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On the Long-range Interactions between Two Hydrogen Atoms and Two Helium Atoms

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The numerical results of the interaction energy between two hydrogen atoms and two helium atoms are examined with the use of exact formulae of the second-order perturbation energy using the Unsöld approximation. It is found that the analytic expression gives a good long-range interaction energy between two hydrogen atoms comparable to the best variational results so far obtained. In the case of two helium atoms, the result lies in between experimental data for large nuclear distances; this seems to support the reliability of the present estimation. Finally, the effectiveness of the Unsöld approximation is remarked on.

In calculating the dispersion energy between two atoms, it happens that the multipole expansion of the perturbation leads to nonconvergent results.[1] To solve this difficulty, exact analytical expressions of the second-order perturbation energy within the framework of the Unsöld approximation have been derived by several authors for the hydrogen molecule ion[2] and for two hydrogen atoms and two helium atoms.[3] One particularly useful advantage is that they are so simple that one can use them for further calculations of the chemical or physical properties of atoms and molecules. On the other hand, a recent calculation[4] using the variation-perturbation technique, even though it avoided the divergence difficulty, is still given in expanded form in each angular component and is, as a consequence, too complicate to be applied to further calculations. Therefore, it is important to investigate whether or not the results obtained by the Unsöld approximation are numerically reliable, especially at a large separation. In the present paper, we will examine the numerical results with the use of the formulae previously obtained in two hydrogen and two helium cases[3] and will compare them with those of several authors.

On the interatomic force between two hydrogen atoms, many calculations have hitherto been carried out by both the variation and perturbation techniques. Among them, one of the most reliable techniques for the potential values in the range of $R>4.5$, where R is the interatomic separation in atomic units, is the variational technique proposed by Hirschfelder-Linnett with a nonexpanded Hamiltonian[5] for $4.5<R<8.0$, and another is that of Pauling and Beach,[6] with an expanded form for $9.0<R<12.0$. The present second-order perturbation energy is comparable to the above-mentioned values. Furthermore, the limit of the Unsöld approximation with the conventional asymptotic expansion is made clear numerically.

In the case of two helium atoms, the best theoretical potential curve is given by superimposing the results of Rosen, Margenau, and Page.[7] Unfortunately, the

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[1] F. C. Brooks, *Phys. Rev.*, **86**, 92 (1952).

[2] G. M. Roe, *ibid.*, **88**, 659 (1952).

[3] K. Fukui and T. Yamabe, *Intern. J. Quantum Chem.*, **2**, 359 (1968): This paper involves an error in one of the formulae, which has been corrected recently by the same authors.

[4] H. Kreek and W. J. Meath, *J. Chem. Phys.*, **50**, 2289 (1969).

[5] L. O. Hirschfelder and J. Y. Linnett, *ibid.*, **18**, 130 (1950).

[6] L. Pauling and J. Y. Beach, *Phys. Rev.*, **47**, 686 (1935).

[7] P. Rosen, *J. Chem. Phys.*, **18**, 1182 (1950); H. Margenau, *Phys. Rev.*, **56**, 1000 (1939); C. H. Page, *Phys. Rev.*, **53**, 426 (1938): These results are quoted and combined to one curve by J. O. Hirschfelder, C. F. Curtiss, and R. Bird, "Molecular Theory of Gasses and Liquids," John Wiley and Sons, Inc., New York, 1954, p. 1067.

curve lies under the experimental curves[8,9] for separations larger than 3.8 Å, although one has, of course, to consider the error involved in the experimental data. On the other hand, the interaction energy estimated in this paper lies between these values, at $R>4.0$ Å; this seems to support the present results. It seems that it would be of interest to examine whether or not this discrepancy is attributable to an essential error which is often brought about in the perturbation treatment. In this aspect, the dispersion energy is discussed in relation to that reported by Margenau and Page. Other theoretical calculations due to the molecular orbital theories have been made by several authors.[10,11] None of them gives satisfactory results in the van der Waals region.

