

AB INITIO CALCULATION OF INTERMOLECULAR POTENTIALS AND PREDICTION OF SECOND VIRIAL COEFFICIENTS FOR DIMER H₂ - F₂

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ABSTRACT

The results presented in this paper are the intermolecular potentials and the prediction of second virial coefficient, $B_2(T)$ of the system H₂-F₂. The ab initio potentials were proposed from the quantum chemical calculations using at high level of theory CCSD(T) with basis sets of Dunning's valence correlation-consistent aug-cc-pVmZ ($m = 2, 3$); the calculated ab initio energies were extrapolated to complete basis set limit aug-cc-pV23Z. The method MP_n ($n = 2, 3, 4$) and other basis sets than 6-31G(d), Dunning's basis sets cc-pVmZ ($m = 2, 3$) were also considered in the convergence of ab initio energies for the orientation T-shape, but the results presented inferior. The ab initio energies derived by the exponential extrapolation were used to construct the 5-site pair potential functions. The virial coefficients for this dimer were predicted from those with integration. The predicted virial coefficients were corrected to first-order quantum effects. The results turn out to be good agreement with experimental data and those from empirical correlation method. The quality of 5-site potentials proved the reliability for prediction of molecular thermodynamic properties.

Keywords: ab initio 5-site potentials, second virial coefficients, ab initio energy.

I - INTRODUCTION

The development of new intermolecular potentials is most important theoretically and practically. The intermolecular potentials proved accurately the interaction between particles in the microscopic system. This could help to understand the macroscopic phenomena. The second virial coefficient $B_2(T)$ is an important parameter presenting the 2-body interactions of molecular system. The mixture of hydrogen and fluorine was applied for several industrial branches. The mixture of gases hydrogen and fluorine produced a kind of rocket fuel [1]. The thermodynamic properties of this mixture were not able to measure experimentally. Therefore, the estimate of

thermodynamic parameters for this mixture is very important for practical application. The theoretical way is suitable for prediction of thermodynamic properties and vapor-liquid equilibria of this system.

The Lennard-Jones-style potential was used for several systems to describe the molecular interaction. There was a lot of pair potentials were developed from this potential. However, the Lennard-Jones-style potentials exhibited the disadvantage, it that was not able to describe the intermolecular forces in long-rang and short-rang area. Deiters and Leonhard developed a potential for argon, krypton the from the function form proposed by Korona [2]. A near-experimental accuracy for neon was dealt in the

first work of Deiters, Hloucha and Leonhard [6]. Nasrabad and Deiters even predicted phase high-pressure vapour-liquid phase equilibria of noble-gas mixtures [3, 4]. Other mixed-dimer potentials for noble gases published by López Cacheiro [5], but not used for phase equilibrium predictions, yet. Moreover, Leonhard and Deiters used a 5-site Morse-style potential to represent the pair potential of nitrogen [7] and they predicted successfully vapour pressures and orthobaric densities. Bock et al. also used a 5-site pair potential for carbon dioxide [8]; they furthermore applied the first-order quantum correction to the virial coefficients developed by Pack [9].

In present work, we report the calculated *ab initio* intermolecular energies of dimer hydrogen-fluorine using at a high theoretical level. The 5-site pair potentials for this are constructed from these *ab initio* energies. The virial coefficients for dimer H_2-F_2 are calculated using these 5-site potential functions. The virial coefficients resulting from these potentials are compared to experimental data and those from empirical correlation method to represent the

reliability of *ab initio* 5-site potentials.

II - COMPUTATIONAL DETAILS

1. Molecular orientation

In this work hydrogen and fluorine molecules are represented as 5-site models, with two sites placed on the atoms (H or F), one site in the center of gravity (M), and two sites halfway between the atoms and the center (N). The molecules are treated as rigid; the interatomic distances are set to 0.7413 Å for hydrogen and 1.418 Å for fluorine [10]. As hydrogen and fluorine are linear molecules, the intermolecular pair potential is a function of distance r (distance 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°. Care was taken to recognize identical configurations in order to reduce the computational workload.

