basis.

CI calculations have been performed for five excited HeH^+ states covering a wide range of internuclear distances. The CI wave functions have been submitted to a natural spin orbital analysis. The strongly occupied NSOs are compared with the original model functions.

Key words: HeH^+ – Diatomic molecular wave functions

1. Introduction and Construction of Model

In connection with scattering problems there is renewed interest in the application of shielded diatomic orbitals to small diatomics [1–6]. On the other hand, very refined CI calculations have been performed on excited states of the helium hydride ion HeH^+ [7–11]. We therefore compare the results of our model calculations presented in 1971 [12][1] with the results of these two approaches.

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* Dedicated to Professor Hermann Hartmann on occasion of his 65th birthday on May 4th, 1979.

[1] A limited number of copies of [12] is available from the author on request.

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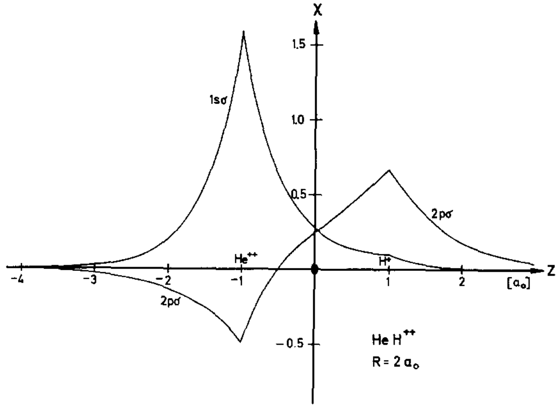

Fig. 1. Values of the wave functions $1s\sigma$ and $2p\sigma$ for HeH^{++} along the internuclear axis z

For each internuclear distance R and each electronic state chosen the construction of the model is performed in three steps:

In the first step, exact solutions of the screened two-centre Coulomb problem with potential energy

$$U(\alpha_k, \beta_k) = -\frac{2 - \alpha_k}{r_a} - \frac{1 - \beta_k}{r_b} \tag{1}$$

are computed by methods described in [13]. Here r_a denotes the distance between the electron and the helium nucleus, r_b the distance between the electron and the proton, and α_k, β_k are screening parameters.

For the one basis function $1s\sigma(\beta_i)$ which is used mainly to describe the "inner" or core electron, α_i is put equal to 0. β_i is a nonlinear variational parameter. The case $\beta_i = 0$ (HeH^{++}) is shown in Fig. 1.

For all the other one-electron basis functions which are used mainly to describe the "outer" electron, β_o is put equal to 0 and α_o is a common nonlinear variational parameter. The special case $\alpha_o = 1$, which essentially is H_2^+, is exhibited in Fig. 2.

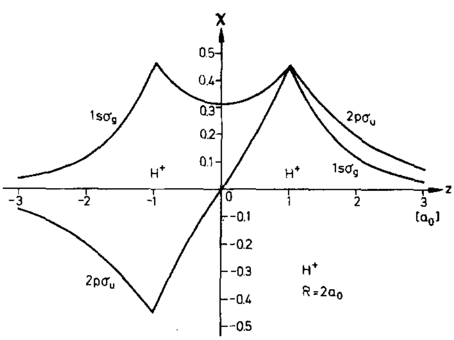

Fig. 2. Values of the wave functions $1s\sigma_g$ and $2p\sigma_u$ for H_2^+ along the internuclear axis z

For instance, one basis used for the $2\,^3\Sigma^+$ state was (II):

i: $1s\sigma(\beta)$

o: $1s\sigma_g'(0)$, $2s\sigma_g(0)$, $2p\sigma_u(0)$

in which full shielding ($\alpha_o = 1$) was assumed for the last three basis functions.

The first step ends with a Gram-Schmidt-orthogonalization procedure.

In the second step, a CI calculation with all configurations resulting from the orthogonalized one-electron basis set is performed. Details are described in [12] and [14]. The method of calculation of the two-electron integrals is due to Ruedenberg [15]; our method of transforming the two-electron integrals is described in the appendix of [14]. In the outmost loop of the program the nonlinear variational parameters β_i and α_o are optimized for the state under consideration at the internuclear distance R chosen.

