Variational Calculation of Atoms and Molecules by a Modified Hassé Method Using Hulthén Functions.[1] III. Long-range Interactions between Hydrogen Atom and Proton and between Two Hydrogen Atoms

Tokio YAMABE, Shingo ISHIMARU, and Kenichi FUKUI

Department of Hydrocarbon Chemistry, Kyoto University, Sakyo-ku, Kyoto 606

(Received February 2, 1973)

The variation method using the wave function of the modified Hassé form is applied to the problem of long-range interactions between hydrogen atom and proton and between two hydrogen atoms. The interaction energy is also related to the perturbation energy under the Unsöld approximation by the use of several pertinent approximations, and an "improved second-order Unsöld energy," which will be higher than the exact second-order perturbation energy, is newly proposed. The numerical results show that the present trial wave function is quite effective; particularly, at $R \gtrsim 10$ (a.u.), the dispersion energy between hydrogen atoms is better than that of Hirschfelder-Linnett, which might be the best variational result at a large nuclear separation. Furthermore, the importance of considering the degeneracy in treating the induction energy is numerically disclosed for an example of H–H$^+$ interaction. The coefficients in the asymptotic form of the dispersion energy between two hydrogen atoms are briefly discussed, and, finally, a new method for the calculation of the second-order energy is suggested.

It is desirable that an expression of the long-range interaction energy between atoms and molecules has the following properties: (1) the result is an upper or lower bound to the exact value, (2) it is given in a simple analytical closed form, and (3) it gives a reasonable asymptotic form when expanded in inverse powers of the nuclear separation, R. Many works have been devoted to obtaining an energy which satisfies the above conditions, particularly for such simple but essential systems as H—H$^+$, H—H and He—He. Among these, one of the most brilliant successes is the exact second-order perturbation energy, E_2, of H—H$^+$ obtained by Dalgarno and Lynn.[2] On the other hand, within the framework of the Unsöld approximation,[3] exact analytical expressions of the second-order perturbation energy, $\overline{E}_2$(Unsöld), which satisfies the latter two properties, have been derived by several authors[4,5] for the above molecular systems. Moreover, in our own previous paper,[6] the results of two hydrogen atoms and two helium atoms were examined and it was found that, at a large R value, the analytical formula gives an energy which is almost an upper bound to the exact one, if the absolute value of the energy in the ground state, E_0, of the isolated system, H_0, is applied to the average excitation energy, $\langle \Delta E \rangle_{\text{Av}}$, in:

$$\overline{E}_2\,(\text{Unsöld}) = -\frac{(H_1{}^2)_{00} - (H_1)_{00}{}^2}{\langle \Delta E \rangle_{\text{Av}}}\,, \tag{1}$$

where H_1 is the non-expanded perturbation and where $(F)_{00}$ signifies the expectation value, $\langle \phi_0 | F | \phi_0 \rangle$, of the operator, F, concerning the unperturbed wave function of the ground state, ϕ_0. The charge overlap effect, which was extensively discussed by Kreak and Meath,[7] is automatically involved in $\overline{E}_2$(Unsöld). Therefore, considering that the Unsöld approximation corresponds to the following form for the first-order perturbation function:[8]

$$\phi_1 \sim AH_1\phi_0\,, \tag{2}$$

the variational function including the above first-order wave function may be expected to give a fairly good interaction energy, especially at a large R value. Indeed, in order to get the result which is an upper bound and which, besides, includes the preferable properties at a large R value, the following variational function was employed in treating the problem of the long-range interaction between two atoms:[9]

$$\phi = (1 + AH_1)\phi_0. \tag{3}$$

An approximate upper bound can thus be obtained, provided that $(H_1H_0H_1)_{00}$ and $(H_1{}^3)_{00}$ are small enough compared with $(H_1{}^2)_{00}$.

It has been pointed out by several authors,[10,11] however, that the variational function of Eq. (3) often gives unreasonable results for the perturbation energy; for example, if H_1 is the exact Coulombic interaction and if ϕ_0 is a 1s-like atomic orbital, $(H_1H_0H_1)_{00}$ and $(H_1{}^3)_{00}$ are infinite, as will be demonstrated in the case of H—H$^+$. To overcome this type of difficulty, the present authors[11] previously proposed a modified Hassé form and, in the atomic cases of hydrogen and helium, showed that the divergence of the above integrals can not only be easily removed, but that the variational function applied is quite effective. The wave function will be also favorable for the calculation of the long-range interaction energy, because the correction is mainly brought about for the exponentially decreasing terms and the asymptotic behavior through the third-order energy is retained.

---

[1] Part II: Ref. 6.

[2] A. Dalgarno and N. Lynn, *Proc. Phys. Soc. Ser. A*, **70**, 223 (1957).

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

[4] G. M. Roe, *Phys. Rev.*, **88**, 659 (1952).

[5] K. Fukui and T. Yamabe, *Intern. J. Quantum Chem.*, **2**, 359 (1968).

[6] T. Yamabe, S. Ishimaru, and K. Fukui, This Bulletin, **45**, 1384 (1972).

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

[8] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 686 (1931): H. R. Hassé, *Proc. Cambridge Phil. Soc.*, **27**, 66 (1931).

[9] L. I. Shiff, "*Quantum Mechanics*", second ed., McGraw-Hill Book Co., New York (1955), p. 179.

[10] B. Kirtman and M. L. Benston, *J. Chem. Phys.*, **46**, 472 (1967).

[11] T. Yamabe, S. Ishimaru, and K. Fukui, This Bulletin, **43**, 2012 (1970).

Another type of variational function[12] usually involves ionic and polarization terms, and the effect of the electron exchange and the associated Laguerre function or the Slater-type orbital are often used for the radial part of the trial function. However, if the exact perturbation is applied in the calculation, this wave function gives only exponentially decreasing terms and a part of the correct asymptotic form, so the potential will be rather higher than the true one at a large nuclear separation.

Therefore, in the present article, we will investigate the long-range interaction energy by using the wave function of the modified Hassé form and by sorting the results into perturbation energies, which makes it possible to discuss the reliability of the Unsöld-type perturbation energy. Two cases of H—H+ and H—H systems will be examined numerically.

The Variation Method Applied and Its Relation to the Perturbation Method

We assume the perturbation acting between two atoms to be the sum of the Coulombic interactions:

$$H_1 = \frac{Z_a Z_b}{R} - \sum_{j=1}^{n_a} \frac{Z_b}{r_{bj}} - \sum_{k=1}^{n_b} \frac{Z_a}{r_{ak}} + \sum_{j=1}^{n_a} \sum_{k=1}^{n_b} \frac{1}{r_{jk}} \tag{5}$$

where $n_{a(b)}$ is the number of electrons of the atom a(b) with a nuclear charge, $Z_{a(b)}$ and where $r_{bj(ak)}$ is the distance between the nucleus of the b(a) atom and the $j(k)$ electron belonging to the atom a(b) (all in atomic units). In order to remove the divergence difficulty mentioned in the introduction, we replace H_1 in Eq. (3) by the following function:[11]

$$\begin{aligned}\overline{H}_1 = {} & \frac{Z_a Z_b}{R} - \sum_{j=1}^{n_a} \frac{Z_b(1-e^{-m_b r_{bj}})}{r_{bj}} \\ & - \sum_{k=1}^{n_b} \frac{Z_a(1-e^{-m_a r_{ak}})}{r_{ak}} + \sum_{j=1}^{n_a} \sum_{k=1}^{n_b} \frac{(1-e^{-k r_{jk}})}{r_{ik}},\end{aligned} \tag{6}$$

in which m_a, m_b, and k are supposed to be positive parameters, and use the variational function of the modified Hassé form:

$$\overline{\phi} = (1 + A\overline{H}_1)\phi_0 \,. \tag{7}$$

The upper bound, $\overline{E}$, of the total energy, E, of the perturbed system, H, is then obtained as follows:

$$\begin{aligned}\overline{E} = {} & E_0 + E_1 \\ & + \frac{2A[(\overline{H}_1 H_1)_{00} - E_1(\overline{H}_1)_{00}] + A^2(\overline{H}_1(H_0 - E_0 + H_1 - E_1)\overline{H}_1)_{00}}{1 + 2A(\overline{H}_1)_{00} + A^2(\overline{H}_1{}^2)_{00}} \\ & \geqq E,\end{aligned} \tag{8}$$