In the last section of this paper, the theoretical foundation of the applicability of the Unsöld approximation is discussed with the use of a variational approach, which confirms the effectiveness of the Unsöld approximation, taking the ground-state energy of the system as the average excitation energy.

The Interaction Energy between Two Hydrogen Atoms

It is well known that, in the framework of the Unsöld approximation, the second-order perturbation energy $E_2(R)$, of the interaction between two hydrogen atoms in their ground states may be represented as follows:

$$E_2(R) = \frac{(H'^2)_{00} - (H')^2_{00}}{\langle \varDelta E \rangle_{\mathrm{Av}}}. \tag{1}$$

$<\varDelta E>_{\mathrm{Av}}$ is an "average excitation energy" after Unsöld. $(H')_{00}$ and $(H'^2)_{00}$ are given by:

$$\begin{Bmatrix} (H')_{00} \\ (H'^2)_{00} \end{Bmatrix} = \iint \phi^2_{Ha}(1)\phi^2_{Hb}(2) \begin{Bmatrix} H' \\ H'^2 \end{Bmatrix} \mathrm{d}v_1 \mathrm{d}v_2, \tag{2}$$

where H' is the usual perturbation at an interatomic distance of R;

$$H' = \frac{1}{R} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} + \frac{1}{r_{12}} \text{ (in atomic units)},$$

ϕ_{Ha} and ϕ_{Hb} are the 1*s* functions of the *a* and *b*, hydrogen atoms and the exchange of two electrons, 1 and 2, is neglected.

In our previous paper,[3] Eq. (1) was evaluated exactly without resorting to a series expansion and was given in a closed analytical form applicable to an arbitrary interatomic distance, R, as follows:

$$(H')_{00} = \mathrm{e}^{-2R}\left(R^{-1} + \frac{5}{8} - \frac{3}{4}R - \frac{1}{6}R^2\right) \equiv U(R), \tag{3}$$

$$(H'^2)_{00} = V_{\mathrm{S}}(R) + V_{\mathrm{L}}(R) \equiv V(R), \tag{4}$$

$$V_{\mathrm{S}}(R) = V_1(R)\mathrm{e}^{-2R} + V_2(R)\mathrm{e}^{-4R} + \mathrm{e}^{2R}Ei(-4R)\left(4 - \frac{2}{R}\right), \tag{5}$$

$$V_{\mathrm{L}}(R) = \frac{1}{R^2} - \frac{7}{12} + \mathrm{e}^{2R}Ei(-2R)\left(\frac{11}{16R} - \frac{11}{8} - \frac{1}{2}R + \frac{1}{6}R^2\right) + \mathrm{e}^{-2R}\widetilde{Ei}(2R)\left(-\frac{11}{16R} - \frac{11}{8} + \frac{1}{2}R + \frac{1}{6}R^2\right), \tag{6}$$

where:

$$V_1(R) = -\frac{2}{R^2} + \left(4 + \frac{2}{R}\right)\log 4\gamma R - \frac{11}{4R} - \frac{9}{2} + \frac{5}{3}R,$$

$$V_2(R) = 2 + \frac{4}{R} + \frac{2}{R^2},$$

$$Ei(-x) = -\int_x^\infty \frac{\mathrm{e}^{-t}}{t}\mathrm{d}t, \quad \widetilde{Ei}(x) = -\int_{-x}^\infty \frac{\mathrm{e}^{-t}}{t}\mathrm{d}t$$

and where $\log \gamma$ is Euler's constant, 0.5772156649…….

Some interesting features of the $V_{\mathrm{S}}(R)$ and $V_{\mathrm{L}}(R)$ functions presented above may be remarked on (Fig. 1). The $V_{\mathrm{S}}(R)$ function is the part of $V(R)$, which attenuates exponentially with increase in R, while the $V_{\mathrm{L}}(R)$ function is the origin of the well-known expression of asymptotic expansion in the inverse powers of R for large R values.