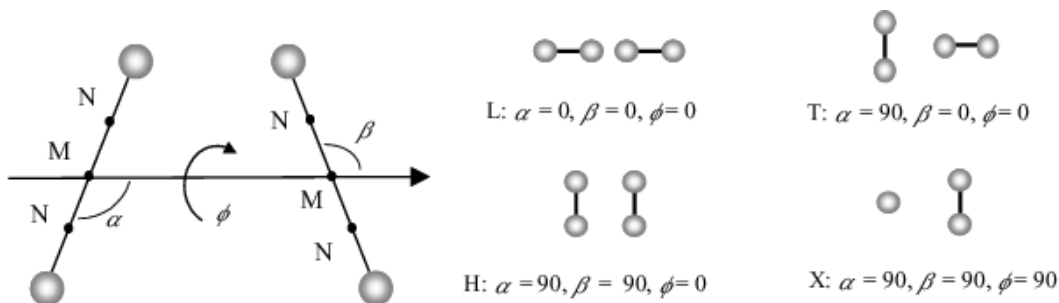


Figure 1: 5-site model of dimer H_2-F_2 and special orientations

2. Quantum chemical calculations

A full configuration interaction treatment (CI) of electron correlations requires enormous computational resources. Fortunately there are several other post-SCF methods that can capture at least a part of the electron correlation effects, e.g., Møller–Plesset perturbation theory MP_n with various orders ($n = 2, 3, 4$) and coupled-

cluster methods (CC). These methods improved for the accurate description of molecular interaction. Experience shows that especially the CCSD(T) method appears to account for the most significant electron correlation effects. The convergent quality of various basis sets, in this study was considered using a small polar basis set 6-31G(d) and two kinds of correlation

consistent basis sets of Dunning [11]: first kinds are not augmented to take care of diffuse functions: cc-pVDZ (for hydrogen: 4s1p/ 2s1p and for fluorine: 9s4p1d/ 3s2p1d), cc-pVTZ (for hydrogen: 5s2p1d/ 3s2p1d and for fluorine: 10s5p2d1f/4s3p2d1f), and second kinds are augmented to take care of diffuse functions: aug-cc-pVDZ (for hydrogen: 5s2p/ 3s2p and for fluorine: 10s5p2d/ 4s3p2d) and aug-cc-pVTZ (for hydrogen: 6s3p2d/ 4s3p2d and for fluorine: 11s6p3d2f/ 5s4p3d2f). The *ab initio* energies were corrected for the basis set superposition error (BSSE) with the counterpoise correction method proposed by Boys and Bernardi [12]:

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

where E_{AB} the total electronic energy of 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 [13, 14]:

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

with $m = 2$ (for cc-pVDZ and aug-cc-pVDZ) or 3 (for cc-pVTZ and aug-cc-pVTZ). *Ab initio* calculations were carried out with the Gaussian03 program package [17].

The influence of the theory level and the basis sets is shown in Fig. 2a and 2b for the T configuration. In all cases the extrapolation to the basis set limit has a significant effect on the calculated energies. This also proves that the molecules are not significantly deformed upon making contact with each other, or that vibrational excitation is not to be expected with low-speed collisions. The potential energies of dimer $H_2 - F_2$ for all distances and orientations were calculated with the CCSD(T) method and basis sets aug-cc-pV m Z ($m = 2, 3, 23$).

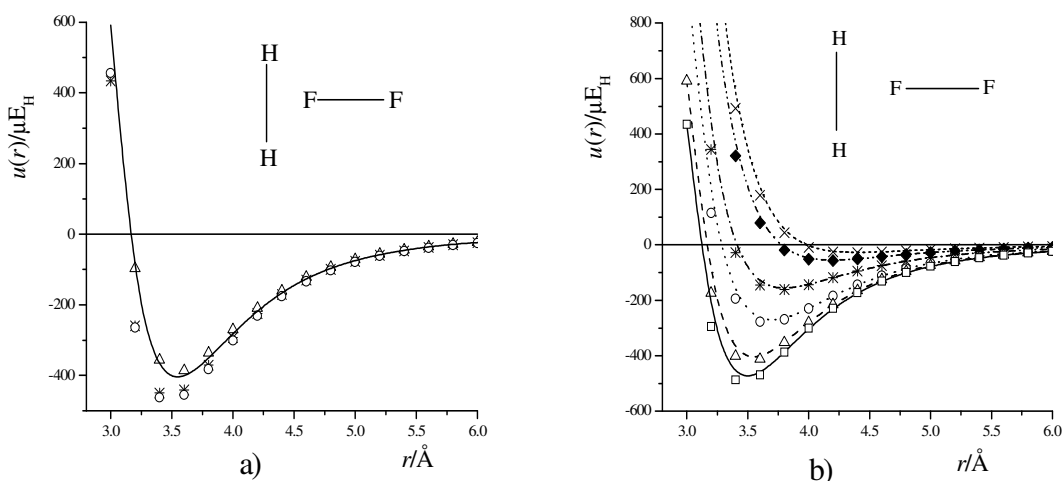


Figure 2: a) Interaction energy of T-shape as a function of theoretical levels using the basis set aug-cc-pVTZ. Symbol: *, MP₂; Δ, MP₃; ○, MP₄; —, CCSD(T).

