

PDF hosted at the Radboud Repository of the Radboud University Nijmegen

This full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/16344>

Please be advised that this information was generated on 2014-11-13 and may be subject to change.

INTERACTION POTENTIAL FOR He-H₂ IN THE REGION OF THE VAN DER WAALS MINIMUM

P.J.M. GEURTS, P.E.S. WORMER and A. VAN DER AVOIRD

Institute of Theoretical Chemistry, University of Nijmegen, Nijmegen, The Netherlands

Received 4 July 1975

Interaction energies for the He-H₂ system have been computed by a VB method for the intermolecular distances $5.2 \leq R \leq 20.0$ bohr and two different orientations of the H₂ molecule ($\theta = 0^\circ, 90^\circ$). The results, especially for the anisotropy, are in good agreement with experiment. The dispersion constants C_6 and C_8 and the corresponding anisotropy constants α_6 and α_8 are presented.

1. Introduction

As one of the simplest systems with a multi-dimensional potential surface, the He-H₂ complex is of experimental as well as theoretical interest. Integral total collision cross sections [1], spin-lattice relaxation times [2] and Raman line shapes [3] have yielded experimental information on the He-H₂ potential surface, and not long ago an analytic intermolecular potential has been proposed by Shafer and Gordon [4] (from here on referred to as SG) which accurately fits all these experimental data.

Theoretical investigations have concentrated either on the short range (repulsive) potential [5-7] or on the long range dispersion forces [8]. Tsapline and Kutzelnigg [9] (henceforth referred to as TK) were the first to calculate van der Waals minima for He-H₂. Their minima are close to the experimental results. However, TK predict the linear configuration of the He-H₂ system to be favoured by 2.35×10^{-5} hartree above the perpendicular geometry, whereas the empirical results of SG show the linear geometry to be slightly less stable than the perpendicular one (by an amount of 0.3×10^{-5} hartree). Also the theoretical and experimental van der Waals radii are not in complete agreement.

It could be supposed that this discrepancy is caused by the neglect of intra-monomer correlation in the calculations and more specifically by the coupling of intra- with inter-monomer correlation

[9,10]. However, as it seems hard to accept that this correlation effect could be responsible for such a relatively large error in the anisotropy, we thought it worthwhile to perform some of the calculations as well, using another formalism [11-13] and another basis of atomic orbitals, but also neglecting the effects of intra-monomer correlation. Interaction curves for two different geometries are presented:

- (i) the perpendicular geometry with an angle $\theta = 90^\circ$ between the molecular axis of H₂ and the vector \mathbf{R} connecting the midpoint of H₂ with He and
- (ii) the linear geometry with $\theta = 0^\circ$.

The distance R has been varied from 5.2 to 20.0 bohr, the H-H distance has been kept constant (1.40 bohr).

2. Method

The method employed in this work is essentially a multistructure valence-bond method based on VB structures containing AO's on He and MO's on H₂. In this formalism it is possible, by using local symmetry, to separate the different terms in the multipole expansion of the dispersion energy [11], although the complete unexpanded form of the interaction operator is used in our calculations. To obtain the contribution from a certain component of the multipole operator the basis must include at least one VB structure representing a locally excited state that combines with the monomer ground state under this multipole component.

Table 1
Atomic orbital basis

| | $N_{\text{contr}}^{\text{a)}$ | $\zeta^{\text{b)}$ | Optimization method | Ref. |
|------|-------------------------------|--------------------|---|-----------|
| He s | 6 | — | SCF calculation He | [17] |
| p | 2 | 1.30 | van der Waals int. in He ₂ | [12] |
| d | 1 | 1.45 ^{c)} | van der Waals int. in He ₂ | [13] |
| H s | 6 | 1.2 | SCF calculation in H ₂ ^{d)} | this work |
| p | 2 | 2.0 | SCF calculation in H ₂ | this work |
| p' | 2 | 1.1 | van der Waals int. in He-H ₂ | this work |
| d | 1 | 1.1 ^{e)} | van der Waals int. in He-H ₂ | this work |

a) Number of primitive GTO's in contracted set.

b) Contracted set represents STO with exponent ζ (bohr⁻¹).

c) Exponent GTO: $\alpha = 0.2738$ (bohr⁻²).

d) Contraction coefficients optimized.

e) Exponent GTO: $\alpha = 0.1576$ (bohr⁻²).

