

Ab initio CALCULATION OF THE INTERMOLECULAR POTENTIAL AND PREDICTION OF SECOND VIRIAL COEFFICIENTS FOR DIMER H₂-H₂

Received 20 January 2007

PHAM VAN TAT¹, U. K. DEITERS²

¹Department of Chemistry, University of Dalat

²University of Cologne, Germany

SUMMARY

The intermolecular pair potentials of the dimer H₂-H₂ were constructed from quantum mechanics using method CCSD(T) with Dunning's correlation-consistent basis sets aug-cc-pV_mZ ($m = 2, 3, 4$); *ab initio* energies were extrapolated to the complete basis set limit. The interaction energies were corrected for the basis set superposition error (BSSE) with the counterpoise scheme. The second virial coefficients of hydrogen resulting from *ab initio* potential functions were obtained by integration; corrections for quantum effects were included too. The results agree well with experimental data.

Keywords: *ab initio* potential, dimer H₂-H₂, second virial coefficients, BSSE.

I - INTRODUCTION

Hydrogen and the mixture hydrogen-oxygen are used in several industrial applications. It could become the most important energy carrier of tomorrow [3]. Liquid hydrogen, oxygen are the usual liquid fuels for rocket engines [2]. The National Aeronautics and Space Administration (NASA) is the largest user of liquid hydrogen in the world [1, 4].

Computer simulations have become indispensable tools for studying fluids and fluid mixtures. One of the first attempts Nasrabad and Deiters predicted phase high-pressure vapour-liquid phase equilibria of noble-gas mixtures [5, 6] from the global simulations using the intermolecular potentials. Other mixed-dimer pair potentials for noble gases were published by Lúpez Cacheiro et al. [7], but not used for phase equilibria predictions, yet.

Leonhard and Deiters used a 5-site Morse potential to represent the pair potential of nitrogen [8] and were able to predict vapour pressures and orthobaric densities. Bock et al. also used a 5-site pair potential for carbon dioxide [9]; Naicker et al. developed the 3-site pair potentials for hydrogen chloride [11]; they predicted successfully the vapour-liquid phase equilibria of hydrogen chloride with GEMC (Gibbs Ensemble Monte Carlo simulations [12]. Recently Diep and Johnson carried out the *ab initio* calculations with post-SCF methods MP n ($n = 2, 3, 4$) and CCSD(T) with the basis sets aug-cc-pV_mZ ($m = 2, 3, 4$) and the complete basis set limit [13, 14].

In this work we report quantum mechanical calculations at a sufficiently high level of approximation to obtain pair potential data of the dimer H₂-H₂. These data are then represented by analytical pair potential functions. These in turn are used to calculate

2nd virial coefficients. The 2nd virial coefficients can then be compared with experimental data as far as such data are available. They can furthermore be used to determine the parameters of a suitable equation of state.

II - COMPUTATIONAL DETAILS

1. Molecular Orientation

Hydrogen molecule is represented as 5-site model with two sites placed on the atoms H, one

site in the center of gravity M, and two sites halfway between the atoms and the center N; the interatomic distance is set to 0.74130 Å for hydrogen [15]. The intermolecular pair potential is a function of distance r (between the centers of gravity) and three angular coordinates, α , β , and ϕ , which are explained in Fig. 1. Interaction energies were calculated for all values of r from 2.6 to 15 Å with increment 0.2 Å; the angles α , β , and ϕ were varied from 0 to 180° with increment 45°.