b) Potential energy of T-shape as a function of basis sets at level CCSD(T). Symbol: ×, 6-31G(d); ◆, cc-pVDZ; *, cc-pVTZ; ○, aug-cc-pVDZ; Δ, aug-cc-pVTZ; □, aug-cc-pV23Z.

3. Potential function

For the calculation of virial coefficients, but especially for the use within computer

simulations, it is desirable to represent the *ab initio* pair potentials. Modeling the molecular anisotropy by spherical harmonics is possible in

principle, but not attempted here for reasons explained in the Introduction. Instead, the multi-center potentials are proposed. Two our new 5-site functional forms were explored in this

work. The first one is developed by incorporating the 5-site pair potential proposed by Deiters for nitrogen [7] with 5-site potential proposed by Bock for carbon dioxide [8]:

$$u(r_{ij}, \alpha, \beta, \phi) = \sum_{i=1}^5 \sum_{j=1}^5 \left[D_e^{ij} ((1 - e^{-\alpha_{ij}(r_{ij} - \beta_{ij})})^2 - 1) + f_1(r_{ij}) \sum_{n=6,8,10} \frac{C_n^{ij}}{r_{ij}^n} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] \quad (3)$$

with $f_1(r_{ij}) = (1 + e^{-2(\delta_{ij} r_{ij} - 2)})^{-15}$

The damping function $f_1(r_{ij})$ is selected from damping function for CO₂ proposed by Bock [8].

Table 1: Optimized parameters of 5-site potential Eq. 3. For all interactions $\delta_{ij} = 2.0 \text{ \AA}^{-1}$ were assumed partial charges for hydrogen: $q_{\text{N/e}} = 0.078329$, $q_{\text{H}} = 0$; for fluorine: $q_{\text{N/e}} = -0.781897132$, $q_{\text{F}} = 0$; $q_{\text{M}} = -2q_{\text{N}}$; $E_{\text{H}} = 4.359782 \cdot 10^{-18} \text{ J}$ (Hartree energy unit)

| Interaction | D_e/E_{H} | $\alpha/\text{\AA}^{-1}$ | $\beta/\text{\AA}^{-1}$ | $(C_6/E_{\text{H}}) \text{\AA}^6$ | $(C_8/E_{\text{H}}) \text{\AA}^8$ | $(C_{10}/E_{\text{H}}) \text{\AA}^{10}$ |
|-------------|------------------------|--------------------------|-------------------------|-----------------------------------|-----------------------------------|---|
| H-F | -1.300.10 ⁰ | 1.360 | -0.081 | -2.576.10 ⁰ | 1.426.10 ¹ | -3.503.10 ¹ |
| H-N | -5.649.10 ⁰ | 1.286 | -5.149 | -7.132.10 ¹ | 3.761.10 ² | -6.514.10 ² |
| H-M | 2.780.10 ⁰ | 1.070 | -2.074 | 1.090.10 ² | -6.449.10 ² | 1.198.10 ³ |
| N-F | 2.075.10 ¹ | 1.401 | -1.052 | 5.370.10 ¹ | -2.594.10 ² | 5.393.10 ² |
| N-N | 3.192.10 ¹ | 1.951 | -0.689 | 1.743.10 ² | -9.437.10 ² | 1.556.10 ³ |
| N-M | -1.620.10 ¹ | 1.979 | -0.342 | -1.222.10 ² | 7.723.10 ² | -1.049.10 ³ |
| M-F | -1.563.10 ¹ | 1.437 | -0.490 | -1.098.10 ² | 5.266.10 ² | -1.079.10 ³ |
| M-M | -4.245.10 ¹ | 1.096 | -1.479 | -1.278.10 ² | 4.217.10 ² | -1.685.10 ³ |

The second functional form is developed from the 5-site pair potential proposed by Deiters for nitrogen [7] with the 3-site potential proposed by Naicker [15, 16]:

$$u(r_{ij}, \alpha, \beta, \phi) = \sum_{i=1}^5 \sum_{j=1}^5 \left[D_e^{ij} ((1 - e^{-\alpha_{ij}(r_{ij} - \beta_{ij})})^2 - 1) + f_2(r_{ij}) \left(\sum_{n=6,8,10,12} \frac{C_n^{ij}}{r_{ij}^n} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) \right] \quad (4)$$