Within the VB framework one can define two quantities $\Delta E^{(1)}$ and $\Delta E^{(2)}$ resembling first- and second-order perturbation energies, respectively. $\Delta E^{(1)}$ is the expectation value of the total hamiltonian over the dimer ground state minus the SCF energies of the free monomers. $\Delta E^{(2)}$ is the difference between the VB multi-structure interaction energy and the just defined first-order energy. This difference is asymptotically equal to London's well-known second-order energy expression [11].

The orbitals on the different monomers do of course overlap, but since we have found previously that a well-chosen orthogonalization does not influence the results to a significant extent, we have orthogonalized the basis, while meeting the following requirements:

the ground state VB structure, and with it $\Delta E^{(1)}$, is left invariant;

the orbitals remain as localized as possible on the respective monomers; consequently they reflect the symmetry of the subsystems.

A careful orthogonalization is of the utmost importance. If, for instance, one allows all orbitals in the dual space to mix among each other, as is done in the method of bi-orthogonal orbitals [14], one finds first-order energies which are very sensitive to the basis set and which sometimes are negative in regions of the potential surface where strong repulsions are expected [14].

3. Basis

The selection of an orbital basis needs special care

in the study of van der Waals interactions, because these are usually very small. It has been found [13], for instance, that the orbitals constituting the excited states must be optimized by maximizing the dispersion energy. Good ground state orbitals are also required: for a reliable estimate of dispersion energies [13] as well as for correct exchange repulsions [15]. Thus, we have included in the AO basis two p-orbitals on each hydrogen: one rather diffuse orbital to obtain the corresponding parts of the dispersion energy and another more compact orbital necessary for the description of the exchange repulsion between He and H₂. The need for at least two p-orbitals in cases such as this has sometimes been overlooked [16]. Contrary to the case of the p-orbitals, one d-orbital per hydrogen atom appears to be sufficient, mainly because the orbital exponent required for getting a good ground state energy of H₂ very nearly optimizes the dispersion energy of He-H₂. One must realize, in this connection, that the dispersion energy is not very sensitive to variations of this exponent in the neighbourhood of the optimum.

The inclusion of an optimized p-orbital on He is necessary to account for the dipole excitations on this atom; one optimized d-orbital on He takes care of the quadrupole excitations.

The AO's used in this work are contracted GTO's with tesseral harmonics as their angular parts. Except for the 1s-orbitals on H and He, they have been fitted to STO's with exponents ζ . The ζ -values have subsequently been optimized. See table 1 for a summary of the basis. We have also experimented with larger contractions of the He and H p-orbitals, but this hardly affected the results.

The MO's of σ -symmetry on H₂ are obtained from

Table 2

| | Present work TK [9] | | HF limit |
|---|---------------------|------------|-------------------------|
| SCF energy He ^{a)} | -2.8611163 | -2.8614912 | -2.86168 ^{c)} |
| SCF energy H ₂ ^{a)} | -1.1330237 | -1.1329092 | -1.133629 ^{b)} |
| quadrupole H ₂ ^{d)} | 0.4931 | - | 0.4933 ^{b)} |

a) Hartree. b) Ref. [18]. c) Ref. [17].

d) $\frac{1}{2}(3\langle z^2 \rangle - \langle r^2 \rangle)$ in au.