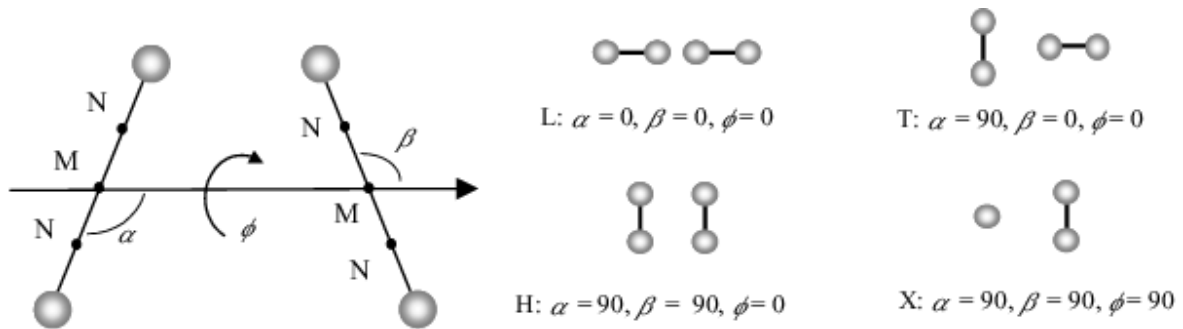


Figure 1: 5-site model and special orientations for quantum chemical approach

2. Quantum chemical calculations

There are several post-SCF methods that can capture at least a part of the electron correlation effects. Experience shows that especially the CCSD(T) method appears to account for the most significant electron correlation effects. The Dunning's correlation-consistent basis sets [16] aug-cc-pVDZ (for hydrogen: 5s2p/3s2p), aug-cc-pVTZ (for hydrogen: 6s3p2d/4s3p2d) and aug-cc-pVQZ (for hydrogen: 6s3p2d1f/4s3p2d1f) were used in this work. The *ab initio* energies were corrected for BSSE with the counterpoise correction method proposed by Boys and Bernardi [17]:

$$\Delta E_{\text{int}} = E_{AB} - (E_{Ab} + E_{aB}) \quad (1)$$

where E_{AB} denotes the total electronic energy of a dimer AB , E_{Ab} the energy of a dimer

consisting of an A atom and a B ghost atom (an atom without nucleus and electrons, but having its orbitals), and E_{aB} vice versa. The electronic energies are then extrapolated to the complete basis set limit [18]:

$$\Delta E(m) = \Delta E(\infty) + cm^{-3} \quad (2)$$

with $m = 2$ for aug-cc-pVDZ or 3 for aug-cc-pVTZ. *Ab initio* calculations were carried out with the Gaussian03 program package [19].

3. Potential function

Two new 5-site pair potential functions were developed by incorporating the repulsive and the dispersive contribution from the terms of the site-site pair potentials in publications [11], [9] and [8]. The damping functions were chosen from the potentials in [8, 9, 20].

$$u = \sum_{i=1}^5 \sum_{j=1}^5 \left[D_e^{ij} e^{-\alpha_{ij} r_{ij}} + f_{1a}(r_{ij}) \sum_{n=6,8,10} \frac{C_n^{ij}}{r_{ij}^n} + f_2(r_{ij}) \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] \quad (3)$$

with $f_{1a}(r_{ij}) = (1 + e^{-2(\delta_{ij}r_{ij}-2)})^{-15}$ and $f_2(r_{ij}) = 1 - e^{-\beta_{ij}r_{ij}}$

$$u = \sum_{i=1}^5 \sum_{i=1}^5 \left[D_e^{ij} e^{-\alpha_{ij}r_{ij}} + f_{1b}(r_{ij}) \sum_{n=6,8,10,12} \frac{C_n^{ij}}{r_{ij}^n} + f_2(r_{ij}) \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] \quad (4)$$

with $f_{1b}(r_{ij}) = 1 - e^{-\delta_{ij}r_{ij}} \sum_{k=0}^{10} \frac{(\delta_{ij}r_{ij})^k}{k!}$ and $f_2(r_{ij}) = 1 - e^{-\beta_{ij}r_{ij}}$

Here the r_{ij} site-site distances, the q_i electric charges of sites, and the C_{ij}^n dispersion coefficients; the leading dispersion term is always proportional to r . The two models differ mostly in the choice of the damping functions $f_{1a}(r_{ij})$ and $f_{1b}(r_{ij})$.

4. Fitting potential function

The adjustable parameters of the *ab initio* pair potential functions can be estimated by nonlinear least-square fitting to the *ab initio* interaction energy values.

Table 1: The statistical results for fitting the intermolecular potentials Eq. 3 and Eq. 4.
The values are in μE_H

Potential	R ²	rms	Residual	
			min	max
Eq. 3	0.9999	0.2329	-6.311	6.284
Eq. 4	0.9999	0.4258	-7.449	7.911

The fit process has to be carried out by two steps. The global minima are coarsely located by means of the Genetic algorithm, and the parameters resulting from the Genetic algorithm are used as initial values for the Marquardt-Levenberg algorithm.

The values of root mean-square deviations (rms), multiple correlation coefficients (R²), and residuals of the fitted analytical potential functions are given in table 1. The statistical estimates here are important for assessing the fitting quality. The residual area for the potential Eq. 3 resulting from the least-square fit is narrower than the residual area of the potential Eq. 4. So the fitting quality for Eq. 3 is better, but this difference is insignificant for 930 interaction energy points. This turned out to be very satisfactory.

III - SECOND VIRIAL COEFFICIENTS

1. Classical virial coefficients

The classical virial coefficients B_{cl}^0 of hydrogen resulting from the formula Eq. 6 using the *ab initio* 5-site pair potentials Eq. 3 and Eq. 4 are depicted in Figs 2a and 2b, respectively. Furthermore, Diep et al. [13,14] computed the second virial coefficients at level of theory.