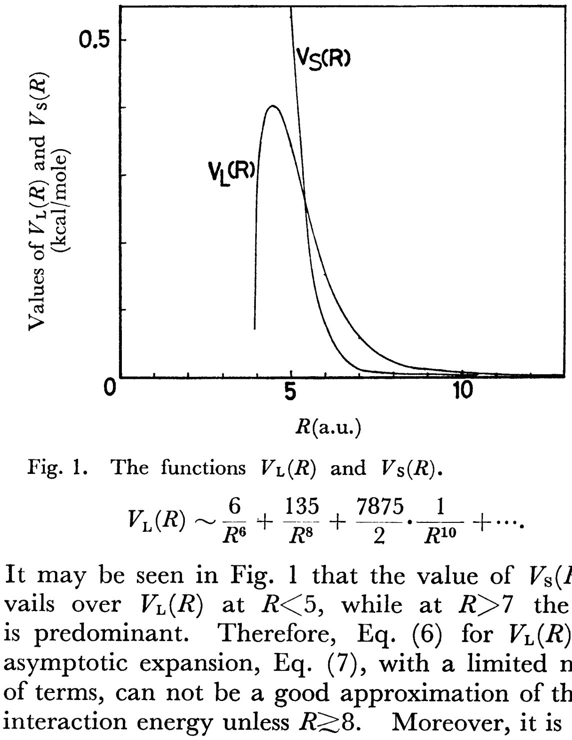

Fig. 1. The functions $V_{\mathrm{L}}(R)$ and $V_{\mathrm{S}}(R)$.

$$V_{\mathrm{L}}(R) \sim \frac{6}{R^6} + \frac{135}{R^8} + \frac{7875}{2} \cdot \frac{1}{R^{10}} + \cdots. \tag{7}$$

It may be seen in Fig. 1 that the value of $V_{\mathrm{S}}(R)$ prevails over $V_{\mathrm{L}}(R)$ at $R<5$, while at $R>7$ the latter is predominant. Therefore, Eq. (6) for $V_{\mathrm{L}}(R)$ or its asymptotic expansion, Eq. (7), with a limited number of terms, can not be a good approximation of the total interaction energy unless $R \gtrsim 8$. Moreover, it is noticeable that the $V_{\mathrm{L}}(R)$ has a maximum value of 0.40502 kcal/mol at $R=4.5$. Accordingly, the value of the interaction energy does not exceed *ca.* 0.4 kcal/mol so long as Eqs. (6) or (7) is adopted as the approximation of the total interaction energy.

In order to compare our results with the best potential energy curves previously obtained by Hirschfelder-Linnett[5] and Pauling-Beach,[6] we make the choice of $<\varDelta E>_{\mathrm{Av}}$, *i.e.* $<\varDelta E>_{\mathrm{Av}} = E_0 = -1.0$ a.u., as was previously suggested by Lennard-Jones.[12] Following this approximation, Eq. (1) and the total energy, E, are rewritten as:

$$E_2(R) = \frac{(H'^2)_{00} - (H')^2_{00}}{E_0} = U^2(R) - V(R), \tag{8}$$

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[8] W. G. Schneider and J. L. Yntema as quoted by P. Rosen, *J. Chem. Phys.*, **18**, 1182 (1950).

[9] R. A. Buckingham, *Trans. Faraday Soc.*, **54**, 453 (1958).

[10] S. Huzinaga, *Prog. Theoret. Phys.* (Kyoto), **20**, 631 (1958); P. Phillipson and R. S. Mulliken which was quoted by B. J. Ransil in Ref. 11.

[11] B. J. Ransil, *J. Chem. Phys.*, **34**, 2109 (1961).