In the third step, the CI wave function is analyzed into natural spin orbitals which appear as linear combinations of the model two-centre functions constructed in the first step. As a rule, in each strongly occupied natural spin orbital one two-centre basis function dominates.

It is seen that our 1971 screening model has two essential differences from Aubert's approach [4]:

1) Screening is variable since α_o and β_i are variational parameters. For the inner electron Aubert has $\alpha_i = \beta_i = 0$ (HeH^{++}) and for the outer electron keeps $\alpha_o = 0.92$ and $\beta_o = 0$ fixed.

2) Wave functions are not restricted to be single configurations. The natural spin orbital analysis, however, shows whether one single configuration composed of strongly occupied NSOs is dominant in the wave function.

Aguilar and Nakamura [6] do allow screening to be variable, giving prescriptions for the screening constants α_k and β_k, but also restrict the wave functions to be single configurations.

2. Basis Sets and Results

For each state treated we now present the following data: The basis set of two-centre functions applied, the variationally determined values of $Z_{bi} = 1 - \beta_i$ and $Z_{ao} = 2 - \alpha_o$ ($\beta_o = 0$ and $\alpha_i = 0$ are fixed), the total energy found and, for comparison, the value of the total energy obtained in one of the previously mentioned CI calculations with larger and different basis sets [6–11].

We do not include the occupation numbers and the coefficients of the NSOs which are contained in [12][1] but use their values for the discussion of the energy plots.

Table 1. $2\,^1\Sigma^+(2\,^1S) \rightarrow He^+(1s) + H(1s)$.
Basis II: i: $1s\sigma$; o: $1s\sigma_g'$, $2s\sigma_g$, $2p\sigma_u$; $Z_{ao} = 1$

R	Z_{bi}	E_{tot} [this work]	E_{tot} [8, Table IV]
0.5	0.979	−0.1708	−0.17436
1.0	0.947	−1.5958	−1.60287
1.5	0.833	−2.0219	
2.0	0.695	−2.2519	−2.25663
2.5	0.507	−2.3799	
3.0	0.308	−2.4463	−2.44813
4.0	0.056	−2.4929	−2.49342
5.0	0	−2.5009	

Table 2. $1\,^3\Sigma^+(2\,^3S) \rightarrow He^+(1s) + H(1s)$.
Basis II: i: $1s\sigma$; o: $1s\sigma_g'$, $2s\sigma_g$, $2p\sigma_u$; $Z_{ao} = 1$

R	Z_{bi}	E_{tot} [this work]	E_{tot} [11]
0.5	0.919	−0.2363	
1.0	0.786	−1.7380	−1.76264
1.5	0.533	−2.1871	
2.0	0.142	−2.3729	−2.37968
2.5	−0.016	−2.4517	
3.0	−0.079	−2.4846	−2.48647
4.0	−0.104	−2.5023	−2.50288
5.0	−0.079	−2.5030	−2.50327

Table 3. $3\,^1\Sigma^+(2\,^1P) \rightarrow He(2\,^1S) + H^+$. Basis III: i: $1s\sigma$; o: $2s\sigma$, $2p\sigma$, $3d\sigma$

R	Z_{bi}	Z_{ao}	E_{tot} [this work]	E_{tot} [8, Table VI]
0.25	1.006	1.005	3.3748	
0.5	0.977	1.122	−0.1435	−0.15368
1.0	0.942	1.153	−1.4602	−1.47259
1.5	0.912	1.178	−1.7531	
2.0	0.891	1.178	−1.8760	−1.88298
2.5	0.897	1.189	−1.9462	
3.0	0.900	1.202	−1.9916	
4.0	0.887	1.263	−2.0542	−2.06024
5.0		1.260	−2.1156	
8.0		1.199	−2.1768	−2.18206
10.0		1.156	−2.1741	−2.17893
12.0		1.134	−2.1651	−2.17020

Table 4. $2\,^3\Sigma^+(2\,^3P) \rightarrow \text{He}\,(2\,^3S) + \text{H}^+$. Basis III: i: $1s\sigma$; o: $2s\sigma$, $2p\sigma$, $3d\sigma$