CCSD(T) with complete basis set limit using the path integral and semiclassical method, respectively. In recent publication the virial coefficients of hydrogen were calculated by Wang [21] using the Lennard-Jones 6-12 potential as described in Fig 2. The classical 2nd virial coefficients B_{cl}^0 of hydrogen resulting from the new potentials Eq. 3 and Eq. 4 at the level of theory CCSD(T) with complete basis set limit aug-cc-pV23Z turn out to be in good agreement with experimental data and those in publications [13, 14, 21, 25].

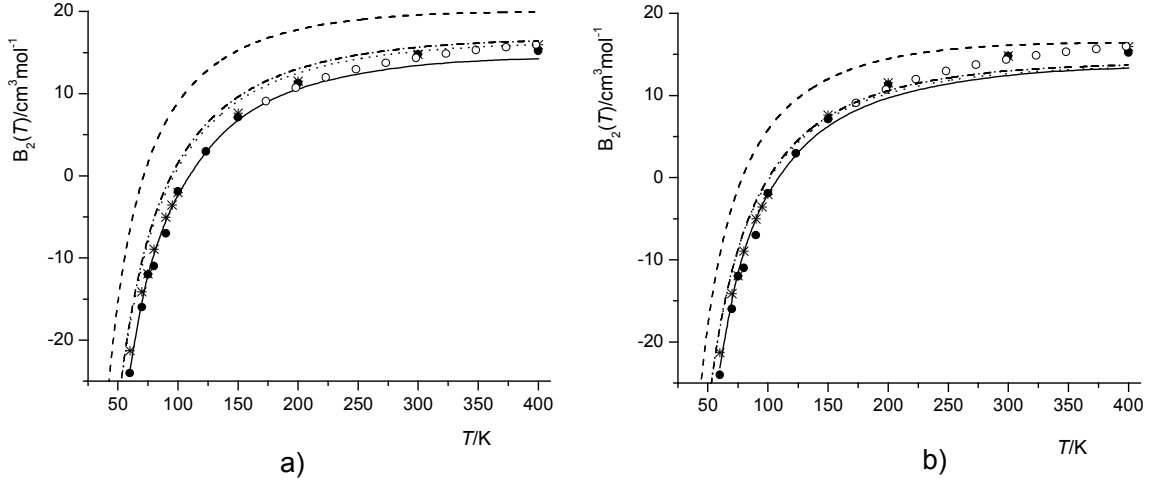


Figure 2: Second virial coefficients B_{cl}^0 of hydrogen resulting from the pair potential functions: a): Eq. 3 and b): Eq. 4 at level of theory CCSD(T); ----: aug-cc-pVDZ; -.-.-: aug-cc-pVTZ;: aug-cc-pVQZ; —: aug-cc-pV23Z; ●: experimental data [23, 24]; ○: Lennard-Jones potential by Wang [21]; *: spherical harmonic potential by Eters and Diep [25, 13, 14].

2. Quantum corrections

In the case of hydrogen the matter is more complicated because of quantum effects. The first-order quantum corrections to the second virial coefficient of linear molecules by Pack [10] and Wang [21] can be written as:

$$B_2 = \frac{N_A}{2u} \iint d\Omega_1 d\Omega_2 \iiint \left\{ 1 - \exp(-u/k_B T) \left[1 + \frac{1}{12(k_B T)^2} H_0 u \right] \right\} dr_1 dr_2 d\Omega_1 d\Omega_2 \quad (5)$$

Here N_A is Avogadro's constant, k_B Boltzmann's constant, T the temperature, and $u(r; \alpha, \beta, \phi)$ the pair potential; H_0 is the translation-rotation Hamiltonian for a pair of molecules.

The classical virial coefficient is given by:

$$B_{cl}^0 = -\frac{N_A}{4} \int_0^{2\pi} d\phi \int_0^\pi \sin \beta d\beta \int_0^\pi \sin \alpha d\alpha \int_0^\infty \left(\exp\left(-\frac{u}{k_B T}\right) - 1 \right) r^2 dr \quad (6)$$

All these integrals were evaluated numerically with a 4D Gauss-Legendre quadrature method [22]. The 2nd virial coefficients $B_2(T)$ including quantum corrections at the level of theory CCSD(T) with the complete basis set limit aug-cc-pV23Z are presented in Fig 3.

IV - CONCLUSION

The second virial coefficients of hydrogen obtained from the two potential functions Eq. 3 and Eq. 4 are very close to experimental data, as

described in Fig 3. The discrepancies between them are insignificant. The second virial coefficients are generated almost within the uncertainties of the experimental measurements. The first-order quantum corrections contribute significantly to the second virial coefficients of hydrogen even at high temperatures. Of these corrections, only the radial term is important; the angular terms are usually much smaller in size. This turned out that new *ab initio* pair potentials of the dimer hydrogen are reliable for predicting the thermodynamic properties.

