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The perturbation calculation of van der Waals potentials

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Summary. The unsymmetrized perturbation theory for interaction potentials is reformulated in such a way that the overlap and exchange effects can be taken into account in a satisfactory and conceptually simple way. This formulation, known as the generalized Heitler–London theory, its shown to be valid regardless of the ultimate limit to which the polarization approximation converges. Within the framework of this theory, the van der Waals potential of the triplet $H_2(^3\Sigma_u)$ state is calculated and shown to be in excellent agreement with the exact *ab initio* results. Both the exchange energy and the polarization energy are obtained from a perturbation calculation.

Key words: Perturbation theory – Interaction potentials – Heitler–London theory

1 Introduction

Quantum-chemical calculations of van der Waals interaction potential were succinctly reviewed by Kutzelnigg [1] in an important 1977 paper. In view of the fact that “standard quantum chemical computational methods even of CI type usually fail for van der Waals interactions”, he concluded “that straightforward Rayleigh–Schrödinger perturbation theory is still the method of choice if one is interested in the asymptotic behaviour of the interaction for $R \to \infty$”. However, he continued to state that “one of the big practical problems is to take overlap and exchange effects on intermolecular forces into account in a satisfactory and conceptually simple way”.

The problem arises from the fact that in order to describe the entire potential energy curve in the van der Waals region, a knowledge of both the long range attractive and short range repulsive potentials as well as the effect of the charge overlap are required. It is well known that the long-range attractive potentials can be described by the dispersion series obtained from the second order Rayleigh–Schrödinger (RS) perturbation theory. The short-range repulsive potential comes mainly from the exchange forces. Up until recently, it was generally

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believed that the exchange potential cannot be obtained from the ordinary (unsymmetrized) RS perturbation theory. Therefore a large amount of effort has been devoted to the development of the so-called symmetry adapted perturbation expansions [2,3]. Unfortunately these expansions are very complicated and give no unique results.

Essentially one can view the symmetry adapted perturbation theories as attempts to extend the Heitler–London treatment to higher orders. Since "a perturbation scheme based on the Heitler–London result is undesirable in the sense that it does not produce in leading order the proper asymptotic behaviour of [the exchange energy],... and no treatment has demonstrated that the correct exponential terms can be obtained this way" [4], serious doubts on the validity of the symmetry adapted perturbation theories for large R have been expressed [5]. Previously it was felt that the correct form of the exponential terms can only be obtained from the asymptotic exchange perturbation theory [6]. This theory was derived rather early in connection with some problems with exchange interactions involved in describing magnetism in solids. It is based on the simple physical concept of relating the exchange energy to the flux of the electrons flowing back and forth between the atoms in the molecule. Previously this theory which involves calculating a surface integral was considered to be "very different in nature from the RS perturbation theory involving special analytical techniques which do not appear capable of systematic improvement" [5].

Recently we have shown that the unsymmetrized perturbation theory can be used with the surface integral to give the exchange energy [7, 8]. Furthermore the energy can be systematically improved. In the framework of the generalized Heitler–London theory [9,10], this exchange energy is modified by the overlap integral and combined with the polarization energy to give the eigenenergies of the system. In this paper we will use the $H_2(^3\Sigma_u)$ potential to illustrate that the van der Waals potential can be constructed from the asymptotic expansions of these energy components. It will be seen that the overlap and exchange effects can indeed be taken into account in a satisfactory and conceptually simple way.

In the next section, we will first re-examine the generalized Heitler–London (HL) theory in the light of yet another one of Kutzelnigg's recent papers [11]. In the new theory the polarization energy and the exchange energy are clearly separated. We will show that this theory is valid regardless of the limit to which the polarization approximation will ultimately converge. In Sect. 3, the asymptotic expressions of the exchange energy and the polarization energy are presented. We will show that although the $1/R$ expansion of the polarization energy is a divergent asymptotic series, it can nevertheless be summed and extended to small distances with a damping function which depends only on the exchange energy. Finally in Sect. 4, these expressions together with the overlap integral are combined according to the generalized HL theory. The result is a remarkably accurate potential in the van der Waals region. All quantities in this paper are in atomic units.