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

Here the function $f_2(r_{ij})$ is taken from Tang and Toennies damping function [18]; r_{ij} site-site distances; q_i electric charge of sites and C_{ij}^n dispersion coefficients; the leading dispersion term is always proportional to r . In

both models the auxiliary N sites (illustrated in Fig. 1), placed on the molecule axis halfway between the outer sites (H or F) and the center (M), carry each a charge of $+q$, and the central M site a charge of $-2q$. The outer sites do not wear electric charges.

Table 2: Optimized parameters of 5-site potential Eq. 4. For all interactions $\delta_{ij} = 5.0 \text{ \AA}^{-1}$ were assumed. See table 1 for the partial charges

| Interaction | D_e/E_H | $\alpha/\text{\AA}^{-1}$ | $\beta/\text{\AA}^{-1}$ | $(C_6/E_H)\text{\AA}^6$ | $(C_8/E_H)\text{\AA}^8$ | $(C_{10}/E_H)\text{\AA}^{10}$ | $(C_{12}/E_H)\text{\AA}^{12}$ |
|-------------|---------------------|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------------|-------------------------------|
| H-F | $3.046 \cdot 10^1$ | 2.520 | -0.225 | $5.047 \cdot 10^1$ | $-2.794 \cdot 10^1$ | $3.642 \cdot 10^2$ | $-2.116 \cdot 10^2$ |
| H-N | $-2.781 \cdot 10^1$ | 2.269 | -0.043 | $-1.703 \cdot 10^2$ | $3.353 \cdot 10^2$ | $-1.500 \cdot 10^3$ | $1.537 \cdot 10^3$ |
| H-M | $6.524 \cdot 10^1$ | 2.938 | 0.280 | $1.448 \cdot 10^2$ | $-1.240 \cdot 10^2$ | $2.068 \cdot 10^3$ | $-2.185 \cdot 10^3$ |
| N-F | $4.202 \cdot 10^1$ | 2.054 | -0.488 | $-5.855 \cdot 10^1$ | $3.163 \cdot 10^2$ | $-2.159 \cdot 10^2$ | $2.525 \cdot 10^2$ |
| N-N | $5.116 \cdot 10^1$ | 2.141 | -0.255 | $3.163 \cdot 10^2$ | $-2.657 \cdot 10^2$ | $-2.259 \cdot 10^2$ | $1.404 \cdot 10^3$ |
| N-M | $-4.467 \cdot 10^1$ | 2.852 | 0.128 | $-1.909 \cdot 10^2$ | $-6.620 \cdot 10^2$ | $5.222 \cdot 10^3$ | $-8.645 \cdot 10^3$ |
| M-F | $-2.489 \cdot 10^1$ | 2.104 | 0.313 | $-8.171 \cdot 10^0$ | $-4.329 \cdot 10^2$ | $-5.434 \cdot 10^2$ | $4.225 \cdot 10^2$ |
| M-M | $-2.554 \cdot 10^1$ | 1.981 | -0.034 | $-6.141 \cdot 10^1$ | $2.261 \cdot 10^3$ | $-1.624 \cdot 10^4$ | $2.434 \cdot 10^4$ |

Fitting the potential functions Eqs. 3 and 4 to the *ab initio* energies is not simple. The object function of fitting problem has got many local minima. So in this study the global minima were coarsely located by means of Genetic algorithm (GA), and then the parameters are optimized with the Marquardt-Levenberg algorithm. The optimized parameters of potential functions Eqs. 3 and 4 are given in tables 1 and 2.

4. Second virial coefficient

The second virial coefficients, B_2 are associated with the intermolecular potential energy by rigorous statistical thermodynamic theory. Therefore, the second virial coefficient

depends on the intermolecular pair potential. In this study, the second virial coefficients of the dimer H_2-F_2 are predicted from our *ab initio* pair potentials Eqs. 3 and 4. For the case of hydrogen is a light gas so the quantum effects would be important. Therefore, the mixture of gas hydrogen and fluorine need to consider for these effects. The quantum correction can be obtained from a perturbation expansion of Planck's constant [19]. The first-order quantum correction to the virial coefficient of linear molecules was proposed by Pack [9] and Wang [20]. Recently, the quantum correction was presented in Wormer's work too [21]. The virial coefficients up to first order can be written as

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

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.