Table 3

First-order, second-order and total interaction energies. Distance in bohr, energy in 10^{-5} hartree

| R | Linear geometry, $\theta = 0^\circ$ | | | Perpendicular geometry, $\theta = 90^\circ$ | | |
|------|-------------------------------------|------------------|-------------------------|---|------------------|-------------------------|
| | $\Delta E^{(1)}$ | $\Delta E^{(2)}$ | ΔE_{tot} | $\Delta E^{(1)}$ | $\Delta E^{(2)}$ | ΔE_{tot} |
| 5.2 | 56.50 | -28.32 | 28.18 | 38.87 | -22.13 | 16.74 |
| 5.6 | 24.40 | -18.71 | 5.69 | 16.79 | -14.91 | 1.88 |
| 6.0 | 10.41 | -12.59 | -2.18 | 7.15 | -10.16 | -3.01 |
| 6.3 | 5.45 | -9.49 | -4.04 | 3.73 | -7.68 | -3.95 |
| 6.5 | 3.52 | -7.91 | -4.39 | 2.41 | -6.41 | -4.00 |
| 6.6 | 2.83 | -7.23 | -4.40 | 1.93 | -5.85 | -3.92 |
| 7.0 | 1.16 | -5.10 | -3.94 | 0.78 | -4.11 | -3.33 |
| 8.0 | 0.11 | -2.26 | -2.15 | 0.07 | -1.81 | -1.74 |
| 9.0 | 0.00 | -1.08 | -1.08 | 0.00 | -0.87 | -0.87 |
| 10.0 | 0.00 | -0.56 | -0.56 | 0.00 | -0.46 | -0.46 |
| 11.0 | 0.00 | -0.32 | -0.32 | 0.00 | -0.26 | -0.26 |
| 12.0 | 0.00 | -0.18 | -0.18 | 0.00 | -0.15 | -0.15 |
| 20.0 | 0.00 | -0.01 | -0.01 | 0.00 | -0.02 | -0.02 |

an SCF calculation on the free molecule, and those of π - and δ -symmetry are simply symmetric and antisymmetric combinations of equivalent orbitals on the atoms.

As in earlier work [11–13] we have found again that VB structures representing the coupling of triplet excited monomers can be omitted. This halves the number of VB structures contributing to the dispersion energy. In total, about 50 of such singlet–singlet structures can be derived from the given orbital basis; all of these have been taken into account in this work.

The quality of the atomic orbital basis may be judged from the values in table 2. Another criterion for the adequacy of the basis is the “saturation test” [19], which is a computation of the SCF energy of each of the single subsystems in the dimer basis. We have found the following small energy improvements at $R = 6.5$ bohr, expressed in 10^{-5} hartree: 0.34 and