R	Z_{bi}	Z_{ao}	E_{tot} [this work]	E_{tot} from Ref. no.	
0.25	0.973	1.240	3.3301		
0.50	1.022	1.480	−0.2055		
1.00	1.051	1.527	−1.5146	−1.52191	[11]
1.50	1.077	1.526	−1.7963		
2.00	1.134	1.512	−1.9097	−1.91747	[11]
2.50	1.196	1.518	−1.9750		
3.00	1.246	1.573	−2.0206	−2.02820	[11]
4.00		1.600	−2.0973	−2.10442	[11]
5.00		1.569	−2.1536	−2.16169	[11]
6.00		1.538	−2.1811	−2.18948	[11]
8.00		1.444	−2.1918	−2.20072	[7]
10.00		1.398	−2.1838	−2.19399	[7]
12.00		1.447	−2.1748	−2.18527	[7]
14.00		1.535	−2.1705	−2.17966	[7]
16.00		1.555	−2.1687	−2.17701	[7]
20.00		1.559	−2.1671		

Table 5. $1\,^3\Pi(2\,^3P) \rightarrow \text{He}\,(2\,^3P) + \text{H}^+$. Basis IV: i: $1s\sigma$; o: $2p\pi_+$, $3d\pi_+$

R	Z_{bi}	Z_{ao}	E_{tot} [this work]	E_{tot} from Ref. no.	
0.25	0.971	1.187	3.34194		
0.5	0.964	1.216	−0.18752		
1.0	0.970	1.241	−1.53687	−1.53807	[11]
1.5	0.977	1.231	−1.83786		
2.0	0.967	1.206	−1.95913	−1.96065	[11]
3.0	0.844	1.163	−2.06589	−2.06749	[11]
4.0	0.624	1.138	−2.10837	−2.10998	[11]
5.0	0.451	1.124	−2.12654	−2.12794	[11]
6.0	0.298	1.118	−2.13442	−2.13545	[11]
8.0	0.080	1.112	−2.13759	−2.13761	[7]
10.0		1.110	−2.13556	−2.13550	[7]
12.0		1.107	−2.13287	−2.13286	[7]
14.0		1.103	−2.13132		
16.0		1.099	−2.13058		
18.0		1.095	−2.13039		
20.0		1.092	−2.13038		

Figure 3 contains the electronic energy of the first two excited singlet sigma states. The natural spin orbital analysis shows that only two natural orbitals 1σ and 2σ are strongly occupied. There is an avoided crossing of the configurations $1s\sigma\, 2s\sigma$ and $1s\sigma\, 2p\sigma$ composed of basis functions.

Figure 4 contains the electronic energy for the corresponding triplet sigma states where also an avoided crossing of the configurations $1s\sigma\, 2s\sigma$ and $1s\sigma\, 2p\sigma$ occurs.

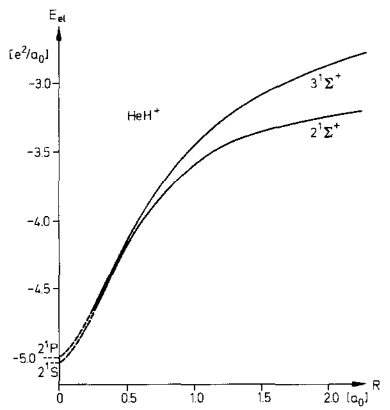

Fig. 3. Electronic energy E_{el} versus the internuclear distance R for the lowest two excited singlet sigma states of HeH^+

Figure 5 gives, for the four sigma states mentioned, the total energies as functions of the internuclear distance.

There is a striking minimum both of the second excited singlet state and the first excited triplet state near $R = 8a_0$. How can it be explained by the model? The natural spin orbital analysis shows that only two natural orbitals 1σ and 2σ are strongly occupied. They are mainly composed of two basis functions, $1s\sigma$ and $3d\sigma$. $1s\sigma$ is the basis function for the description of the core electron. For larger distances $3d\sigma$ becomes the diagonally hybridized linear combination $2s_A - 2p_{oA}$ centred at the helium nucleus. This function also occurs in the treatment of the hydrogen atom in a homogeneous electric field, where it gives rise to a linear Stark effect. Here this function $3d\sigma$ leads to a dipole moment of $3a_0$ due to the polarized electronic charge near the helium nucleus. This dipole interacts with the proton charge from which it originates and is the reason for the lowering of the energy.