[12] J. E. Lennard-Jones, *Proc. Roy. Soc.* (London), **A129**, 598 (1930).

$$E \sim E_0 + (H')_{00} + E_2(R). \qquad (9)$$

As was pointed out by Dalgarno and Lewis,[13] the asymptotic form of Eq. (8) (equivalent to Eq. (7)) provides a good approximation to the variational calculation.[6] Moreover, the variational calculation gives $-6.49\,R^{-6}$ as the first leading term in its expanded form, while the present estimation gives $-6.00\,R^{-6}$ for the corresponding term. These facts imply that the above-mentioned choice of $\langle \Delta E \rangle_{\mathrm{AV}}$ is appropriate.

Table 1. The interaction energy between two hydrogen atoms (kcal/mol)

R (a.u.)	Present result	Pauling and Beach[a]	Hirschfelder and Linnett[b]
6.0	−0.2730	−0.1457	−0.3995
7.0	−0.07848	−0.0507	−0.09190
8.0	−0.02679	−0.0209	−0.02510
9.0	−0.01090		
10.0	−0.005130	−0.0049	−0.004380
11.0	−0.002687		
12.0	−0.001519	−0.0016	−0.001263

a) From Ref. 6. b) From Ref. 5.

In Table 1, the interaction energies between two hydrogen atoms at several interatomic separations larger than 6.0 are shown. Except for one case, at $R=12$, the present results give values below those of Pauling and Beach, which were obtained by the variational calculation taking the perturbation of the first three terms of the asymptotic expansion. Furthermore, at $6<R<7$, our results come close to the energy curve of Hirschfelder-Linnett obtained variationally by the use of the exact H' and by a trial function consisting of 1s functions with a variable exponent and corrected by considering all possible states of electron configurations and polarization effects. In the longer range, $8<R<12$, the present calculations give a lower energy curve than the previous results. As expected, the contribution of the first-order energy becomes negligibly small at all these distances.

The Interaction Energy between Two Helium Atoms

In the case of two helium atoms, the interaction energy was derived in a way analogous to the case of H_2, that is, by using the Unsöld approximation and by neglecting the electron exchange. The same discussion as that in the case of two hydrogen atoms is possible with respect to the $V(ZR)$ function, in which R is the distance between two helium nuclei in atomic units and in which Z is the effective nuclear charge of the isolated helium atom.

We chose the approximate wavefunction, $(Z^3/\pi)e^{-z(r_1+r_2)}$, as the unperturbed state of an isolated helium atom in the ground state, where r_1 and r_2 are the distances from the nucleus of the 1 and 2 electrons respectively. This function gives the energy of $-Z^2$, and the optimum value of Z is 27/16. The second-order perturbation energy is obtained for two cases, in which $\langle \Delta E \rangle_{\mathrm{AV}}$ is approximated by the ground-state energy ($-Z^2$) and by the ionization potential (−0.903695). These cases are denoted by E_2^{U} and E_2^{L} respectively. Following to Unsöld,[14] the value of E_2^{L} is a lower limit to the second-order perturbation energy. The sum of the first- and second-order perturbation energies of these two cases are denoted by E^{U} and E^{L} respectively; they are tabulated in Table 2 together with the experimental and theoretical estimations. The present results give lower energy values than does the molecular orbital theory.[10,11] On the other hand, E^{U} gives higher values, over the whole range, than the combined results of Rosen, Margenau and Page (RMP), which consist of first- and second-order perturbation energies, including the electron exchange, and which are presumably the best theoretical potential energy curves so far obtained. However, in the $R>3.8$ Å range, the energies of RMP are always lower than both the experimental values,[8,9] whereas E^{U} lies between them. In this connection, it is worthwhile examining the dispersion energies obtained by these two theoretical approaches in the 4 Å$<R<$5 Å range in more detail. The results are indicated in Table 3. At $R=3.8$ Å, the difference be-

Table 3. The dispersion energy between two helium atoms (in 10^{-7} a.u.)

R (Å)	Present result		Margenau and Page
	E_2^{U}	E_2^{L}	
3.8	−54.0	−170.2	−129.6
4.0	−38.4	−121.0	− 94.0
4.2	−27.9	− 87.9	− 69.4
4.4	−20.7	− 65.2	− 52.0
4.6	−15.5	− 48.8	− 39.5
4.8	−11.8	− 37.2	− 30.3
5.0	− 9.1	− 28.7	− 23.6

Table 2. Theoretical and experimental data on the interaction energy between two helium atoms (in 10^{-7} a.u.)