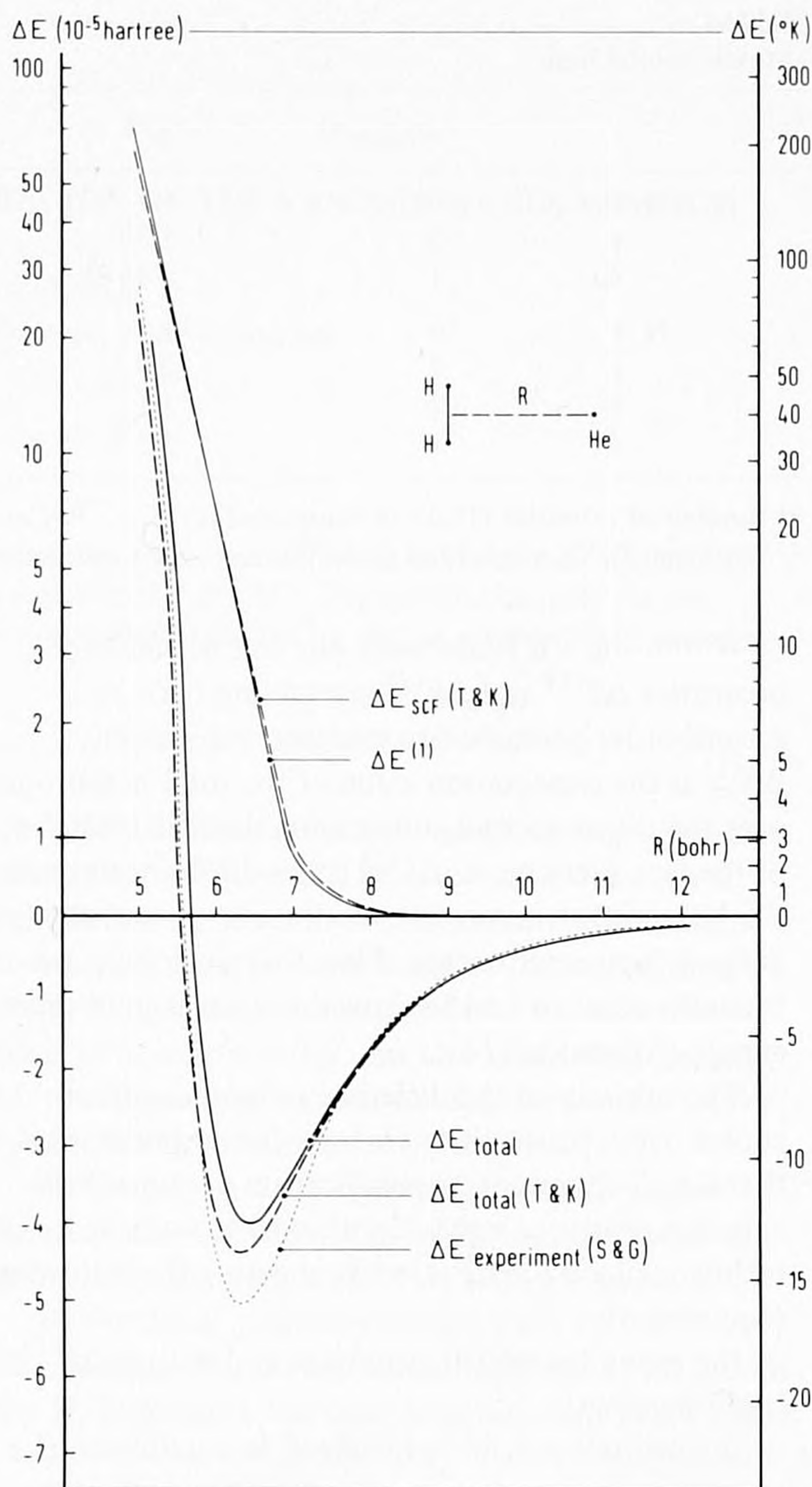


Fig. 1. Perpendicular geometry. Total interaction energy ΔE_{tot} of TK [9], SG [4] and this work. First-order energy $\Delta E^{(1)}$ of this work, SCF-interaction energy ΔE_{SCF} of TK [9]. From 1×10^{-5} hartree upwards the energy scale is logarithmic.

0.26 for He, 0.16 and 0.08 for H₂ in the case of the linear and the perpendicular geometry, respectively. If we had obtained the first-order interaction from SCF calculations on the dimer, we would have had to correct for these small effects, but because we calculate $\Delta E^{(1)}$ directly from the monomer orbitals, the fact that the basis set is not completely saturated does not concern us.