In analogy to the Stark effect in hydrogen, the polarization of the electronic cloud should not occur if the outer electron is in a $2p\pi$-orbital. Therefore

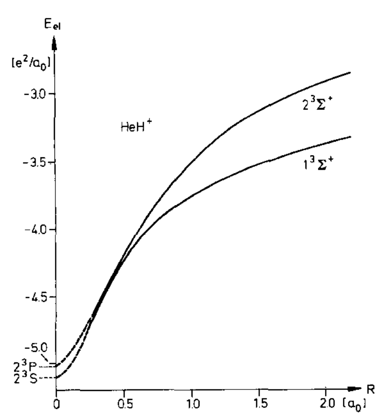

Fig. 4. Electronic energy E_{el} versus the internuclear distance R for the lowest two triplet sigma states of HeH^+

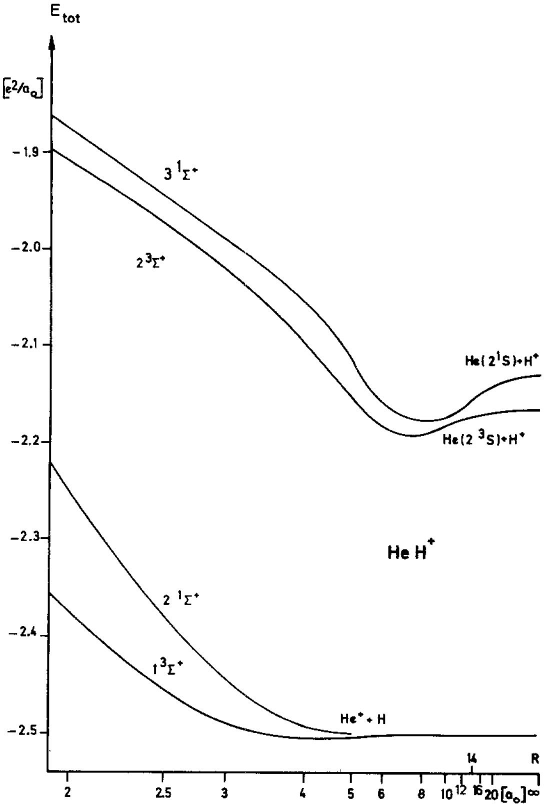

Fig. 5. Total energy E_{tot} versus the internuclear distance R for the lowest four excited sigma states of HeH^+

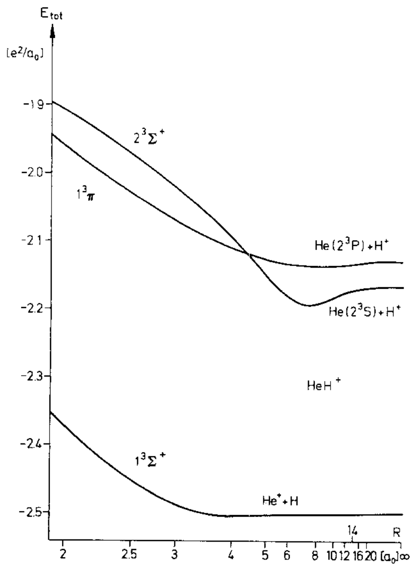

Fig. 6. Total energy E_{tot} versus the internuclear distance R for the lowest three triplet states of HeH^+

we have also treated the state 1 $^3\Pi$ which has no definite minimum (Fig. 6). The NSO analysis shows that 1π is a function with pseudo parity u over the whole range of R.

We finally mention the fact that, for the singlet and triplet sigma states treated, the screening parameter Z_{b1} tends to zero if the system dissociates into $He^+(1s)$ + $H(1s)$ and to approximately 1 if the final products are $He(2\,^{1,3}S) + H^+$. This shows the necessity for using variable screening.

Acknowledgement. The author thanks the Deutsche Forschungsgemeinschaft and the Sonderforschungsbereich Theoretische Chemie for paying computer time and Mrs. M. Dolle and Mrs. A. Schleiff for aid with the manuscript and the figures.

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Received December 27, 1978