R (Å)	Present calculation		Rancil[a]	RMP[b]	Schneider and Yntema[c]	Buckingham[d]	Corrected values
	E^{U}	E^{L}					
3.4	−90.1	−296.9	−41.3	−178	−178	−110	
3.8	−54.0	−170.2	− 9.2	−110	−100	− 32.1	−34.7
4.0	−38.5	−121.0	− 2.3	− 84.2	− 58.5	− 16.5	−28.6
4.5	−18.9	− 56.3					
5.0	− 9.1	− 28.7	0	− 22.0	− 19.3	− 0.5	− 7.5

a) From Ref. 11. b) From Ref. 7. c) From Ref. 8. d) From Ref. 9.

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[13] A. Dalgarno and J. T. Lewis, *Proc. Phys. Soc.* (London), **A69**, 57 (1956).

[14] A. Unsöld, *Z. Phys.*, **43**, 374 (1927).

tween E_2^{U} and the value of Margenau and Page is 76×10^{-7}; this value is 56×10^{-7} at $R=4.0$ Å and 15×10^{-7} at $R=5.0$ Å. By adding these values to the interaction energies of RMP, one obtains the energies through the second-order perturbation energies, including the effect of electron exchange and lying at least between two experimental data. The corrected values of the interaction energy are shown in the last column of Table 2. In our previous paper, the present authors obtained the approximate dispersion energy of $-1.63\,R^{-6}$ (R in a.u.) for E_2^{L}. The value of the above coefficient is 0.517 for E_2^{U}, while Margenau reported 1.45. The former value is obviously too small, but the latter is in good agreement with the other results estimated by many authors over the last ten years.15) However, as will be shown in the next section, the energy through E_2^{U} will give nearly an upper limit to the long-range interaction energy.

In the $R<4.0$ Å range, it is necessary to consider the electron exchange. Adding the approximate first-order exchange energy16) to the above interaction energy gives an equilibrium distance of 3.2 Å, which roughly agrees with the experimental result of 2.8—3.0 Å.8,9)

A Remark on the Applicability of the Unsöld Approximation

In the above discussions, in the cases of both two hydrogen and two helium atoms, it is clear that the analytical formula of the second-order perturbation energy on the basis of the Unsöld approximation gives a good descrpition of the long-range interaction. Here, a theoretical foundation may be required as to the applicability of the Unsöld approach.

For the sake of simplicity, we will discuss the case of the interaction of two hydrogen atoms. According to the variational principle,17) and by the use of the variation function:

$$\psi = \phi_{\mathrm{Ha}}(1)\phi_{\mathrm{Hb}}(2)(1+\mathrm{AH}'), \tag{10}$$

one obtains:

$$\begin{aligned} E \leqq E_0 + (H')_{00} + [&(2A-E_0A^2)(H')_{00}-(H')^2_{00} \\ &+A^2\{(H'H_0H')_{00}+(H'^3)_{00}-E_0(H')^2_{00} \\ &-(H')_{00}(H'^2)_{00}\}]/[1+2A(H')_{00}+A^2(H'^2)_{00}], \end{aligned} \tag{11}$$

where A is the variational parameter, H_0 is the unperturbed Hamiltonian operator, and $(H'H_0H')_{00}$ and (H'^3) are integrals defined similarly to Eq. (2). At large separations, $(H')_{00}$ and $(H'^2)_{00}$ are small compared with unity (*e.g.*, at $R=8$ a.u., $(H')_{00}=-1.8\times10^{-6}$ and $(H'^2)_{00}=4.1\times10^{-5}$ a.u.); hence, they are negligible in the denominator of the third term in the right-hand side of Eq. (11), since A is found to be of the order of unity in the neibourhood of the minimum value of the righthand side of Eq. (11). Thus, Eq. (11) may be rewritten as:

$$\begin{aligned} E \lesssim E_0 + (H')_{00} &+ (2A-E_0A^2)\{(H'^2)_{00}-(H')^2_{00}\} \\ &+ A^2\{(H'H_0H')_{00}+(H'^3)_{00}\}. \end{aligned} \tag{12}$$

Up to the present, no exact evaluation of $(H'H_0H')_{00}$ or $(H'^3)_{00}$ has been found in the literature.