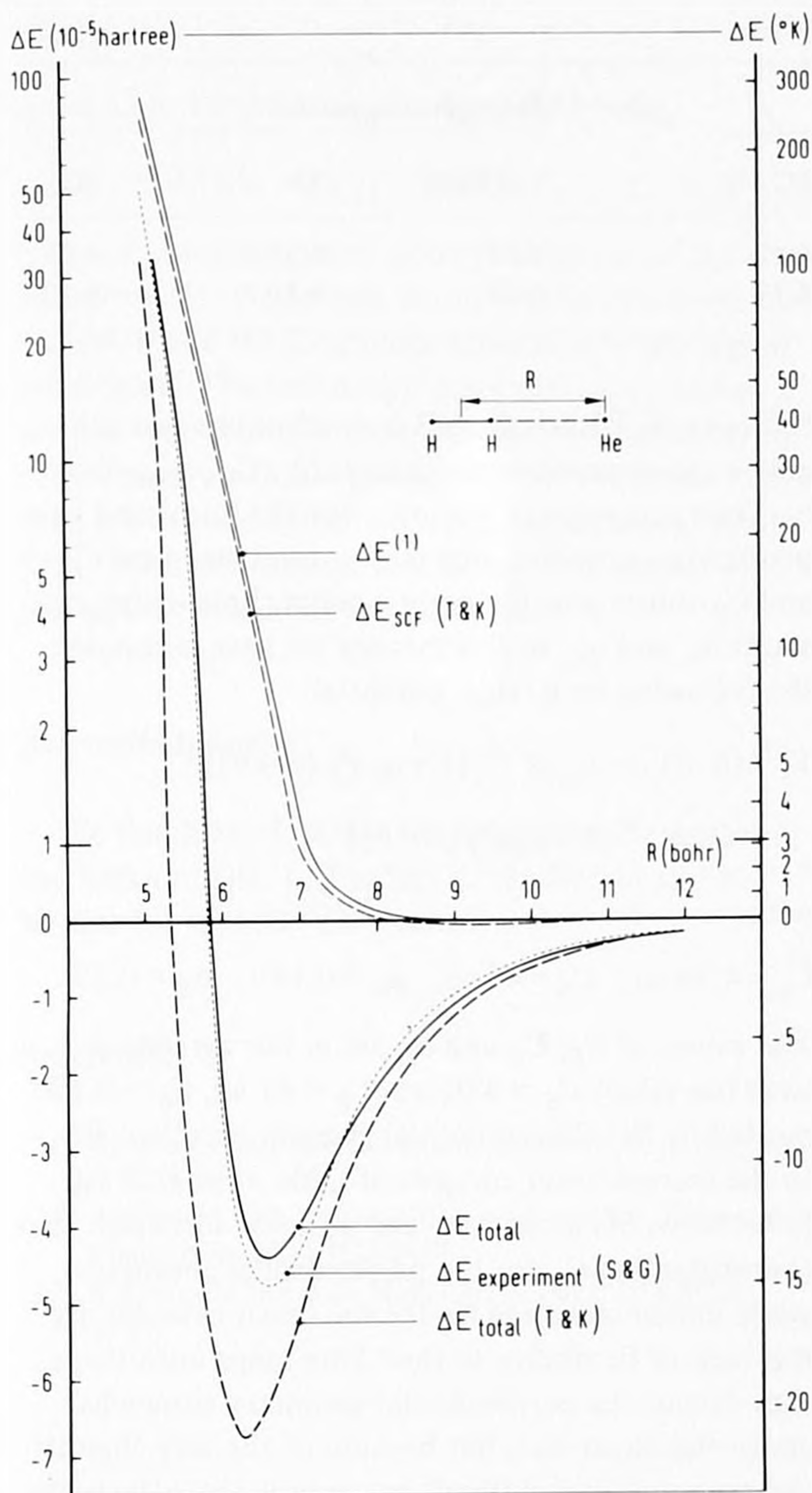


Fig. 2. Linear geometry. Total interaction energy ΔE_{tot} of TK [9], SG [4] and this work. First-order energy $\Delta E^{(1)}$ of this work, SCF-interaction energy ΔE_{SCF} of TK [9]. From 1×10^{-5} hartree upwards the energy scale is logarithmic.

4. Results and discussions

In table 3 the first-order, second-order and total interaction energies are given for the two configurations considered in this work. Figs. 1 and 2 give some of these results graphically, showing also a comparison with the total interaction energies of SG [4] and the SCF and total interaction energies of TK [9].

4.1. First-order energy

For the perpendicular geometry one notes that our first-order energies are very similar to the SCF energies of TK; the hardly significant difference can probably be explained by the differences in the basis sets. In the case of the linear geometry, our first-order results differ a little more from the SCF curve of TK, which is lying lower. The induction part (mainly permanent quadrupole on H_2 , induced dipole on He) of the interaction energy could be a source of this discrepancy, because it is contained in the dimer SCF energy but not in our first-order energy. We have therefore computed the induction energy explicitly, by the VB method, as well as classically using the quadrupole moment of H_2 from table 2 and the polarizability $\alpha = 1.393 \text{ (bohr)}^3$ of He [13]. We find that the two methods agree in all significant figures, which are not many in this case because the effect is very small indeed: 0.05×10^{-5} hartree at 6.5 bohr (linear geometry). In any event this value is too small to explain the difference between TK's and our results. Possibly TK have improved the SCF energies of the subsystems somewhat in the dimer basis, due to a non-saturated monomer basis, and have not subsequently corrected for this effect. This allegation is supported by the occurrence of a minimum in their curve which, although very weak, is still too deep to be caused by induction. Also, our first-order energy at 5.2 bohr compares quite well with the best SCF value of ref. [5] after correction for the induction energy: 56.5×10^{-5} hartree versus 56.3×10^{-5} hartree [5], whereas TK find about 51×10^{-5} hartree (interpolated) for the same value. (For the perpendicular case with the same distance these values are 38.9 (this work), 39.6 [5] and about 37 (TK).)