where $E_0 = (H_0)_{00}$ and $E_1 = (H_1)_{00}$. $\overline{E}$ is further classified into the second- and third-order perturbation energies by regarding $A\overline{H}_1\phi_0$ as the approximate first-order perturbation function, $\overline{\phi}_1$. That is, following the variation-perturbation theory, the upper bound, $\overline{E}_2$, of the second-order energy is given by:

$$\overline{E}_2 = 2\langle\overline{\phi}_1|H_1 - E_1|\phi_0\rangle + \langle\overline{\phi}_1|H_0 - E_0|\overline{\phi}_1\rangle \tag{9}$$

$$= 2A[(\overline{H}_1 H_1)_{00} - E_1(\overline{H}_1)_{00}] + A^2(\overline{H}_1(H_0 - E_0)\overline{H}_1)_{00} \tag{10}$$

$$= 2A[(\overline{H}_1 H_1)_{00} - E_1(\overline{H}_1)_{00}] + \frac{1}{2}A^2(\nabla H_1)_{00}{}^2 \geqq E_2, \tag{10'}$$

which gives the minimum:[13]

$$\overline{E}_2 = -\frac{[(\overline{H}_1 H_1)_{00} - E_1(\overline{H}_1)_{00}]^2}{(\overline{H}_1(H_0 - E_0)\overline{H}_1)_{00}} \geqq E_2 \tag{11}$$

when

$$A = -\frac{(\overline{H}_1 H_1)_{00} - E_1(\overline{H}_1)_{00}}{(\overline{H}_1(H_0 - E_0)\overline{H}_1)_{00}} \,. \tag{12}$$

The third-order energy is, approximately:

$$\overline{E}_3 = -2A\overline{E}_2(\overline{H}_1)_{00} + A^2(\overline{H}_1(H_1 - E_1)\overline{H}_1)_{00} \,. \tag{13}$$

The residue in $\overline{E}$, hence, consists of the fourth- and higher-order terms. At a large R value, the results of Eq. (8) can also be related to the perturbation energy with the Unsöld approximation by the use of several pertinent approximations; *i.e.*, we may put

$$(\overline{H}_1)_{00} \sim (H_1)_{00} \tag{14}$$

$$(\overline{H}_1{}^2)_{00} \sim (\overline{H}_1 H_1)_{00} \sim (H_1{}^2)_{00} \,, \tag{15}$$

because the discrepanicies between them are of the order of e^{-2R}. For instance, the relative magnitudes of these integrals in the case of H—H+, which we will discuss in the next section, are presented in Table 1. The results show that these assumptions are reasonable. Moreover, considering that the denominator of Eq. (8) is almost unity,[6] and using the relations, $|E_0| \gg |E_1|$ and $(H_1{}^2)_{00} \gg (H_1)_{00}$, Eq. (8) can be approximated by:

$$\overline{E} \sim E_0 + E_1 + \frac{(H_1{}^2)_{00} - (H_1)_{00}{}^2}{E_0 - \varDelta} \gtrsim E, \tag{16}$$

where

$$\varDelta = \frac{(\overline{H}_1 H_0 \overline{H}_1)_{00} + (\overline{H}_1 H_1 \overline{H}_1)_{00}}{(H_1{}^2)_{00} - (H_1)_{00}{}^2} \,. \tag{17}$$

Equation (16) shows that, if the $E_0 - \varDelta$ value is chosen as $-\langle\varDelta E\rangle_{\mathrm{AV}}$, Eq. (1) gives almost an upper bound. $\varDelta$ is considered to be a correction depending on the R value and the variational parameters (in our previous derivation of the upper bound,[6] $\varDelta$ was neglected). Ex-

TABLE 1. THE RELATIVE MAGNITUDES OF SEVERAL INTEGRALS IN THE CASE OF H–H+ INTERACTION

R (a.u.)	m	$(\overline{H}_1)_{00}/(H_1)_{00}$	$(\overline{H}_1 H_1)_{00}/(H_1{}^2)_{00}$	$(\overline{H}_1{}^2)_{00}/(H_1{}^2)_{00}$	$(H_1)^2{}_{00}/(H_1{}^2)_{00}$
6.0	4.0	1.270	0.993	0.990	0.561×10^{-7}
8.0	4.3	1.251	1.000	0.999	0.604×10^{-10}
10.0	4.3	1.244	1.000	1.000	0.489×10^{-15}

---

[12] L. O. Hirschfelder and J. Y. Linnett, *J. Chem. Phys.*, **18**, 130 (1950).

[13] Dalgarno got an upper bound to E_2 using the function of the type of Eq. (2) in the perturbation-variation theory as follows:

$$-\frac{[(H_1{}^2)_{00} - (H_1)^2{}_{00}]^2}{(H_1(H_0 - E_0)H_1)_{00}} \geqq E_2 \,.$$

See A. Dalgarno, "Quantum Theory," Vol. 1, ed. by D. R. Bates, Academic Press Inc., New York (1961), p. 193.

panding $1/(E_0-\Delta)$ into the power series of Δ/E_0 and neglecting the higher-order terms than Δ/E_0, one obtains another expression:

$$\overline{E}\sim E_0+E_1{}^{+}+\frac{(H_1{}^2)_{00}-(H_1)_{00}{}^2}{E_0}+\frac{(\overline{H}_1H_0\overline{H}_1)_{00}+(\overline{H}_1H_1\overline{H}_1)_{00}}{E_0{}^2}. \tag{18}$$

Although $(\overline{H}_1H_1\overline{H}_1)_{00}/E_0{}^2$ in Eq. (18) is a part of the third-order energy, $(\overline{H}_1H_0\overline{H}_1)_{00}/E_0{}^2$ should be included in the second-order energy, as may be seen in Eq. (10). Indeed, under the same order of the approximation as the above, Eq. (10) gives:

$$\overline{E}_2\sim\frac{(H_1{}^2)_{00}-(H_1)_{00}{}^2}{E_0}+\frac{(\overline{H}_1H_0\overline{H}_1)_{00}}{E_0{}^2}\gtrsim E_2, \tag{19}$$

which may be called "the improved second-order Unsöld energy" and which is plausible when compared with the modified form of the exact second-order energy given by Lennard-Jones:[14]

$$E_2=\frac{(H_1{}^2)_{00}-(H_1)_{00}{}^2}{E_0}+\sum_i{}'\frac{(H_1)_{0i}E_0{}^i(H_1)_{i0}}{E_0(E_0-E_0{}^i)}, \tag{20}$$

where $E_0{}^i$ is the i-th eigenvalue of H_0(*i.e.*, $H_0\phi_0{}^i=E_0{}^i\phi_0{}^i$ $(\phi_0{}^0=\phi_0,\ E_0{}^0=E_0)$) and where $\sum'$ means that the summation does not include the case of $i=0$. Equation (19) corresponds to the results obtained by replacing $E_0-E_0{}^i$ by $-\langle\Delta E\rangle_{\mathrm{Av}}=E_0$ and by deleting the divergence difficulty. It should be noticed that the second-order energy of Eq. (1) with $\langle\Delta E\rangle_{\mathrm{Av}}=-E_0$ differs from that of the (perturbation-) variation method by the amount of $(\overline{H}_1H_0\overline{H}_1)_{00}/E_0{}^2$, though the correction does not affect the first leading term of the asymptotic form of Eq. (1), as will be shown below.