2 The generalized Heitler–London theory

2.1 Rayleigh–Schrödinger perturbation theory

The Rayleigh–Schrödinger perturbation theory [12] is briefly reviewed here to establish the notation. When electron exchange is neglected in the calculation, this perturbation theory is known as the polarization approximation [13].

In the Born–Oppenheimer approximation, the Hamiltonian of the H_2 molecule, written in the atomic units is

$$H = H_0 + V, \tag{1}$$

with

$$H_0 = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2B}}, \tag{2}$$

$$V = -\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R}. \tag{3}$$

The wavefunction χ_p and the energy E_p of the Schrödinger equation with a zeroth-order Hamiltonian H_0 and a perturbing potential V:

$$(H_0 + \lambda V)\chi_p = E_p \chi_p \tag{4}$$

are both expanded in an infinite series in powers of λ:

$$\chi_p = \sum_{n=0} \lambda^n \phi_n, \tag{5}$$

$$E_p = \sum_{n=0} \lambda^n \varepsilon_n. \tag{6}$$

The different orders of the wavefunction satisfy the following set of equations:

$$n = 0\colon\ (H_0 - \varepsilon_0)\phi_0 = 0, \tag{7}$$

$$n = 1\colon\ (H_0 - \varepsilon_0)\phi_1 + (V - \varepsilon_1)\phi_0 = 0, \tag{8}$$

$$n \geqslant 2\colon\ (H_0 - \varepsilon_0)\phi_n + (V - \varepsilon_1)\phi_{n-1} = \sum_{i=2}^{n} \varepsilon_i \phi_{n-i}, \tag{9}$$

with the condition:

$$\langle \phi_0, \phi_n \rangle = \delta_{n,0}. \tag{10}$$

Since H_0 is the Hamiltonian of the two isolated hydrogen atoms, the zeroth-order wavefunction is simply the product of the 1s orbitals of the two unperturbed hydrogen atoms:

$$\phi_0 = 1S_A(1)\,1S_B(2), \tag{11}$$

and the zeroth-order energy is

$$\varepsilon_0 = -1. \tag{12}$$

The higher orders of energy are then given by

$$\varepsilon_{n+1} = \langle \phi_n, V\phi_0 \rangle. \tag{13}$$

The question of convergence immediately arises. It is known that for small λ, Eq. (6) is convergent, the question is whether it converges for $\lambda = 1$. In a recent paper "Does the polarization approximation converge for large R to primitive or a symmetry-adapted wavefunction?" Kutzelnigg [11] showed that, with certain assumptions, it also converges at $\lambda = 1$, although it converges extremely slowly. In this paper, we will denote the Nth-order approximation of the polarization energy by:

$$\varepsilon_p^N = \sum_{n=1}^{N} \varepsilon_n. \tag{14}$$

2.2 *The Eigenenergies of the system*

Since the total Hamiltonian H is symmetric with respect to the interchange of electrons 1 and 2, the eigenfunctions must be either symmetric or anti-symmetric. The symmetric wavefunction is associated with the singlet state and the anti-symmetric wavefunction with the triplet state. That is

$$H\varphi_s = E_s\varphi_s, \tag{15}$$

$$H\varphi_t = E_t\varphi_t, \tag{16}$$

and

$$P\varphi_s = \varphi_s, \tag{17}$$

$$P\varphi_t = -\varphi_t, \tag{18}$$

where P is the operator which interchanges the coordinates of electrons 1 and 2.

At large R, the two states are nearly degenerate. Half of the difference of the two energies is known as the exchange energy ε_x:

$$\varepsilon_x = \tfrac{1}{2}(E_t - E_s). \tag{19}$$

To see the relationship between various energy components, it is useful to define the Coulomb energy ε_c as