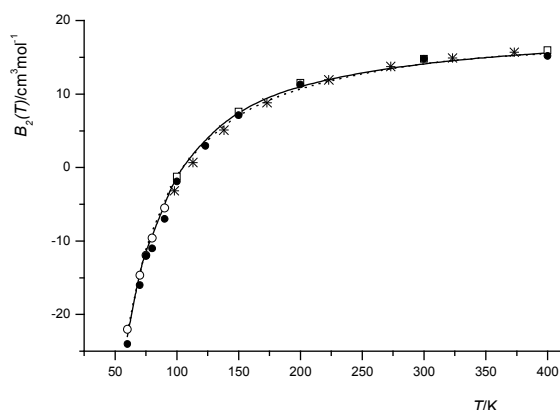


Figure 3: Second virial coefficient $B_2(T)$ of hydrogen are calculated using the pair potentials (this work): —: the pair potential Eq. 3; *...: the pair potential Eq. 4; ●: experimental data [23,24]; ○: path integral [13] and □: semi-classical method [14].

Acknowledgments: *The Regional Computer Center of Cologne (RRZK) contributed to this project by a generous allowance of computer time as well as by efficient software support; we wish to thank Dr. L. Packschies for technical help with the Gaussian03 software. We would like to thank Prof. Dr. J. Karl Johnson (University of Pittsburgh, USA) for providing the virial coefficient results.*

REFERENCES

1. V. P. Dawson. A History of the Rocket Engine Test Facility at the NASA Glenn Research Center, NASA, Glen Research Center, Cleveland (2004).
2. L. J. Krzycki. Build and test small liquid-fuel rocket engines, Rocketlab, Oregon (1967).
3. E. Larry. Homebrew fuel cell and Hydrogen Electrolyser, Home Power, 85, 52 - 59 (2001).
4. T. M. Haarmann and W. Koschel. Proc. Appl. Math. Mech., 2, 360 - 361 (2003).
5. A. E. Nasrabad and U. K. Deiters. J. Chem. Phys., 119, 947 - 952 (2003).
6. A. E. Nasrabad, R. Laghaei, and U. K. Deiters. J. Chem. Phys., 121, 6423 - 6434 (2004).
7. J. Lúpez Cacheiro, B. Fernandez, D. Marchesan, S. Coriani, C. Hattig, and A. Rizzo. J. Mol. Phys., 102, 101 - 110 (2004).
8. K. Leonhard and U. K. Deiters. Mol. Phys., 100, 2571 - 2585 (2002).
9. S. Bock, E. Bich, and E. Vogel. Chem. Phys., 257, 147 - 156 (2002).
10. R. T. Pack. J. Chem. Phys., 78, 7217 - 7222 (1983).
11. P. K. Naicker, A. K. Sum, and S. I. Sandler. J. Chem. Phys., 118, 4086 - 4093 (2003).
12. A. Z. Panagiotopoulos. Mol. Phys., 61, 813 - 826 (1987).
13. P. Diep and J. K. Johnson. J. Chem. Phys., 112, 4465 - 4473 (2000).
14. P. Diep and J. K. Johnson. J. Chem. Phys., 113, 3480 - 3481 (2000).
15. L. E. Sutton. Table of Interatomic Distances and Configurations in Molecules and Ions. Chemical Society, London, 18 (1965).
16. R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison. J. Chem. Phys., 96, 6796 - 6806 (1992).
17. S. F. Boys and F. Bernardi. Mol. Phys., 19, 553 - 566 (1970).
18. P. L. Fast, M. L. Sanchez, and D. G. Truhlar. J. Chem. Phys., 111, 2921 - 2926 (1999).
19. Gaussian03. Revision B.02. Gaussian Inc., Wallingford, CT, USA (2003).
20. K. T. Tang and J. P. Toennies. J. Chem. Phys., 80, 3726 - 3741 (1984).
21. W. F. Wang, J. Quant. Spectrosc. Radiat. Transfer, 76, 23 - 30 (2003).
22. W. Squire. Integration for Engineers and Scientists. Elsevier, New York (1970).
23. J. H. Dymond and E. B. Smith. The Virial Coefficients of Pure Gases and Mixtures. Clarendon Press, Oxford (1980).
24. D. R. Lide. Handbook of Chemistry and Physics. CRC Press, Raton, 85th edition (2000).
25. R. D. Etters, R. Danilowicz, and W. England. Phys. Reviews A, 12, 2199 - 2212 (1975).

26.