H—H+ Interaction

As the simplest example, let us first consider the interaction between a hydrogen atom with a nucleus, a, and a proton, b. The perturbation may be obtained from Eq. (5) as follows:

$$H_1=\frac{1}{R}-\frac{1}{r_{\mathrm{b}1}}. \tag{21}$$

If one applies the variational function of Eq. (3), with the 1s atomic orbital as the unperturbed wave function, the $(H_1{}^3)_{00}$ and $(\overline{H}_1H_0\overline{H}_1)_{00}$ appearing in the expression of the total energy become infinite because of the divergence of integrals:

$$(r_{\mathrm{b}1}{}^{-3})_{00}=\lim_{\varepsilon\to0}4\left(-\log\varepsilon+1-\log 2\gamma+\frac{1}{2R}\right)\mathrm{e}^{-2R}-\frac{2}{R}-2\mathrm{e}^{2R}Ei(-2R)+2\mathrm{e}^{-2R}Ei(2R), \tag{22}$$

$$(r_{\mathrm{b}1}{}^{-4})_{00}=4\mathrm{e}^{-2R}\lim_{\varepsilon\to0}\frac{1}{\varepsilon}, \tag{23}$$

where:

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

and where $\log\gamma$ is the Euler constant, 0.5772156649…. However, if one uses the variational function of Eq. (7), in which $\overline{H}_1$ is, in the present example, given by:

$$\overline{H}_1=\frac{1}{R}-\frac{1-\mathrm{e}^{-mr_{\mathrm{b}1}}}{r_{\mathrm{b}1}}, \tag{24}$$

$(\overline{H}_1H_1\overline{H}_1)_{00}$ and $(\overline{H}_1H_0\overline{H}_1)_{00}$ become finite by the cancellation of singularities so long as m is finite. For large m values, these values are, respectively, approximated by:

$$(\overline{H}_1H_1\overline{H}_1)_{00}\sim-4\mathrm{e}^{-2R}\log m \tag{25}$$

$$(\overline{H}_1H_0\overline{H}_1)_{00}\sim4m\mathrm{e}^{-2R}, \tag{26}$$

which diverge to negative and positive infinity as $m\to\infty$.

Thus, the divergence characters are included in the exponentially decreasing terms, which can not be obtained unless exact calculations are performed. The conventional perturbation calculation with the Unsöld approximation[15] did not solve this problem since the perturbation is usually expanded in powers of R^{-1} and the exponentially decreasing terms are completely omitted. Nevertheless, the conventional calculation is considered to be reliable, because, according to our correction, the divergence character has been excluded and so exerts little influence on the part expressed in the inverse powers of R.[16]

Now, let us calculate the interaction energy, $\overline{E}-E_0$. All of the integrals in Eq. (8) can be written as follows:

$$(H_1)_{00}=\left(1+\frac{1}{R}\right)\mathrm{e}^{-2R} \tag{27}$$

$$(\overline{H}_1)_{00}=(H_1)_{00}+\left(\frac{\mathrm{e}^{-mr_{\mathrm{b}1}}}{r_{\mathrm{b}1}}\right)_{00} \tag{28}$$

$$(H_1{}^2)_{00}=\frac{1}{R^2}-\frac{2}{R}\left(\frac{1}{r_{\mathrm{b}1}}\right)_{00}+\left(\frac{1}{r_{\mathrm{b}1}{}^2}\right)_{00} \tag{29}$$

$$(\overline{H}_1H_1)_{00}=(H_1{}^2)_{00}+\frac{1}{R}\left(\frac{\mathrm{e}^{-mr_{\mathrm{b}1}}}{r_{\mathrm{b}1}}\right)_{00}-\left(\frac{\mathrm{e}^{-mr_{\mathrm{b}1}}}{r_{\mathrm{b}1}{}^2}\right)_{00} \tag{30}$$

$$(\overline{H}_1{}^2)=2(\overline{H}_1H_1)_{00}-(H_1{}^2)_{00}+\left(\frac{\mathrm{e}^{-2mr_{\mathrm{b}1}}}{r_{\mathrm{b}1}{}^2}\right)_{00} \tag{31}$$

$$(\nabla\overline{H}_1)_{00}{}^2=\left(\frac{[1-\mathrm{e}^{-mr_{\mathrm{b}1}}]^2}{r_{\mathrm{b}1}{}^4}\right)_{00}-2m\left(\frac{\mathrm{e}^{-mr_{\mathrm{b}1}}[1-\mathrm{e}^{-mr_{\mathrm{b}1}}]}{r_{\mathrm{b}1}{}^3}\right)_{00}+m^2\left(\frac{\mathrm{e}^{-2mr_{\mathrm{b}1}}}{r_{\mathrm{b}1}{}^2}\right)_{00} \tag{32}$$

---

[14] J. E. Lennard-Jones, *Proc. Roy. Soc. Ser. A*, **129**, 598 (1930).

[15] A. Dalgarno and J. T. Lewis, *Proc. Phys. Soc. Ser. A*, **69**, 57 (1956).

[16] For example, assuming $r_{\mathrm{a}1}<R$ and α is a constant not equal to zero,

$$\left(\frac{\mathrm{e}^{-\alpha r_{\mathrm{b}1}}}{r_{\mathrm{b}1}{}^3}\right)_{00}=\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}(2l+1)\int\frac{r_{\mathrm{a}1}{}^{m+n}}{\sqrt{r_{\mathrm{a}1}R}\,R^{m+n+2}}\times P_l(\cos\theta)\,P_m(\cos\theta)\,P_n(\cos\theta)\,I_{l+1/2}(\alpha r_{\mathrm{a}1})\,K_{l+1/2}(\alpha R)\,\phi_0{}^2\mathrm{d}\tau$$
$$=\frac{2\,\mathrm{e}^{-\alpha R}}{(\alpha R)^3}\left[\frac{\alpha^2}{(2-\alpha)^2}-\frac{\alpha^2}{(2+\alpha)^2}\right]+\frac{4\,\mathrm{e}^{-\alpha R}}{(\alpha R)^4}\left[\frac{2\alpha^3}{(2+\alpha)^3}+\frac{2\alpha^3}{(2-\alpha)^3}+\frac{\alpha^2}{(2+\alpha)^2}-\frac{\alpha^2}{(2-\alpha)^2}\right]+\frac{16\,\mathrm{e}^{-\alpha R}}{(\alpha R)^5}\left[\frac{\alpha^4}{(2-\alpha)^4}-\frac{\alpha^4}{(2+\alpha)^4}\right]+\mathrm{e}^{-\alpha R}\,\mathrm{O}([\alpha R]^{-6}),$$

where θ is the angle between $r_{\mathrm{a}1}$ and R and $I_\nu(z)$ and $K_\nu(z)$ are well-known Bessel functions of purely imaginary argument. This integral can be neglected for large R.

TABLE 2. THE INTERACTION ENERGIES BETWEEN HYDROGEN AND PROTON WITHOUT THE RESONANCE EFFECT (in a.u.)

R (a.u.)	The present result			Dalgarno and Lynn[a]
	m	A	$E-E_0$	
5.0	3.8	−2.350	-0.4712×10^{-2}	-0.462×10^{-2}
6.0	4.0	−2.183	-0.1980×10^{-2}	-0.206×10^{-2}
7.0	4.1	−2.088	-0.9743×10^{-3}	-0.105×10^{-2}
8.0	4.2	−2.042	-0.5414×10^{-3}	-0.595×10^{-3}
9.0	4.3	−2.020	-0.3278×10^{-3}	-0.365×10^{-3}
10.0	4.3	−2.009	-0.2111×10^{-3}	-0.235×10^{-3}

a) Ref. 17.

$$(\overline{H}_1H_1\overline{H}_1)_{00} = \frac{1}{R^3} - \frac{1}{R^2}[2(\overline{H}_1)_{00} + (H_1)_{00}]$$

$$+ \frac{1}{R}[2(\overline{H}_1H_1)_{00} + (\overline{H}_1{}^2)_{00}] - \left(\frac{[1-\mathrm{e}^{-mr_{\mathrm{b}1}}]^2}{r_{\mathrm{b}1}{}^3}\right)_{00} . \quad (33)$$

The integrals on the right-hand sides are given in Appendix A. The interaction energies, optimized at each R value with respect to m, are listed in Table 2. The results are comparable with those obtained through the second-order perturbation energy under the Unsöld approximation and without the resonance effect.[17] That the values of m are finite means that the divergence difficulty is deleted and that, as expected, A approaches $1/E_0=-2.0$ at large R values.