$$\varepsilon_c = \tfrac{1}{2}(E_t + E_s). \tag{20}$$

Thus, it is clear that

$$E_g = \varepsilon_c - \varepsilon_x, \tag{21}$$

$$E_t = \varepsilon_c + \varepsilon_x. \tag{22}$$

2.3 *The equation that governs the polarization wavefunction*

In the above-mentioned recent paper [11] Kutzelnigg concluded that the polarization approximation will converge, in infinite order, to the symmetrical ground state wavefunction. However, he goes on to state that "the wavefunction of the polarization approximation is genuinely primitive (localized) to any finite order". This is the dilemma of the conventional perturbation theory. In principle it converges to the ground state and yet one can never achieve it in any actual calculation. Earlier we have shown that if the polarization expansion is assumed to converge to the primitive wavefunction:

$$\Phi_a = \frac{1}{\sqrt{2}}(\varphi_s + \varphi_t), \tag{23}$$

one can obtain not only the polarization energy in excellent agreement with all practical calculations [9, 10], but one can also obtain the exchange energy through the surface integral [7, 8]. Recently Cwiok et al. [14] carried the perturbation calculation for H_2 to 150th order. While their result still did not converge to the ground state, they used an elaborate extrapolation method to show that it will eventually converge to the ground state in infinite order. It seems that at present the conventional polarization approximation is not a convenient way to calculate the potential energy. On the other hand, when the polarization series is substituted into the equations of the generalized HL theory, it leads to a series which converges very rapidly [9, 10].

Next, we will show by a nearly trivial calculation that this theory is always valid. All we have to do is to demonstrate that the formulas derived are in fact independent of the convergence limit of the polarization approximation. We start with an Ansatz for the wavefunction of the polarization approximation which covers all possible eventualities of convergence discussed above.

$$\chi_p = \frac{1}{(1 + k^2(R))^{1/2}} (\varphi_s + k(R)\varphi_t). \tag{24}$$

If χ_p converges to φ_s for all R, then $k(R) = 0$. If at large R, it converges to the localized wavefunction of Eq. (23), then $k(\infty) = 1$. We then develop a set of energy expressions which are independent of k.

It is easy to show that Eq. (24) satisfies the following equation, which is the basis of the generalized Heitler–London theory:

$$(H_0 + V)\chi_p = (\varepsilon_c - \varepsilon_x P)\chi_p. \tag{25}$$

The left side of this equation is

$$\begin{aligned}(H_0 + V)\chi_p &= (H_0 + V)\frac{1}{(1 + k^2)^{1/2}} (\varphi_s + k\varphi_t)\\ &= \frac{1}{(1 + k^2)^{1/2}}(E_s\varphi_s + kE_t\varphi_t).\end{aligned} \tag{26}$$

The right side of Eq. (25) can be expressed as

$$(\varepsilon_c - \varepsilon_x P)\chi_p = \frac{1}{(1 + k^2)^{1/2}}[(\varepsilon_c - \varepsilon_x P)\varphi_s + k(\varepsilon_c - \varepsilon_x P)\varphi_t]. \tag{27}$$

Using Eqs. (17), (18), (21), and (22) we have

$$(\varepsilon_c - \varepsilon_x P)\chi_p = \frac{1}{(1 + k^2)^{1/2}}(E_s\varphi_s + kE_t\varphi_t)\cdot \tag{28}$$

Since Eq. (28) is identical with Eq. (26), Eq. (25) is clearly established to be independent of the value of k.

2.4 Energies according to the generalized Heitler–London theory

To get a solution to all orders we first substitute Eq. (5) into Eq. (25) with $\lambda = 1$.

$$(H_0 + V)| \sum_{n=0} \phi_n\rangle = (\varepsilon_c - \varepsilon_x P)| \sum_{n=0} \phi_n\rangle. \tag{29}$$

Forming the inner product with $\langle\phi_0|$, we obtain

$$\varepsilon_0 + \sum_{n=0} \langle\phi_0, V\phi_n\rangle = \varepsilon_c - \varepsilon_x \sum_{n=0} \langle\phi_0, P\phi_n\rangle. \tag{30}$$

Using Eqs. (6) and (13), this equation can be written as

$$E_p = \varepsilon_c - \varepsilon_x \sum_{n=0} \langle\phi_0, P\phi_n\rangle. \tag{31}$$