The first-order repulsion can be fitted quite satisfactorily by the following potential, valid for $R \geq 5.2$ bohr. (The θ -dependency is given by a second-order Legendre polynomial.)

$$V^{(1)}(R, \theta) = A e^{-\beta R} [1 + \gamma P_2(\cos \theta)] .$$

The optimal parameters are:

$$A = 34.5 \text{ hartree}, \quad \beta = 2.16 \text{ (bohr)}^{-1}, \quad \gamma = 0.267.$$

The β -value is somewhat larger than any of the values proposed in ref. [5] for $3.8 \leq R \leq 5.2$ (bohr), a range which is different from ours, though. Since a

Table 4

| | Linear geometry | | | Perpendicular geometry | | |
|----------------------------|-----------------|--------|--------|------------------------|------|------|
| | this work | TK [9] | SG [4] | this work | TK | SG |
| R_m (bohr) | 6.58 | 6.25 | 6.58 | 6.42 | 6.29 | 6.30 |
| E_m (10^{-5} hartree) | 4.40 | 6.75 | 4.77 | 4.02 | 4.40 | 5.06 |

small deviation in β gives a considerable effect on A , it is not surprising that our A -value differs by a factor of about 3 from the values of ref. [5].

4.2. Total energy

With regard to the total energy, we see from table 4 that for the perpendicular geometry TK's calculations agree better with the experimental results than ours, although our values do not deviate too much either. We have observed before that our method has a tendency to underestimate the dispersion energy to some extent. Using a comparable basis we have found for He-He [13] a dispersion energy $\Delta E^{(2)}$ which is 90% of the value computed in a much larger basis including f-orbitals [20].

As to the linear geometry, the results of this work are in full agreement with the experimental R_m -value and, again, underestimate the experimental well depth somewhat, whereas TK find too deep a minimum at too short a distance (table 4)*.

So, although the anisotropy found in this work is much less pronounced than that of TK [9], we still predict the wrong geometry to be more stable, that is, comparing with SG [4]. To explain this discrepancy one may point out several inaccuracies in this work, such as the neglect of intra-monomer correlation or a possible geometry-dependent underestimate of the dispersion, but it must also be noted that SG's potential lacks some flexibility in the long range part. The following discussion may clarify

* When informed about our results Professor Kutzelnigg has communicated that their potential curves become very similar to ours when they extended their formalism in order to account for the coupling between inter- and intra-monomer correlations. In comparing these results it must be remembered, though, that the relative contributions from inter- and intra-monomer terms depend on the degree of localization of the orbitals on the subsystems.

this remark. Within the VB formalism one can calculate the dispersion coefficients C_6 , C_8 , etc., directly. Thus computing C_6 and C_8 for the linear and perpendicular geometry, one may extract averaged C_6 - and C_8 -values plus the corresponding anisotropy constants α_6 and α_8 . In this manner we have computed the following long range potential:

$$V^{(2)}(R, \theta) = -C_6 R^{-6} [1 + \alpha_6 P_2(\cos \theta)] \\ - C_8 R^{-8} [1 + \alpha_8 P_2(\cos \theta)] ,$$

with

$$C_6 = 4.34 \text{ au}, \quad C_8 = 49 \text{ au}, \quad \alpha_6 = 0.149, \quad \alpha_8 = 0.23 .$$

The values of C_6 , C_8 and α_6 are in fair agreement with the values $C_6 = 4.01$ au, $C_8 = 41$ au, $\alpha_6 = 0.105$ quoted by SG. This potential gives an excellent fit to the second-order energies of table 3 for $R \geq 7.0$ bohr. Now, SG assume α_6 and α_8 to be identical, thus overestimating C_8 for the perpendicular geometry, while underestimating C_8 for the linear case. So, by this lack of flexibility in their long range anisotropy they favour the perpendicular geometry somewhat above the linear one, but because of the way they fit the potential, it is difficult to see how this affects the minima.