Next, let us examine the second- and third-order perturbation energies in connection with the above variational calculation. At large enough R values, exponentially decreasing terms can be neglected and $(H_1{}^2)_{00}$ and $(\overline{H}_1H_0\overline{H}_1)_{00}$ can be simplified only to the parts which are the origin of the well-known expression of a power series of R^{-1}, namely:

$$(H_1{}^2)^{\mathrm{L}}{}_{00} = -\frac{1}{R^2} + \left(1+\frac{1}{2R}\right)\mathrm{e}^{-2R}Ei(2R)$$

$$+ \left(1-\frac{1}{2R}\right)\mathrm{e}^{2R}Ei(-2R) \quad (34)$$

$$\sim\sum_{n=1}^{\infty}\frac{4(n+1)(2n)\,!}{(2R)^{2n+2}}, \quad (34')$$

$$(\overline{H}_1H_0\overline{H}_1)^{\mathrm{L}}{}_{00} = \frac{1}{2R^2} + \left(\frac{1}{2}-\frac{3}{4R}\right)\mathrm{e}^{-2R}Ei(2R)$$

$$+\left(\frac{1}{2}+\frac{3}{4R}\right)\mathrm{e}^{2R}Ei(-2R) \quad (35)$$

$$\sim\sum_{n=1}^{\infty}\frac{2n(2n+2)\,!}{(2R)^{2n+4}}. \quad (35')$$

From Eq. (1),

$$\overline{E}_2{}^{\mathrm{L}}(\text{Unsöld}) = -2(H_1{}^2)^{\mathrm{L}}{}_{00} \quad (36)$$

and from Eq. (19),

$$\overline{E}_2{}^{\mathrm{L}} = \frac{4}{R}\left[\frac{1}{R} - \mathrm{e}^{-2R}Ei(2R) + \mathrm{e}^{2R}Ei(-2R)\right]. \quad (37)$$

According to the results of Dalgarno and Lynn,[2] the exact second-order energy without exponentially decreasing terms is given by:

$$E_2{}^{\mathrm{L}} = \frac{1}{R^2}\left[\frac{5}{2}-(R+1)^2\mathrm{e}^{-2R}Ei(2R)-(R-1)^2\mathrm{e}^{2R}Ei(-2R)\right]. \quad (38)$$

On expanding the exponential integrals, Eqs. (36)—(38) are reduced to:

$$\overline{E}_2{}^{\mathrm{L}}(\text{Unsöld}) \sim -\sum_{n=1}^{\infty}\frac{(n+1)(2n)\,!}{2^{2n-1}R^{2n+2}} \quad (36')$$

$$\overline{E}_2{}^{\mathrm{L}} \sim -\sum_{n=1}^{\infty}\frac{2(2n)\,!}{2^{2n-1}R^{2n+2}} \quad (37')$$

$$E_2{}^{\mathrm{L}} \sim -\sum_{n=1}^{\infty}\frac{(2n+1)(n+2)}{4n}\,\frac{(2n)\,!}{2^{2n-1}R^{2n+2}}\,. \quad (38')$$

From Eqs. (37′) and (38′), it may easily be seen that $\overline{E}_2{}^{\mathrm{L}}$ is higher than $E_2{}^{\mathrm{L}}$ in all terms of the series, that is, that the relation of Eq. (19) is still kept for the non-exponentially decreasing terms:

$$\overline{E}_2{}^{\mathrm{L}} > E_2{}^{\mathrm{L}}\,. \quad (39)$$

$\overline{E}_2{}^{\mathrm{L}}$(Unsöld) is, however, so only in the first term, probably because the higher multipole transition has a larger excitation energy than does the lowest dipole transition. The numerical results, presented in Table 3, show that the non-exponentially decreasing terms are negligible and that the expressions of $\overline{E}_2{}^{\mathrm{L}}$(Unsölid)

TABLE 3. THE PERTURBATION ENERGIES BETWEEN HYDROGEN AND PROTON ESTIMATED BY SEVERAL METHODS (in a.u.)

R (a.u.)	E_1	$\overline{E}_2$(Unsöld)	$\overline{E}_2{}^{\mathrm{L}}$(Unsöld)	$\overline{E}_2$	$\overline{E}_2{}^{\mathrm{L}}$
5.0	0.5448×10^{-4}	-0.4153×10^{-2}	-0.4109×10^{-2}	-0.2639×10^{-2}	-0.3768×10^{-2}
6.0	0.7168×10^{-5}	-0.1833×10^{-2}	-0.1828×10^{-2}	-0.1569×10^{-2}	-0.1716×10^{-2}
7.0	0.9503×10^{-6}	-0.9358×10^{-3}	-0.9353×10^{-3}	-0.8761×10^{-3}	-0.8958×10^{-3}
8.0	0.1266×10^{-6}	-0.5307×10^{-3}	-0.5306×10^{-3}	-0.5120×10^{-3}	-0.5148×10^{-3}
9.0	0.1692×10^{-7}	-0.3246×10^{-3}	-0.3246×10^{-3}	-0.3170×10^{-3}	-0.3174×10^{-3}
10.0	0.2267×10^{-8}	-0.2101×10^{-3}	-0.2101×10^{-3}	-0.2064×10^{-3}	-0.2065×10^{-3}

R (a.u.)	E_2	$E_2{}^{\mathrm{L}}$	$\overline{E}_3$	$\overline{E}_3{}^{\mathrm{L}}$
5.0	-0.4093×10^{-2}	-0.4331×10^{-2}	-0.2179×10^{-2}	-0.7515×10^{-3}
6.0	-0.1929×10^{-2}	-0.1963×10^{-2}	-0.4271×10^{-3}	-0.2355×10^{-3}
7.0	-0.1008×10^{-3}	-0.1019×10^{-2}	-0.1008×10^{-3}	-0.7756×10^{-4}
8.0	-0.5829×10^{-3}	-0.5836×10^{-3}	-0.3013×10^{-4}	-0.2685×10^{-4}
9.0	-0.3590×10^{-3}	-0.3591×10^{-3}	-0.1103×10^{-4}	-0.1053×10^{-4}
10.0	-0.2333×10^{-3}	-0.2333×10^{-3}	-0.4722×10^{-5}	-0.4646×10^{-5}

---

[17] A. Dalgarno and N. Lynn, *Proc. Phys. Soc. Ser. A*, **69**, 821 (1956).

TABLE 4. THE INTERACTION ENERGIES BETWEEN TWO HYDROGEN ATOMS (in a.u.)

R (a.u.)	The present result				Hirschfelder and Linnett[a)]
	m	k	A	$\overline{E}-E_0$	
6.0	3.5	2.9	−0.419	-0.1922×10^{-3}	-0.6367×10^{-3}
7.0	3.2	2.6	−0.553	-0.6774×10^{-4}	-0.1465×10^{-3}
8.0	3.1	2.5	−0.694	-0.2883×10^{-4}	-0.4000×10^{-4}
9.0	3.0	2.4	−0.819	-0.1400×10^{-4}	
10.0	2.9	2.4	−0.897	-0.7288×10^{-5}	-0.6980×10^{-5}
11.0	2.8	2.4	−0.935	-0.3993×10^{-5}	
12.0	2.8	2.4	−0.949	-0.2295×10^{-5}	-0.2013×10^{-5}

a) Ref. 12.

and $\overline{E}_2{}^{\mathrm{L}}$ are quite effective.

Similarly, the third-order energy in Eq. (18) is approximated by:

$$\begin{aligned}\overline{E}_3{}^{\mathrm{L}} &= (\overline{H}_1H_1\overline{H}_1)^{\mathrm{L}}{}_{00}/E_0{}^2\\ &= 4\left[\frac{2}{R}-\frac{2}{R^3}-\left(2-\frac{3}{R}-\frac{3}{2R^2}\right)\mathrm{e}^{-2R}Ei(2R)\right.\\ &\qquad\left.+\left(2+\frac{3}{R}-\frac{3}{2R^2}\right)\mathrm{e}^{2R}Ei(-2R)\right], \qquad (40)\end{aligned}$$

which is, in the form of a power series of R^{-1}:

$$\overline{E}_3{}^{\mathrm{L}} \sim -\sum_{n=1}^{\infty}\frac{n(n+2)(2n+2)\,!}{2^{2n+1}R^{2n+5}} \qquad (41)$$

and which leads to the same result as that of Dalgarno and Lewis[15)] except for the difference in the average energy. The numerical results are also listed in Table 3.