Let us define various orders of overlap integrals as

$$S_n = \langle\phi_0, P\phi_n\rangle, \tag{32}$$

then Eq. (31) becomes

$$\varepsilon_c = E_p + \varepsilon_x \sum_{n=0} S_n. \tag{33}$$

Substituting Eq. (33) into Eqs. (21) and (22), we obtain the desired generalized Heitler–London expressions for the energies of the singlet ${}^1\Sigma_g$ and the triplet ${}^3\Sigma_u$ states of H_2 for all distances:

$$E_s = E_p - \left(1 - \sum_{n=0} S_n\right)\varepsilon_x, \tag{34}$$

$$E_t = E_p + \left(1 + \sum_{n=0} S_n\right)\varepsilon_x. \tag{35}$$

In a previous publication we expanded these expressions up to fourth order and expressed them in terms of the usual Coulomb and exchange integrals [10]. The first-order term is simply the usual Heitler–London formula. The second-order term is identical to that of the symmetry-adapted Murrel–Shaw [15] and Musher–Amos [16] theory obtained by Chałasinski and Jeziorski [17]. The entire series was recently shown [18] to be equivalent to the symmetrized Rayleigh–Schrödinger expansion of Jeziorski et al. [19]. However, here we wish to emphasize that with ε_x in Eqs. (34) and (35) calculated by the surface integral method, then already in first order the results are different from those of the above mentioned symmetry adapted theories as has been demonstrated [20, 8] for both H_2^+ and H_2.

If ε_x can be calculated from the polarization approximation, as is discussed in the next section, we will achieve our objective of calculating both E_s and E_t with the unsymmetrized RS perturbation theory. The paramount question is how fast will the series converge to the respective energies? We have demonstrated previously that with only two orders, the ground-state energies of H_2^+ and H_2 already converge to within a few percent in the entire region of the chemical bond [9, 20]. Here we will show that this is equally true for the H_2 triplet state van der Waals potential. Moreover, near the van der Waals minimum and at smaller distances, the asymptotic expressions can still be used to accurately describe these potentials.

3 Asymptotic theory of the interaction potential

3.1 Asymptotic exchange energy

Following the pioneering work of Gor'kov and Pitaevski [21] and Herring and Flicker [22] the exchange energy can be written as

$$\varepsilon_x = \frac{-\int_{\Sigma} (P\Phi_a)\nabla^6 \Phi_a \cdot \mathbf{n}\, d^5 s}{1 - 2\int_{\text{far}} \Phi_a^2\, d^6 r}, \tag{36}$$

where Φ_a is the localized wavefunction of Eq. (23), $\mathbf{n}$ is a vector normal to the hyperplane, and ∇^6 is the gradient operator in the six dimensional space of the two electrons. The five dimensional surface integral is over the hyperplane Σ which consists of all planes perpendicular to the internuclear axis in ordinary three dimensional space. The six-dimensional volume integral in the denominator is over the far side of Σ where the localized wavefunction is exponentially decaying. At large internuclear distances the denominator goes to unity, however at small distances the volume integral increases and the denominator has an increasing effect.

With the exchange energy defined in Eq. (19), this expression is exact. Recently we have shown [8] that even with the simplest zeroth order approximation for Φ_a ($\Phi_a = \phi_0$), the exchange energy obtained from this formula for H_2 closely follows the exact value over the entire range of internuclear distances down to $R = 0.5$ a.u. In this respect it performs just as well as conventional symmetrized Heitler–London theory. As already pointed out by Herring and Flicker the big advantage of the new calculation is that it does not exhibit the incorrect behavior at $R \approx 50$ a.u. which already in 1961 Bingel and coworkers realized to be a problem with conventional Heitler–London theory [23]. For large R, it can be shown [24] that the asymptotic exchange energy calculated from Eq. (36) using the higher-order polarization approximation for calculating Φ_a leads to the previously reported result of Herring and Flicker [22, 25]:

$$\varepsilon_x \underset{R\to\infty}{=} 0.818\, R^{5/2} e^{-2R}. \tag{37}$$

Previously Kolos and Wolniewicz established that this result is in excellent agreement with "exact" *ab initio* calculations down to about $R = 7$ a.u. [26]. Our use of the polarization approximation via Eq. (36) demonstrates that by using perturbed wavefunctions the effect of the dispersion forces can be included in a systematic way. In this approach the exchange energy is associated with the physical exchange of electrons between the two nuclei. This concept, although still not generally accepted in the chemistry community [27], is demonstrated to be correct by the excellent results obtained [8].