It may be permitted at large separations to estimate the relative magnitude of the integrals in Eq. (12) by the first leading terms of their asymptotic expansion.18) The results are:

$$(H'^2)_{00} \sim -\frac{6}{R^6}, \tag{13}$$

$$(H'H_0H')_{00} \sim +\frac{45}{2}\frac{1}{R^8}, \tag{14}$$

$$(H'^3)_{00} \sim -\frac{2430}{R^{11}}. \tag{15}$$

At $R=8$, these one-term approximations give $(H'H_0H')_{00}\sim-0.0625\,\tilde{a}$ and $(H'^3)_{00}\sim+0.0124\,\tilde{a}$, while at $R=10$, $(H'H_0H')_{00}\sim-0.0375\,\tilde{a}$ and $(H'^3)_{00}\sim+0.0041\,\tilde{a}$ respectively. Where $\tilde{a}$ represents the values of $-6/R^6$ at each R. Consequently, if R is so large that the residual main term $(H'H_0H')_{00}$ can be neglected, Eq. (12) may be reduced to:

$$E \lesssim E_0 + (H')_{00} + (2A-E_0A^2)\{(H'^2)_{00}-(H')^2_{00}\}. \tag{16}$$

The right-hand side of this equation approaches approximately from the upper side to the upper limit of Eq. (11) with an increase in R. Now, we can easily find that Eq. (16) has a minimum with respect to the variation in A when $A=1/E_0$, in which case Eq. (16) becomes:

$$E \lesssim E_0 + (H')_{00} + \frac{(H'^2)_{00}-(H')^2_{00}}{E_0}. \tag{17}$$

The right-hand side of Eq. (17) agrees with Eq. (9). From the above discussions, it may be concluded that, if the energy of two isolated hydrogen atoms, E_0, is adopted for the value of $<\Delta E>_{\mathrm{AV}}$ in the Unsöld approximation, the results give almost an upper limit for the energy; therefore, our previous result3) and the numerical estimation presented in this paper are reliable. For a long-range interaction of two helium atoms, there is no essentially new problem and one will be able to treat it in the same way as in the case of two hydrogen atoms.

It becomes clear from the theoretical and numerical aspects that, if one uses the Unsöld approximation with the choice of the ground-state energy of the system considered as the average excitation energy, the resulting formula obtained analytically gives an energy value very close to the upper limit of the exact one. The evidence encourages us to investigate long-range forces between atoms and molecules, which are especially interesting in view of the chemical bond formation, in the simple manner described above.

The evidence reported in this paper may support the conclusion that the dispersion force is of the same nature as the chemical bond formation, being only a portion abstracted as acting at larger distances than ordinary bond lengths.

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15) The data are summarized in the following paper: G. Starkshall and R. G. Gordon, *J. Chem. Phys.*, **54**, 663 (1971).

16) K. Fukui, "Quantum Chemistry," Asakura-Shoten, Inc., Tokyo 1968, p. 337.

17) L. I. Shiff, "Quantum Mechanics," second ed., McGraw-Hill Book Co., 1955, p. 179.

18) Mathematically, the integrals, $(H'H_0H')_{00}$ and $(H'^3)_{00}$ are infinite. However, one can avoid this difficulty in the manner previously developed by the present authors (This Bulletin, **43**, 2012 (1970)) and so find results not very different from those obtained by the use of the asymptotic expansion. A more detailed discussion of this point will be presented elsewhere.