H—H Interaction

In the case of two hydrogen atoms, the perturbation is given by:

$$H_1 = \frac{1}{R}-\frac{1}{r_{\mathrm{b1}}}-\frac{1}{r_{\mathrm{a2}}}+\frac{1}{r_{12}}. \qquad (42)$$

According to Eq. (6), $\overline{H}_1$ is written as follows:

$$\overline{H}_1 = \frac{1}{R}-\frac{1-\mathrm{e}^{-mr_{\mathrm{b1}}}}{r_{\mathrm{b1}}}-\frac{1-\mathrm{e}^{-mr_{\mathrm{a2}}}}{r_{\mathrm{a2}}}+\frac{1-\mathrm{e}^{-kr_{12}}}{r_{12}}. \qquad (43)$$

In Table 4, the interaction energy optimized with respect to m and k is shown, together with the best variational results for large separations calculated by Hirschfelder and Linnett[12)] (HL) using the exact perturbation and the trial function, which consists of the 1s atomic orbital with a variable exponent and which is corrected by considering the ionic states, the polarization effect, and the electron exchange. As a matter of course, the values of HL are better than ours at $R\leqq8$, where the exchange effect plays an important role. However, at a longer distance, where only the Coulombic interaction is dominant, the present energy becomes lower than that of HL in spite of its simple expression.

In Table 5, the perturbation energies through the third-order are listed and the second-order perturbation energy is compared with the result previously obtained by the present authors.[6)] The second-order energy of the Unsöld type approaches $\overline{E}_2$ at large R values; this is consistent with the previous observation.[6)]

Following our calculation, the third-order energy, $\overline{E}_3$, is positive, while the asymptotic form[18)] gives a negative value ($-3986\,R^{-11}$). The difference may be partly due to the fact that the present result includes the charge-overlap effect,[19)] which is usually repulsive in the order of e^{-2R}, and partly to the fact that, in the calculation of $(\overline{H}_1H_1\overline{H}_1)_{00}$, we neglected the $-(\mathrm{e}^{-kr_{12}}/r_{\mathrm{b1}}r_{12}r_{\mathrm{a2}})_{00}+(\mathrm{e}^{-mr_{\mathrm{b1}}}\mathrm{e}^{-kr_{12}}/r_{\mathrm{b1}}r_{12}r_{\mathrm{a2}})_{00}$ terms, which are of the e^{-2R} order and which are totally negative (the $\overline{E}_3$ and $\overline{E}$ thus obtained are, accordingly, higher than the respective exact values). Therefore, it is not strange that $\overline{E}_3$ is positive for not sufficiently large nuclear distances.

For such large R values that the exponentially decreasing terms can be neglected, the non-exponentially decreasing terms of $(H_1{}^2)_{00}$, which are the same as those in $(\overline{H}_1H_1)_{00}$ and $(\overline{H}_1{}^2)_{00}$, were obtained in our previous paper[6)] as follows:

$$\begin{aligned}(H_1{}^2)^{\mathrm{L}}{}_{00} &= \frac{1}{R^2}-\frac{7}{12}+\mathrm{e}^{2R}Ei(-2R)\left(\frac{11}{16R}-\frac{11}{8}-\frac{R}{2}+\frac{R^2}{6}\right)\\ &\quad+\mathrm{e}^{-2R}Ei(2R)\left(-\frac{11}{16R}-\frac{11}{8}+\frac{R}{2}+\frac{R^2}{6}\right). \qquad (44)\end{aligned}$$

Hence, $\overline{E}_2{}^{\mathrm{L}}$(Unsöld) is in the expanded form:

$$\begin{aligned}\overline{E}_2{}^{\mathrm{L}}(\text{Unsöld}) &= \frac{1}{E_0}(H_1{}^2)^{\mathrm{L}}{}_{00}\\ &\sim -\frac{1}{3}\sum_{n=1}^{\infty}\frac{n(n+7)(2n+4)\,!}{(2n+3)(2R)^{2n+4}}\\ &\sim -\frac{6.0}{R^6}-\frac{135.0}{R^8}-\frac{3937.5}{R^{10}}-\cdots. \qquad (45)\end{aligned}$$

Moreover, the second-order perturbation energy of Pauling and Beach[20)] is:

$$E_2{}^{\mathrm{L}} = -\frac{6.49903}{R^6}-\frac{124.399}{R^8}-\frac{3285.828}{R^{10}}-\cdots. \qquad (46)$$

By comparing Eqs. (45) and (46), it may easily be seen that, as in the case of H-H$^+$, the Unsöld approxima-

---

18) Y. M. Chan and A. Dalgarno, *Mol. Phys.*, **14**, 101 (1968).

19) At $R=10$, for example, $\mathrm{e}^{-2R}=0.2\times10^{-8}$ and $-3986\ R^{-11}=-4\times10^{-8}$. So the effect of the charge overlap will surpass that of the asymptotic form in the region $R<10$.

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

TABLE 5. THE PERTURBATION ENERGIES BETWEEN TWO HYDROGEN ATOMS (in a.u.)

R (a.u.)	E_1	$\overline{E}_2$	$\overline{E}_2$ (Unsöld)[a]	$\overline{E}_3$
6.0	-0.5965×10^{-4}	-0.1534×10^{-3}	-0.4351×10^{-3}	0.2092×10^{-4}
7.0	-0.1052×10^{-4}	-0.6470×10^{-4}	-0.1251×10^{-3}	0.7469×10^{-5}
8.0	-0.1791×10^{-5}	-0.2965×10^{-4}	-0.4269×10^{-4}	0.2605×10^{-5}
9.0	-0.2972×10^{-6}	-0.1466×10^{-4}	-0.1737×10^{-4}	0.7513×10^{-6}
10.0	-0.4832×10^{-7}	-0.7443×10^{-5}	-0.8176×10^{-5}	0.2041×10^{-6}
11.0	-0.7727×10^{-8}	-0.4054×10^{-5}	-0.4282×10^{-5}	0.6946×10^{-7}
12.0	-0.1219×10^{-8}	-0.2333×10^{-5}	-0.2421×10^{-5}	0.3919×10^{-7}

a) Ref. 6.

TABLE 6. THE INTERACTION ENERGIES BETWEEN HYDROGEN AND PROTON WITH THE RESONANCE EFFECT (in a.u.)

R (a.u.)	The present result			Dalgarno and Lynn[a]	The exact value[b]
	m	A	$\overline{E}-E_0$		
2.0	2.5	-1.185	-0.9428×10^{-1}	-0.6591×10^{-1}	-0.1026
3.0	1.9	-1.442	-0.7479×10^{-1}	-0.6546×10^{-1}	-0.7756×10^{-1}
4.0	1.3	-1.797	-0.4506×10^{-1}	-0.4393×10^{-1}	-0.4608×10^{-1}
5.0	1.1	-2.103	-0.2398×10^{-1}	-0.2368×10^{-1}	-0.2442×10^{-1}
6.0	0.9	-2.326	-0.1169×10^{-1}	-0.1151×10^{-1}	-0.1197×10^{-1}
7.0	1.3	-2.250	-0.5416×10^{-2}	-0.5295×10^{-2}	-0.5595×10^{-2}
8.0	1.5	-2.200	-0.2455×10^{-2}	-0.2395×10^{-2}	-0.2570×10^{-2}
9.0	3.1	-2.136	-0.1126×10^{-2}	-0.1095×10^{-2}	-0.1195×10^{-2}
10.0	6.5	-2.092	-0.5388×10^{-3}	-0.5250×10^{-3}	-0.5800×10^{-3}

a) Ref. 17. b) Ref. 23.

tion with $\langle \Delta E\rangle_{\mathrm{Av}}=-E_0$ tends to underestimate the coefficient of the first leading term, while overestimating those of the higher-order terms. Therefore, if one chooses the average excitation energy so that correct coefficient of R^{-6} may be obtained, the adjustment unfortunately increases errors in the coefficients of the second- and higher-order terms.[21] On the other hand, the correction terms, $(\overline{H}_1H_0\overline{H}_1)^{\mathrm{L}}{}_{00}$, is:

$$(\overline{H}_1H_0\overline{H}_1)^{\mathrm{L}}{}_{00}=\frac{5}{12}-\frac{1}{R^2}+\mathrm{e}^{2R}Ei(-2R)\left(\frac{R^2}{6}+\frac{R}{2}-\frac{7}{8}-\frac{25}{16R}\right)$$
$$+\,\mathrm{e}^{-2R}Ei(2R)\left(\frac{R^2}{6}-\frac{R}{2}-\frac{7}{8}+\frac{25}{16R}\right), \tag{47}$$

which is written in the following power series:

$$(\overline{H}_1H_0\overline{H}_1)_{00}\sim\frac{2}{3}\sum_{n=1}^{\infty}\frac{n(n+1)(n+5)(2n+4)\,!}{(2R)^{2n+6}}. \tag{48}$$