3.2 Asymptotic polarization energy

In the asymptotic region, it is well known that the interaction potential is correctly described by the long range dispersion series [28]. This series can be obtained from the RS perturbation theory by expanding the perturbation energy in powers of R^{-1}. The advantage of this approach is that each individual term can be given a direct physical interpretation as the induced multipole interaction. As is well known the series is actually divergent [29] since it is based on the assumption that the overlap of the atomic wavefunctions is negligible. It is possible however to correct for charge overlap, by writing the dispersion series as [30]:

$$\varepsilon_2(R) = -\sum_{2n=6} f_{2n}(R)\, C_{2n} R^{-2n}, \tag{38}$$

where the C_{2n} are the asymptotic dispersion coefficients and the $f_{2n}(R)$ are damping functions which are less than one in the region of small internuclear distances. The dispersion coefficients are known for many systems and for H_2 essentially exact values are available [30, 31]: $C_6 = 6.499$, $C_8 = 124.4$, $C_{10} = 3.286 \times 10^3$, $C_{12} = 1.215 \times 10^5$, $C_{14} = 6.061 \cdot 10^6$. In recent years, considerable effort has gone into the *ab initio* calculation of the damping functions [30]. With the availability of accurate calculations, it has been possible to develop analytical expressions for the damping functions. One especially simple and successful expression is given by [32]:

$$f_{2n}(R) = 1 - \exp(-bR) \sum_{k=0}^{2n} \frac{(bR)^k}{k!}, \tag{39}$$

where b is the range parameter of the repulsive part of the potential. Eq. (39) was derived on the assumption that the short range repulsive potential is described by the Born–Mayer form $A \exp(-bR)$. Referring to Eq. (35) we see that in the context of the generalized Heitler–London theory, that the repulsive part of the triplet state potential can be attributed almost entirely to the exchange energy ε_x since the overlap integral S_0 is very small in the van der Waals region (see Table 2). As seen from Eq. (37), ε_x is in fact not purely exponential. For such a case, under these circumstances we have recently proposed that the parameter b should be given by [33]:

$$b(R) = -\frac{\mathrm{d}}{\mathrm{d}R} \ln(\varepsilon_x). \tag{40}$$

and will thus be a function of R.

In the case of triplet H_2, with ε_x given by Eq. (37):

$$b = 2 - \frac{5}{2}\left(\frac{1}{R}\right). \tag{41}$$

The minimum position of the $H_2(^3\Sigma_u)$ state potential is at $R_m = 7.8$ a.u., for which according to Eq. (41), $b(R_m) = 1.68$. It is gratifying to see that this is in good agreement with the value of $b = 1.66$ used and obtained previously from a Born–Mayer fit of SCF calculations [32]. This shows that our previous choice was consistent with the generalized Heitler–London equation at least in the region of the van der Waals minimum. When the damping functions calculated with Eqs. (39) and (41) are compared with the nearly "exact" values of the damping functions of the H_2 system [30], the agreement is very similar to that previously reported in Ref. [32]. Near the van der Waals minimum ($R \sim 8.0$ a.u.), the present results and our previous results [32] with a constant b agree very well with the exact values as expected. For $R > 8.0$ a.u., the present results are much better especially for terms of higher n and are almost identical with the exact values. For $R < 7$ a.u. the present damping functions deviate from the exact values. This is not unexpected as the asymptotic exchange energy of Eq. (37) becomes less accurate at smaller R.

In order to implement Eq. (35) we also need the first order polarization energy ε_1, which for H_2 is given by [34]:

$$\varepsilon_1 = \left(\frac{1}{R} + \frac{5}{8} - \frac{3}{4}R - \frac{1}{6}R^2\right)\exp(-2R). \tag{42}$$

Like the exchange energy, ε_1 is exponentially decreasing at large R. However, it is not yet completely negligible at the minimum of the triplet state potential. It contributes almost 10% at the well depth (see Table 2).