This expression can be broken down into a classical term and first-order quantum corrections (radial part, angular part proportional to I^{-1} (moment of inertia), angular part proportional to μ^{-1} (reduced mass)):

$$B(T) = B_{cl}^0(T) + B_r^1(T) + B_{al}^1(T) + B_{am}^1(T) \quad (6)$$

The classical virial coefficient is given by:

$$B_{cl}^0 = -\frac{N_A}{4} \int_0^{2\pi} d\varphi \int_0^\pi \sin\beta d\beta \int_0^\pi \sin\alpha d\alpha \int_0^\infty \left(\exp\left(-\frac{u}{k_B T}\right) - 1 \right) r^2 dr \quad (7)$$

The terms $u_{l_1 l_2 l}(r) A_{l_1 l_2 l}(\alpha, \beta, \phi)$ represent a spherical harmonics expansion of the interaction potential. All these integrals were evaluated numerically with 4D Gauss-Legendre quadrature method [22]. The predicted virial coefficients are compared to those from empirical correlation method in the percent deviation:

$$\%Dev = \left| \frac{B_{cal} - B_{correl}}{B_{correl}} \right| 100\% \quad (8)$$

Where B_{cal} the predicted second virial coefficient from our pair potentials; B_{correl} the calculated second virial coefficient from empirical correlation equation [23]. The resulting virial coefficients of dimer H_2 - F_2 included the first-order quantum corrections are given in Fig. 3.

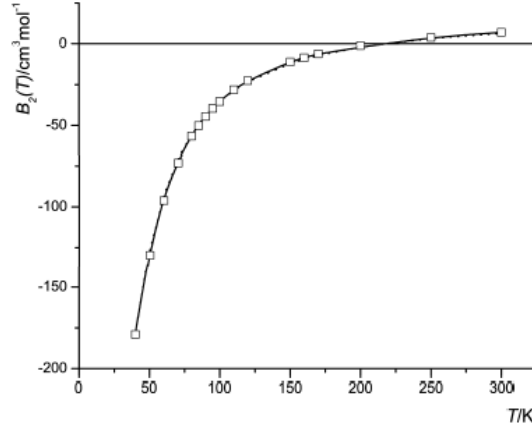


Figure 3: Cross second virial coefficient of H_2 - F_2 system. —: *ab initio* prediction (this work) based on Eq. 3, - - -: *ab initio* prediction (this work) based on Eq. 4; \square : empirical correlation [23]

Recently Estela-Urbe and Jaramillo [23] published empirical correlation equations for virial coefficients which are based on the corresponding - states of Lee and Kesler [24]. In their work, binary interactions are characterized by so-called pseudo-critical parameters, which are interpolations of the pure-fluid critical temperatures and densities:

$$\rho_{c,ij}^{-1/3} = \frac{1 + d_{ij}}{2} (\rho_{c,i}^{-1/3} + \rho_{c,j}^{-1/3}) T_{c,ij} = \frac{(1 - k_{ij})(T_{c,i} T_{c,j})^{1/2}}{1 + c / (M_{ij} T)} \quad (9)$$

$$\text{with } M_{ij}^{-1} = \frac{1}{2} (M_i^{-1} + M_j^{-1}) \text{ and } k_{ij} = 1 - \frac{a_{ij} \rho_{c,ij}}{(\rho_{c,i} \rho_{c,j})^{1/2}} \quad (10)$$

Here the M_i denote molar masses of the pure components, M_{ij} an interaction molar mass, and c is a constant (21.8 K g/mol). It turns out that the adjustable parameters a_{ij} and d_{ij} are very close to zero for a large number of chemical compounds. We have set these two correlation

parameters to zero for the H₂-F₂ interaction and used the correlations of Estela-Uribe and Jaramillo to predict cross second virial coefficients. The results, presented in Fig. 3, show a remarkably good agreement with the predictions from quantum mechanics.

III - CONCLUSION

We conclude that our ab initio pair potential for the hydrogen-fluorine interaction is reliable, and that the calculation of thermodynamic properties from quantum mechanical results can be useful, if experimental data are scarce.

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**TÍNH TOÁN *AB INITIO* CÁC THỂ TƯƠNG TÁC PHÂN TỬ VÀ
DỰ ĐOÁN CÁC HỆ SỐ VIRIAL BẬC HAI CỦA DIME H₂ - F₂**