Hence, from Eqs. (19), (44) and (47), $\overline{E}_2{}^{\mathrm{L}}$ is obtained as follows:

$$\overline{E}_2{}^{\mathrm{L}}=\frac{1}{6}-\left(\frac{R^2}{3}-\frac{9}{4}-\frac{7}{8R}\right)\mathrm{e}^{2R}Ei(-2R)$$
$$-\left(\frac{R^2}{3}-\frac{9}{4}+\frac{7}{8R}\right)\mathrm{e}^{-2R}Ei(2R)$$
$$\sim-4\sum_{n=1}^{\infty}\frac{n(n+3)(2n+2)\,!}{(2R)^{2n+4}}$$
$$\sim-\frac{6.0}{R^6}-\frac{112.5}{R^8}-\frac{2835.0}{R^{10}}-\cdots. \tag{49}$$

Equation (49) gives the upper values for all orders of R^{-1}, as in the case of H–H$^+$.

Discussion

It has been stressed by several authors[7,15,22] that the major factor limiting the accuracy of the long-range interaction energy between the hydrogen atom and the proton is the neglect of the degeneracy arising from the identity of the nuclear fields. Therefore, let us now examine the energy, including the effect of the degeneracy. The wave function for the $1s\sigma_g$ is given by:

$$\psi_{1s\sigma_g}=(1+P)(1+A\overline{H}_1)\phi_0 \tag{50}$$

where P is a usual projection operator which interchanges the two nuclei, a and b. Performing the integration analytically with some manipulations, and optimizing with respect to m in $\overline{H}_1$, the results shown in Table 6 are obtained. It is remarkable that the present result is, for all nuclear distances, superior to that calculated by Dalgarno and Lynn[17] by the use of a modification of a trial function given by HL for the H–H system. That there is a great discrepancy between the results in Tables 1 and 6 demonstrates the importance of considering the degeneracy particularly in treating the induction force, because, as has been mentioned above, the present dispersion energy for H–H, even without any exchange effect, is better than that of HL for $R\gtrsim10$.

It is of interest that Eq. (49) gives good coefficients when multiplied by the value of 6.499/6.0 so that the coefficient of the first leading term may become the

---

[21] G. Starkschall and R. G. Gordon, *J. Chem. Phys.*, **56**, 2801 (1972).

[22] H. Margenau, *Phys. Rev.*, **56**, 1000 (1939).

exact value; that is:

$$\frac{6.499}{6.0}E_2^{\mathrm{L}} \sim \frac{6.499}{R^6}-\frac{121.9}{R^8}-\frac{3070.8}{R^{10}}-\cdots . \tag{51}$$

This coincidence implies the utility of the conditions in Eq. (19). However, the correction for the coefficient of R^{-6} should be essentially brought about by use of the sum in Eq. (20),[14] which corresponds to $(\bar{H}_1H_0\bar{H}_1)_{00}/E_0^2$ in the present treatment, whereas, as is shown in Eq. (48), $(\bar{H}_1H_0\bar{H}_1)_{00}/E_0^2$ does not include the term of R^{-6}, but begins with R^{-8}. The difference may be caused by the average energy approximation applied. Followingly, it seems more legitimate to correct the result of Eq. (45) by adding $-(\bar{H}_1H_0\bar{H}_1)_{00}/E_0\langle\Delta E\rangle_{\mathrm{Av}}$, in which $\langle\Delta E\rangle_{\mathrm{Av}}$ is adjusted so as to give the preferable coefficient of R^{-8}. Indeed, if the value of 2.122 is adopted for $\langle\Delta E\rangle_{\mathrm{Av}}$, the coefficients of R^{-8} and R^{-10} become 124.4 and 3417.9 respectively; the latter is better than the value, 3724, obtained by Starkschall and Gordon.[21]

Furthermore, one can easily improve the numerical accuracy by the combination of our method with that presented by Goodisman,[24] who also treated the divergence problem in the calculation of $(\bar{H}_1H_0\bar{H}_1)_{00}$. If the complete set of eigenfunctions $\{\phi_0{}^i\}$ of the unperturbed Hamiltonian H_0 is available, the following first-order variational function, $\bar{\phi}_1{}^{(n)}$, can be used instead of $\bar{\phi}_1$:

$$\bar{\phi}_1{}^{(n)} = A[\bar{H}_1\phi_0 - \sum_{i=1}^{n}\bar{V}_i\phi_0{}^i] - \sum_{i=1}^{n}\frac{V_i\phi_0{}^i}{\varepsilon_i}, \tag{52}$$

where:

$$V_i = \langle\phi_0{}^i|H_1|\phi_0\rangle \tag{53}$$

$$\bar{V}_i = \langle\phi_0{}^i|\bar{H}_1|\phi_0\rangle \tag{54}$$

$$\varepsilon_i = E_0{}^i - E_0 . \tag{55}$$

Substituting Eq. (52) into Eq. (9) gives:

$$\bar{E}_2{}^{(n)} = -\sum_{i=1}^{n}\frac{V_i^2}{\varepsilon_i} + 2A[(\bar{H}_1H_1)_{00}-E_1(\bar{H}_1)_{00}-\sum_{i=1}^{n}\bar{V}_iV_i] + A^2[(\bar{H}_1(H_0-E_0)\bar{H}_1)_{00} - \sum_{i=1}^{n}\varepsilon_i\bar{V}_i^2] \geqq E_2 . \tag{56}$$

which is reduced to Eq. (10) when the terms of the summation concerning i are omitted and to the exact value when $n=\infty$. Minimizing Eq. (56) with respect to A, one obtains:

$$\bar{E}_2{}^{(n)} = -\sum_{i=1}^{n}\frac{V_i^2}{\varepsilon_i} + \frac{[(\bar{H}_1H_1)_{00}-\sum_{i=1}^{n}\bar{V}_iV_i]^2}{\sum_{i=1}^{n}\varepsilon_i\bar{V}_i^2-(\bar{H}_1(H_0-E_0)\bar{H}_1)_{00}} \geqq E_2 . \tag{57}$$

In the above equation, no divergence difficulty appears in the denominator. The improvement made possible by applying this expression is now under investigation in our laboratory.

Appendix A. The basic integrals used in the case of H–H⁺

$$(\mathrm{e}^{-mr_{\mathrm{b1}}})_{00} = \left[-I_2{}^- - \left(\frac{I_2{}^-}{2}+2I_3{}^+\right)\frac{1}{R}\right]\mathrm{e}^{-2R} + \left[\left(\frac{I_1{}^-}{2}+I_2{}^+\right)+\left(\frac{I_2{}^-}{2}+2I_3{}^+\right)\frac{1}{R}\right]\mathrm{e}^{-mR} \tag{A1}$$

$$\left(\frac{\mathrm{e}^{-mr_{\mathrm{b1}}}}{r_{\mathrm{b1}}}\right)_{00} = \left[-I_1{}^- - \left(\frac{I_1{}^-}{2}+I_2{}^+\right)\frac{1}{R}\right]\mathrm{e}^{-2R} + \left(\frac{I_1{}^-}{2}+I_2{}^+\right)\frac{\mathrm{e}^{-mR}}{R} \tag{A2}$$

$$\left(\frac{\mathrm{e}^{-mr_{\mathrm{b1}}}}{r_{\mathrm{b1}}{}^2}\right)_{00} = \left[-\log\left|\frac{m-2}{m+2}\right| - \left(I_1{}^+ + \frac{1}{2}\log\left|\frac{m-2}{m+2}\right|\right) \times\frac{1}{R}\right]\mathrm{e}^{-2R} + \frac{I_1{}^+}{R}\mathrm{e}^{-mR} + \left(1-\frac{1}{2R}\right)\mathrm{e}^{2R}Ei(-[m+2]R) + \left(1+\frac{1}{2R}\right)\mathrm{e}^{-2R}Ei(-[m-2]R) \tag{A3}$$