The overlap integrals are also decreasing exponentially as R increases. In the van der Waals minimum region, only the zeroth order overlap [34]:

$$S_0 = (1 + R + \tfrac{1}{3}R^2)^2 \exp(-2R) \tag{43}$$

has a small effect (see Table 2).

4 Results and discussion

With ε_x, ε_1, ε_2 and S_0 given by Eqs. (37), (42), (38), and (43) respectively, we calculate the singlet state energy E_s and the triplet state energy E_t according to Eqs. (34) and (35). The results are listed in Table 1. They are compared with the "exact" *ab initio* results of Kolos and Wolniewicz [26]. For E_s, the agreement is very good down to $R = 8.0$ a.u. but the predictions are too small by about 20% at $R = 6.0$ a.u. For E_t the agreement is excellent over the entire range down to $R = 3.0$ a.u.

The individual components of the energy are tabulated in Table 2. The asymptotic exchange energy of Eq. (37), as noted before [26], is too small by about 5% at $R = 8$ a.u. and with a much smaller error at larger distances. The absolute value of the damped dispersion series of Eq. (38) is too small by about 4% at 8. a.u. as compared with the second-order polarization energy calculated by Koide et al. [30]. Most of the discrepancy comes from the neglect of induction and spherical dispersion which together still contribute about 3% of the second-order energy at $R = 8.$ a.u. As seen from Eqs. (34) and (35), the errors in the exchange energy and the polarization energy will add up in the singlet state energy E_s, but will cancel each other in the triplet state energy E_t. This explains why in Table 1 the errors in E_t are much smaller than in E_s.

The ${}^3\Sigma_u$ potential of the H_2 molecule is an important prototype of the van der Waals potentials [35]. The potential energy, defined as $V = E_t - \varepsilon_0$, is thus given in second order by

$$V = \varepsilon_p^2 + (1 + S_0)\varepsilon_x. \tag{44}$$

Here we have neglected the high-order overlap integrals, since they are very small. For example, at $R = 8$ a.u., $S_1 = 0.10 \times 10^{-4}$ which is one order of magnitude smaller than S_0 [36]. $V(R)$ is shown in Fig. 1 together with the "exact" *ab initio* values. They are practically indistinguishable. The numerical values of V and the percentage of error as compared with the "exact" *ab initio* calculations are also listed in Table 2. Except near the zero crossing, where small differences are exaggerated, the agreement is within 1 percent in the entire well region.

Previously we have proposed a similar model where the repulsive part is given by a SCF calculation [32]. It was found that the SCF results have to be multiplied by a factor of 1.14 in order to obtain an accurate potential. This 14% correction was attributed to the neglect of the dispersion exchange term, which had to be estimated semi-empirically. In the present theory this term is included in ε_x via Eq. (36) by using the polarization perturbed wavefunction. In the present theory, there is no adjustable parameter.

We feel the generalized HL theory is appealing in that it shows how the energies of the dispersion forces and of the exchange forces are quantitatively combined to give the total energy. It is well known that the dispersion forces are due to the induced multipole interactions [28] and are mediated by photons [37]. With the aid of Eq. (36) we have recently demonstrated that the exchange forces leading to chemical bonding are mediated by electrons which are constantly trading places [8]. Thus this theory not only gives us a practical way of calculating van der Waals potentials, but it also makes the underlying physics more transparent. It seems to us that the validity of the present theory is unequivocally demonstrated by the excellent results of the present study. Thus the 1977 challenge posed by Kutzelnigg [1] "how to take overlap and exchange effects into account in a satisfactory and conceptually simple way" has now been finally successfully met!