It could be presumed that the superposition, $V^{(1)} + V^{(2)}$, of the short and the long range potential can yield a reasonable fit for the whole range. This is not so, mainly because of the inadequacy of $V^{(2)}$ to represent charge-penetration effects. A better fit would require some extra (exponential) terms to account for charge penetration.

Since scattering experiments are often interpreted by the use of Lennard-Jones potentials [21], we have computed the following analytic form from the positions and the depths of the minima:

$$V_{L-J}(R, \theta) = -2\epsilon(R_0/R)^6 [1 + q_{2,6} P_2(\cos \theta)] \\ + \epsilon(R_0/R)^{12} [1 + q_{2,12} P_2(\cos \theta)] ,$$

with

$$\epsilon = 4.13 \times 10^{-5} \text{ hartree}, \quad R_0 = 6.48 \text{ bohr},$$

$$q_{2,6} = 0.164, \quad q_{2,12} = 0.271.$$

The L-J potential gives a good description of the computed van der Waals well, but overestimates both the repulsion and the long range attraction in the region considered. The anisotropy constants $q_{2,12}$ and $q_{2,6}$ are not very different from our corresponding asymptotic values $\gamma = 0.267$ and $\alpha_6 = 0.149$. Furthermore, they are in good agreement with experimental results [22] obtained from the scattering of molecular H_2 beams with several of the noble gases.

Acknowledgement

We thank Dr. J. Reuss for suggesting the problem, and him and Drs. L. Zandee, T. van Berkel and F. Mulder for valuable discussions.

References

- [1] R. Gengenbach and Ch. Hahn, Chem. Phys. Letters 15 (1972) 604.
- [2] J.W. Riehl, C.J. Fisher, J.D. Baloga and J.L. Kinsey, J. Chem. Phys. 58 (1973) 4571.
- [3] B.K. Gupta and A.D. May, Can. J. Phys. 50 (1972) 1747.
- [4] R. Shafer and R.G. Gordon, J. Chem. Phys. 58 (1973) 5422.
- [5] M.D. Gordon and D. Secrest, J. Chem. Phys. 52 (1970) 120.
- [6] M. Krauss and F.M. Mies, J. Chem. Phys. 42 (1965) 2703.
- [7] C.S. Roberts, Phys. Rev. 131 (1963) 203.
- [8] P. Langhoff, R.G. Gordon and M. Karplus, J. Chem. Phys. 55 (1971) 2126, and references therein.
- [9] B. Tsapline and W. Kutzelnigg, Chem. Phys. Letters 23 (1973) 173.
- [10] B. Liu and A.D. McLean, J. Chem. Phys. 59 (1973) 4557.
- [11] P.E.S. Wormer and A. van der Avoird, J. Chem. Phys. 62 (1975) 3326.
- [12] P.E.S. Wormer, T. van Berkel and A. van der Avoird, Mol. Phys. 29 (1975) 1181.
- [13] F. Mulder, P. Geurts and A. van der Avoird, Chem. Phys. Letters 33 (1975) 215.
- [14] E. Kochanski and J.F. Gouyet, Mol. Phys. 29 (1975) 693.
- [15] J.G.C.M. van Duijneveldt-van de Rijdt and F.B. van Duijneveldt, Chem. Phys. Letters 17 (1972) 425.
- [16] E. Kochanski, J. Chem. Phys. 58 (1973) 5823.
- [17] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.
- [18] W. Kołos and C.C.J. Roothaan, Rev. Mod. Phys. 32 (1960) 219.
- [19] W. Kutzelnigg, V. Staemmler and C. Hoheisel, Chem. Phys. 1 (1973) 27.
- [20] D.R. McLaughlin and H.F. Schaefer III, Chem. Phys. Letters 12 (1971) 244.
- [21] H. Moerkerken, L. Zandee and J. Reuss, Chem. Phys. 11 (1975), to be published.
- [22] L. Zandee and J. Reuss, private communication.