$$\left(\frac{\mathrm{e}^{-mr_{\mathrm{b1}}}}{r_{\mathrm{b1}}{}^3}\right)_{00} = \left[-4\lim_{\varepsilon\to0}\log\varepsilon\gamma + 4-(m+2)\log(m+2) + (m-2)\log|m-2| + \left(2+\frac{m}{2}\log\left|\frac{m-2}{m+2}\right|\right)\frac{1}{R}\right]\mathrm{e}^{-2R} - \frac{2}{R}\mathrm{e}^{-mR} - \left(m+2-\frac{m}{2R}\right)\mathrm{e}^{2R}Ei(-[m+2]R) - \left(m-2+\frac{m}{2R}\right)\mathrm{e}^{-2R}Ei(-[m-2]R) \tag{A4}$$

$$\left(\frac{\mathrm{e}^{-mr_{\mathrm{b1}}}}{r_{\mathrm{b1}}{}^4}\right)_{00} = \left[4\lim_{\varepsilon\to0}\left(\frac{1}{\varepsilon}+m\log\varepsilon\gamma\right) - \frac{m}{R} - \left(6m+\frac{(m-2)^2}{2}\log|m-2| - \frac{(m+2)^2}{2}\log|m+2|\right) - \frac{m^2-4}{4R}\log\left|\frac{m-2}{m+2}\right|\right]\mathrm{e}^{-2R} + \frac{m}{R}\mathrm{e}^{-mR} + \left[\frac{(m+2)^2}{2}-\frac{m^2-4}{4R}\right]\mathrm{e}^{2R}Ei(-[m+2]R) + \left[\frac{(m-2)^2}{2}+\frac{m^2-4}{4R}\right]\mathrm{e}^{-2R}Ei(-[m-2]R) , \tag{A5}$$

where

$$I_n{}^+ = \frac{1}{(m+2)^n} + \frac{1}{(m-2)^n}$$

and

$$I_n{}^- = \frac{1}{(m+2)^n} - \frac{1}{(m-2)^n} .$$

Appendix B. The additional integrals necessary in the case of H–H. Most integrals in the case of two hydrogen atoms are easily obtained by the use of the results in Appendix A repeatedly. Only the integrals below which appear in the third-order energy should be newly calculated:

$$(\mathrm{e}^{2r_{\mathrm{b1}}}Ei(-[m+2]r_{\mathrm{b1}}) + \mathrm{e}^{-2r_{\mathrm{b1}}}Ei(-[m-2]r_{\mathrm{b1}}))_{00} = \left[\left(\frac{1}{2}I_2{}^- - \frac{1}{4}I_1{}^+\right) + \frac{1}{R}\left(\frac{2}{3}I_3{}^+ - \frac{1}{4}I_1{}^+\right) - \frac{1}{8}\left(1+\frac{1}{R}\right)\log\left|\frac{m-2}{m+2}\right|\right]\mathrm{e}^{-2R} + \left[\frac{I_1{}^+}{6}R - \left(\frac{1}{4}I_1{}^- + \frac{1}{6}I_2{}^+\right) - \left(\frac{2}{3}I_3{}^+ - \frac{1}{4}I_1{}^+\right)\frac{1}{R}\right]\mathrm{e}^{-mR} + \mathrm{e}^{2R}Ei(-[m+2]R)\left(\frac{R^2}{6}-\frac{R}{4}+\frac{1}{4}-\frac{1}{8R}\right)$$

---

[23] D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc., Ser A*, **246**, 215 (1953).

[24] J. Goodisman, *J. Chem. Phys.*, **47**, 2707 (1967).

$$+\mathrm{e}^{-2R}Ei(-[m-2]R)\left(\frac{R^2}{6}+\frac{R}{4}+\frac{1}{4}+\frac{1}{8R}\right) \tag{B1}$$

$$\begin{aligned}
&(\mathrm{e}^{2r_{\mathrm{b1}}}Ei(-[m+2]r_{\mathrm{b1}})-\mathrm{e}^{-2r_{\mathrm{b1}}}Ei(-[m-2]r_{\mathrm{b1}}))_{00}\\
&=\left[\left(\frac{1}{2}I_2{}^{+}+\frac{1}{4}I_1{}^{-}\right)+\frac{1}{R}\left(\frac{2}{3}I_3{}^{-}+\frac{1}{4}I_1{}^{-}+\frac{1}{2}I_2{}^{+}\right)\right]\mathrm{e}^{-2R}\\
&+\left[\frac{I_1{}^{-}}{6}R-\left(\frac{1}{4}I_1{}^{+}+\frac{1}{6}I_2{}^{-}\right)-\frac{1}{R}\left(\frac{2}{3}I_3{}^{-}+\frac{1}{4}I_1{}^{-}\right.\right.\\
&\left.\left.+\frac{1}{2}I_2{}^{+}\right)\right]\mathrm{e}^{-mR}+\frac{1}{4}\mathrm{e}^{2R}Ei(-[m+2]R)\left(\frac{2}{3}R^2-R+\frac{1}{2}\right)\\
&-\frac{1}{4}\mathrm{e}^{-2R}Ei(-[m-2]R)\left(\frac{2}{3}R^2+R+\frac{1}{2}\right)
\end{aligned} \tag{B2}$$

$$\begin{aligned}
&\left(\frac{\mathrm{e}^{2r_{\mathrm{b1}}}Ei(-[m+2]r_{\mathrm{b1}})+\mathrm{e}^{-2r_{\mathrm{b1}}}Ei(-[m-2]r_{\mathrm{b1}})}{r_{\mathrm{b1}}}\right)_{00}\\
&=\left[I_1{}^{-}+\frac{1}{2R}\left(I_2{}^{+}+\frac{I_1{}^{-}}{2}\right)\right]\mathrm{e}^{-2R}+\left[\frac{I_1{}^{+}}{2}-\frac{1}{2R}\left(I_2{}^{+}\right.\right.\\
&\left.\left.+\frac{I_1{}^{-}}{2}\right)\right]\mathrm{e}^{-mR}-\left(\frac{1}{4}-\frac{R}{2}\right)\mathrm{e}^{2R}Ei(-[m+2]R)\\
&+\left(\frac{1}{4}+\frac{R}{2}\right)\mathrm{e}^{-2R}Ei(-[m-2]R)
\end{aligned} \tag{B3}$$

$$\begin{aligned}
&\left(\frac{\mathrm{e}^{2r_{\mathrm{b1}}}Ei(-[m+2]r_{\mathrm{b1}})-\mathrm{e}^{-2r_{\mathrm{b1}}}Ei(-[m-2]r_{\mathrm{b1}})}{r_{\mathrm{b1}}}\right)_{00}\\
&=\left[I_1{}^{+}+\frac{1}{2R}\left(I_2{}^{-}+\frac{3}{2}I_1{}^{+}\right)+\left(\frac{1}{2}+\frac{3}{8R}\right)\right.\\
&\left.\times\log\left|\frac{m-2}{m+2}\right|\right]\mathrm{e}^{-2R}+\left[\frac{I_1{}^{-}}{2}-\frac{1}{2R}\left(I_2{}^{-}+\frac{3}{2}I_1{}^{+}\right)\right]\\
&\times\mathrm{e}^{-mR}+\mathrm{e}^{2R}Ei(-[m+2]R)\left(\frac{R}{2}-\frac{3}{4}+\frac{3}{8R}\right)\\
&-\mathrm{e}^{-2R}Ei(-[m-2]R)\left(\frac{R}{2}+\frac{3}{4}+\frac{3}{8R}\right)
\end{aligned} \tag{B4}$$