Table 1. Singlet ($X\,^1\Sigma_g$) energy E_s and triplet ($b\,^3\Sigma_u$) energy E_t of the H_2 molecule

	E_s(a.u.)		E_t(a.u.)	
R(a.u)	Present[a]	"Exact"[b]	Present[c]	"Exact"[b]
1.0	– 0.933255	– 1.124538	– 0.711847	– 0.621523
1.2	– 1.011908	– 1.164934	– 0.777792	– 0.718964
1.4	– 1.052232	– 1.174474	– 0.821516	– 0.784150
1.6	– 1.070843	– 1.168580	– 0.854899	– 0.831724
1.8	– 1.076608	– 1.155067	– 0.882294	– 0.868291
2.0	– 1.074792	– 1.138131	– 0.905288	– 0.897064
2.2	– 1.068739	– 1.120123	– 0.924546	– 0.919859
2.4	– 1.060631	– 1.102413	– 0.940488	– 0.937905
2.6	– 1.051877	– 1.085781	– 0.953502	– 0.952135
2.8	– 1.043348	– 1.070670	– 0.963983	– 0.963299
3.0	– 1.035537	– 1.057312	– 0.972322	– 0.972010
3.2	– 1.028682	– 1.045783	– 0.978888	– 0.978772
3.4	– 1.022850	– 1.036058	– 0.984010	– 0.983991
3.6	– 1.018008	– 1.028027	– 0.987973	– 0.987998
3.8	– 1.014062	– 1.021530	– 0.991016	– 0.991056
4.0	– 1.010898	– 1.016369	– 0.993335	– 0.993378
4.2	– 1.008391	– 1.012337	– 0.995092	– 0.995130
4.4	– 1.006427	– 1.009230	– 0.996412	– 0.996446
4.6	– 1.004901	– 1.006870	– 0.997399	– 0.997425
4.8	– 1.003724	– 1.005092	– 0.998131	– 0.998150
5.0	– 1.002823	– 1.003763	– 0.998671	– 0.998685
5.2	– 1.002135	– 1.002774	– 0.999065	– 0.999076
5.4	– 1.001613	– 1.002042	– 0.999352	– 0.999360
5.6	– 1.001219	– 1.001503	– 0.999558	– 0.999564
5.8	– 1.000921	– 1.001107	– 0.999706	– 0.000709
6.0	– 1.000696	– 1.000834	– 0.999810	– 0.999813
6.2	– 1.000527	– 1.000619	– 0.999883	– 0.999885
6.4	– 1.000401	– 1.000462	– 0.999934	– 0.999934
6.6	– 1.000305	– 1.000346	– 0.999967	– 0.999967
6.8	– 1.000234	– 1.000260	– 0.099990	– 0.999990
7.0	– 1.000181	– 1.000197	– 1.000003	– 1.000004
7.2	– 1.000139	– 1.000151	– 1.000012	– 1.000012
7.4	– 1.000108	– 1.000116	– 1.000017	– 1.000017
7.6	– 1.000085	– 1.000090	– 1.000020	– 1.000020
7.8	– 1.000067	– 1.000070	– 1.000021	– 1.000020
8.0	– 1.000054	– 1.000055	– 1.000020	– 1.000020
8.5	– 1.000032	– 1.000032	– 1.000017	– 1.000017
9.0	– 1.000020	– 1.000020	– 1.000014	– 1.000013
9.5	– 1.000013	– 1.000013	– 1.000010	– 1.000010
10.0	– 1.000009	– 1.000009	– 1.000008	– 1.000008
11.0	– 1.000005	– 1.000005	– 1.000004	– 1.000004
12.0	– 1.000003	– 1.000003	– 1.000003	– 1.000003

[a] Calculated from Eq. (34) with Eqs. (37), (38), (42), and (43)

[b] *ab initio* calculation of Kolos and Wolniewicz (Ref. [26])

[c] Calculated from Eq. (35) with Eqs. (37), (38), (42), and (43)

While in this paper we present only the results of the prototype van der Waals potential of the H_2 systems, the theory should be applicable to other systems as well. The long-range dispersion coefficient are now available for a large number of systems [38, 39]. The asymptotic exchange energies of many systems have also