$$\begin{aligned}
&\left(\frac{\mathrm{e}^{(2-k)r_{\mathrm{b1}}}Ei(-[m+2]r_{\mathrm{b1}})+\mathrm{e}^{-(2+k)r_{\mathrm{b1}}}Ei(-[m-2]r_{\mathrm{b1}})}{r_{\mathrm{b1}}}\right)_{00}\\
&=\frac{1}{2}\mathrm{e}^{-2R}\left[\frac{1}{k}\left(R-\frac{1}{k}+\frac{1}{2}\right)\log\left|\frac{m-2}{m+k-2}\right|\right.\\
&-\frac{1}{4+k}\left(R+\frac{1}{4+k}+\frac{1}{2}\right)\log\left|\frac{m-2}{m+k+2}\right|-\frac{1}{k}\left(R+\frac{1}{k}\right.\\
&\left.+\frac{1}{2}\right)\log\left|\frac{m+2}{m+k+2}\right|-\frac{1}{4-k}\left(R+\frac{1}{4-k}+\frac{1}{2}\right)\\
&\times\log\left|\frac{m+2}{m+k-2}\right|-\frac{1}{k(m+k+2)}-\frac{1}{(4+k)(m+k+2)}\\
&\left.-\frac{1}{k(m+k-2)}+\frac{1}{(4-k)(m+k-2)}\right]+\frac{1}{2}\mathrm{e}^{-(m+k)R}\\
&\times\left[\frac{1}{k(m+k+2)}+\frac{1}{(4+k)(m+k+2)}+\frac{1}{k(m+k-2)}\right.\\
&\left.-\frac{1}{(4-k)(m+k-2)}\right]+\frac{1}{2}\mathrm{e}^{(2-k)R}Ei(-[m+2]R)\\
&\times\left[\frac{1}{k}\left(\frac{1}{k}+\frac{1}{2}\right)+\frac{1}{4-k}\left(\frac{1}{4-k}+\frac{1}{2}\right)\right]\\
&+\frac{1}{2}\mathrm{e}^{-(2+k)R}Ei(-[m-2]R)\left[\frac{1}{k}\left(\frac{1}{k}-\frac{1}{2}\right)\right.\\
&\left.+\frac{1}{4+k}\left(\frac{1}{4+k}+\frac{1}{2}\right)\right]+\frac{1}{2}\mathrm{e}^{2R}Ei(-[m+k+2]R)\\
&\times\left[\frac{1}{k}\left(R-\frac{1}{k}-\frac{1}{2}\right)+\frac{1}{4+k}\left(R-\frac{1}{4+k}-\frac{1}{2}\right)\right]\\
&+\frac{1}{2}\mathrm{e}^{-2R}Ei(-[m+k-2]R)\left[\frac{1}{k}\left(R-\frac{1}{k}+\frac{1}{2}\right)\right.\\
&\left.-\frac{1}{4-k}\left(R+\frac{1}{4-k}+\frac{1}{2}\right)\right]
\end{aligned} \tag{B5}$$

$$\begin{aligned}
&\left(\frac{\mathrm{e}^{(2-k)r_{\mathrm{b1}}}Ei(-[m+2]r_{\mathrm{b1}})-\mathrm{e}^{-(2+k)r_{\mathrm{b1}}}Ei(-[m-2]r_{\mathrm{b1}})}{r_{\mathrm{b1}}{}^2}\right)_{00}\\
&=\frac{\mathrm{e}^{-2R}}{R}\left[\frac{1}{k}\log\left|\frac{m-2}{m+k-2}\right|+\frac{1}{4+k}\log\left|\frac{m-2}{m+k+2}\right|\right.\\
&\left.-\frac{1}{k}\log\left|\frac{m+2}{m+k+2}\right|+\frac{1}{4-k}\log\left|\frac{m+2}{m+k-2}\right|\right]\\
&+\frac{\mathrm{e}^{(2-k)R}}{R}Ei(-[m+2]R)\left(\frac{1}{k}-\frac{1}{4-k}\right)-\frac{\mathrm{e}^{-(2+k)R}}{R}\\
&\times Ei(-[m-2]R)\left(\frac{1}{k}+\frac{1}{4+k}\right)-\frac{\mathrm{e}^{2R}}{R}Ei(-[m+k+2]R)\\
&\times\left(\frac{1}{k}+\frac{1}{4+k}\right)+\frac{\mathrm{e}^{-2R}}{R}Ei(-[m+k-2]R)\left(\frac{1}{k}+\frac{1}{4-k}\right)\\
&-\left(1-\frac{1}{2R}\right)X+\left(1+\frac{1}{2R}\right)\mathrm{e}^{-2R}Y
\end{aligned} \tag{B6}$$

where

$$\begin{aligned}
X&=\int_R^\infty\frac{\mathrm{e}^{-kx}}{x}[Ei(-[m+2]x)-\mathrm{e}^{-4x}Ei(-[m-2]x)]\mathrm{d}x\\
&=\frac{\mathrm{e}^{-(m+k)R}}{R}\sum_{n=1}^{\infty}\left[\frac{1}{(m-2)^n}-\frac{1}{(m+2)^n}\right]\frac{(-1)^{n+1}}{n}\\
&\qquad\times\sum_{s=1}^{N}\frac{(-1)^{s+1}(n+s-1)\,!}{(m+k+2)^sR^{n+s-1}}
\end{aligned} \tag{B7}$$

in which N is the s that minimizing $(n+s-1)\,!/(m+k+2)^s\times R^{n+s-1}$, and where

$$\begin{aligned}
Y&=\int_0^R\frac{\mathrm{e}^{-kx}}{x}[\mathrm{e}^{4x}Ei(-[m+2]x)-Ei(-[m-2]x)]\mathrm{d}x\\
&-\int_0^R\frac{\mathrm{e}^{-kx}}{x}[Ei(-[m+2]x)-\mathrm{e}^{-4x}Ei(-[m-2]x)]\mathrm{d}x\\
&-X\\
&=\log\gamma R\sum_{i=1}^{\infty}\frac{R^i}{i\,i!}[(-[k-4])^i-2(-k)^i+(-[k+4])^i]\\
&-\sum_{i=1}^{\infty}\frac{R^i}{i^2\,i!}[(-[k-4])^i-2(-k)^i+(-[k+4])^i]\\
&+\log|m+2|\sum_{i=1}^{\infty}\frac{R^i}{i\,i!}[(-[k-4])^i-(-k)^i]\\
&-\log|m-2|\sum_{i=1}^{\infty}\frac{R^i}{i\,i!}[(-k)^i-(-[k+4])^i]\\
&+\sum_{i=1}^{\infty}\frac{(-[k-4])^i-(-k)^i}{i\,!}R^i\sum_{j=1}^{\infty}\frac{(-[m+2])^jR^j}{j\,j!\ (i+j)}\\
&-\sum_{i=1}^{\infty}\frac{(-k)^i-(-[k+4])^i}{i\,!}R^i\sum_{j=1}^{\infty}\frac{(-[m-2])^jR^j}{j\,j!\ (i+j)}\\
&-X
\end{aligned} \tag{B8}$$

in which the infinite series are truncated so that they give necessary accuracy.

$$\begin{aligned}
&\left(\frac{\mathrm{e}^{-mr_{\mathrm{b1}}}\mathrm{e}^{-kr_{\mathrm{a2}}}}{r_{\mathrm{b1}}r_{12}r_{\mathrm{a2}}}\right)_{00}\\
&=\frac{R^3}{2}\sum_{\tau=0}^{\infty}(2\tau+1)\left[W_\tau{}^0\left(1,1;\frac{R}{2}(2+k),\frac{R}{2}(2+m)\right)\right.\\
&\times G_\tau{}^0\left(0,\frac{R}{2}(2-k)\right)G_\tau{}^0\left(0,\frac{R}{2}(m-2)\right)
\end{aligned}$$

$$\begin{aligned}
&-W_\tau^0\left(1,0;\frac{R}{2}(2+k),\frac{R}{2}(2+m)\right) \\
&\qquad\times G_\tau^0\left(0,\frac{R}{2}(2-k)\right)G_\tau^0\left(1,\frac{R}{2}(m-2)\right) \\
&+W_\tau^0\left(0,1;\frac{R}{2}(2+k),\frac{R}{2}(2+m)\right) \\
&\qquad\times G_\tau^0\left(1,\frac{R}{2}(2-k)\right)G_\tau^0\left(0,\frac{R}{2}(m-2)\right) \\
&-W_\tau^0\left(0,0;\frac{R}{2}(2+k),\frac{R}{2}(2+m)\right) \\
&\qquad\times G_\tau^0\left(1,\frac{R}{2}(2-k)\right)G_\tau^0\left(1,\frac{R}{2}(m-2)\right)\Bigg]
\end{aligned} \tag{B9}$$

where W_τ^0 and G_τ^0 refer to the notation of Ref. 25.

---

25) M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, "Table of Molecular Integrals," 2nd ed., Maruzen Co., Tokyo (1963).