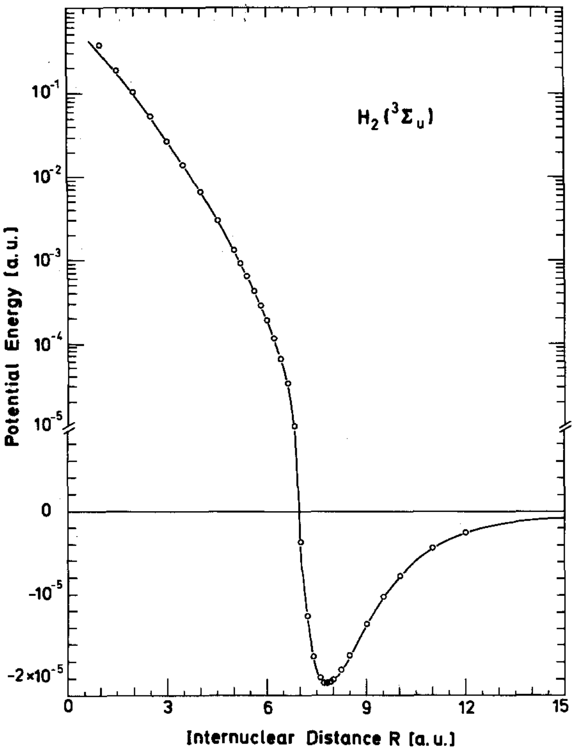

Fig. 1. The van der Waals potential $V(R)$ of the $H_2(^3\Sigma_u)$ system; —— present; ○ "exact" ab initio calculation of Kolos and Wolniewicz (Ref. [26])

Table 2. The energy components of the van der Waals potential $V(R)$ of the $H_2(^3\Sigma_u)$ system

R(a.u.)	S_0^a	ε_1(a.u.)^b	$-\varepsilon_2$(a.u.)^c	ε_x(a.u.)^d	V(a.u.) Present^e	% error^f
1.0	0.73683	0.95862 − 1^g	0.28750 − 1	0.11070	0.28815	− 23.9
2.0	0.34393	− 0.19079 − 1	0.13434 − 1	0.84752 − 1	0.94712 − 1	− 8.0
3.0	0.12146	− 0.69199 − 2	0.49117 − 2	0.31607 − 1	0.27678 − 1	− 1.1
4.0	0.03582	− 0.16074 − 2	0.16870 − 2	0.87811 − 2	0.66646 − 2	0.6
5.0	0.00933	− 0.32196 − 3	0.58318 − 3	0.20760 − 2	0.13294 − 2	− 1.1
6.0	0.00222	− 0.59650 − 4	0.21120 − 3	0.44320 − 3	0.19012 − 3	1.5
7.0	0.00049	− 0.10518 − 4	0.82246 − 4	0.88181 − 4	− 0.35036 − 5	− 7.2
8.0	0.00010	− 0.17912 − 5	0.34922 − 4	0.16664 − 4	− 0.20247 − 4	0.5
9.0	0.00002	− 0.29720 − 6	0.16203 − 4	0.30273 − 5	− 0.13576 − 4	0.6
10.0	0.00000	− 0.48317 − 7	0.81617 − 5	0.53317 − 6	− 0.77065 − 5	0.6
11.0	0.00000	− 0.77270 − 8	0.44144 − 5	0.91571 − 7	− 0.43377 − 5	0.4
12.0	0.00000	− 0.12191 − 8	0.25345 − 5	0.15404 − 7	− 0.25218 − 5	0.2
13.0	0.00000	− 0.19013 − 9	0.15290 − 5	0.25466 − 8	− 0.15270 − 5	
14.0	0.00000	− 0.29366 − 10	0.96139 − 6	0.41479 − 9	− 0.96107 − 6	

[a] Calculated from Eq. (43)

[b] Calculated from Eq. (42)

[c] Calculated from Eq. (38) with *b* given by Eq. (41); summed from $2n = 6$ to $2n = 14$

[d] Calculated from Eq. (37)

[e] Calculated from Eq. (44)

[f] % error = (V(present) − V(exact))/V(exact) with V(exact) taken from Ref. [26]

[g] 0.95862 − 1 means 0.95862×10^{-1}

been calculated [40], mostly by Russian authors [41]. Up to now, they are used almost exclusively in the charge exchange scattering calculations [42]. We are presently using these results for calculating van der Waals potentials of alkali and rare gas systems. For these systems, the calculations are more complicated since even the zeroth-order wavefunction has to be approximated. Nevertheless, preliminary results are very encouraging.

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