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Long-range Interaction between a Hydrogen Atom and a Hydride Ion

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The long-range force between a hydrogen atom and a hydride ion has been studied by means of the second-order perturbation theory. This H–H$^-$ system has been chosen as the simplest example of a system composed of a neutral atom and an anion. The results seem to suggest that the analytical closed form of the second-order energy is desirable for any discussion of the long-range interaction between H and H$^-$ in place of the usual multipole expansion. According to the multipole expansion until the R^{-12} term, the nature of the long-range interaction operating in this system seems to be dispersive, and it seems to become inductive at a much larger R because of the existence of the leading R^{-4} term.

Generally, long-range forces among atoms and molecules are conveniently classified into two categories: the induction force and the dispersion force. The former is due to the long-range interaction energy between a neutral system and a cationic one, and the latter, to that between two neutral systems. Numerous theoretical studies have been devoted to these forces, particularly the systems composed of combinations of H$^+$, H, and He; the perturbation theory or equivalent variational methods have been used.[1] As a matter of course, the long-range interaction between a cation and an anion is Coulombic. Now, then, what kind of interaction operates between a neutral system and an anionic one? In order to clarify the nature of the interaction energy between such systems, we will try, as the first step, to investigate the long-range force between H and H$^-$ as the simplest system.

The long-range force between H and H$^-$ actually has an important role in the dissociation process of the H$_2^-$ molecule ion into H and H$^-$ in the solar corona[2] and is referred to as considerably strong in spite of its anionic nature.[3] Theoretical investigations of the H–H$^-$ long-range force have been done only by Dalgarno and Kingston[4] and by Davison[5] using the usual multipole expansion of the second-order perturbation energy. The latter has evaluated the coefficients of the R^{-4}, R^{-6}, and R^{-8} terms in the series expansion of the inverse powers of the internuclear distance, R, between H and H$^-$ (hereafter we will briefly representthe above quantities as C_4, C_6, C_8, *etc.* and will use the atomic units for energies and distances throughout this paper). The results, however, were too poor for us to get the interaction energy by means of the multipole expansion, since the convergency of the series was bad, even in the asymptotic sense:

$$\bar{E}_2(\text{Davison}) = -\left(\frac{2.25}{R^4}+\frac{93}{R^6}+\frac{7\cdot 10^3}{R^8}\right) \tag{1}$$

For instance, the values of these terms are comparable at $R=10$; hence, we need to estimate the higher-order terms at least in the region of *ca.* $R=10$.

In view of this inherent defect in the series expansion, an analytical form is desirable instead. In preceding papers,[6a–6d] we have already investigated the analytical formulae for the second-order perturbation energies with respect to the H–H$^+$, H–H, and He–He systems, neglecting exchange in the framework of the Unsöld approximation. Similarly, in this paper, we will try to obtain a closed form of the second-order perturbation energy of the interaction between H and H$^-$, both in their ground states, and afterwards, will try to show an expansion form again derived from the closed one in order to discuss the nature of the force operating in this system.

Method of Calculation

As is well known, in the framework of the Unsöld approximation,[7] neglecting the exchange for a larger R, the second-order perturbation energy caused by a perturbation, H_1, can be represented by:

$$\bar{E}_2(\text{Unsöld}) = -\frac{\langle H_1{}^2\rangle_{00}-\langle H_1\rangle_{00}{}^2}{\langle \Delta E\rangle_{\text{AV}}}, \tag{2}$$

where 0 means the eigenfunction, Φ_0, in the ground state with respect to the unperturbed Hamiltonian, H_0; $\langle \Delta E\rangle_{\text{AV}}$ is called an 'average excitation energy,' after Unsöld. In the cases of the H–H$^-$ system, neglecting the exchange, Φ_0 appears as follows:

$$\Phi_0 = \Psi_{\text{a}}(1)\Psi_{\text{b}}(2,3), \tag{3}$$

where $\Psi_{\text{a}}(1)$ is the 1s-function of a hydrogen atom, a, and where $\Psi_{\text{b}}(2,3)$ is a wavefunction of a hydride ion, b. In order to get an analytical form of $\bar{E}_2$ (Unsöld), we need a wavefunction, $\Psi_{\text{b}}(2,3)$, simple enough to be used for Φ_0, but also accurate enough to show the stability of H$^-$. The simplest form is one for the 1s^2 ^{1}S state, but it gives no stabilization of H$^-$.[8] The form we employ here is a linear combination of the product of the 1s-like functions with different orbital exponents, z and z', for different spins:

$$\Psi_{\text{b}}(2,3) = \frac{1}{\sqrt{2(1+s^2)}}[\Psi_{\text{b}}(2)\Psi_{\text{b}}'(3)+\Psi_{\text{b}}(3)\Psi_{\text{b}}'(2)], \tag{4}$$

where:

$$\Psi_{\text{b}}(i) = \frac{z^{3/2}}{\sqrt{\pi}}\exp[-zr_i], \tag{5-a}$$

and

$$\Psi_{\text{b}}'(j) = \frac{z'^{\,3/2}}{\sqrt{\pi}}\exp[-z'r_j], \tag{5-b}$$

and where:

$$s = \left(\frac{2\sqrt{zz'}}{z+z'}\right)^3. \tag{6}$$

The notations in the H–H$^-$ system are shown in Fig. 1. This wavefunction, which was first obtained by Chandrasekhar[9] and was thereafter used by Dalgarno *et al.*[3] and Fischer-Hjalmars[10] for the calculation of

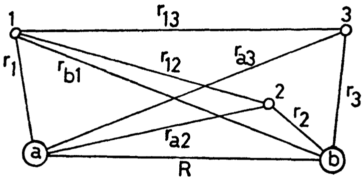

Fig. 1. Notation for distances among electrons 1, 2, and 3, and nuclei a and b in the H-H⁻ system.

the energy of H_2^-, predicts the stability of H^- when $z' \simeq z/3$; hence, we assume that this wavefunction is the correct one for H^-. Using this $\Psi_b(2,3)$, we construct an unperturbed wavefunction as follows:

$$\Phi_0 = \left(\frac{zz'}{\pi}\right)^{3/2} \cdot \frac{1}{\sqrt{2(1+s^2)}} \exp[-r_1]\{\exp[-zr_2] \times \exp[-z'r_3] + \exp[-zr_3]\exp[-z'r_2]\}. \tag{7}$$

The perturbation, H_1, between H and H^- at an internuclear distance, R, is written by:

$$H_1 = \frac{1}{R} - \frac{1}{r_{a2}} - \frac{1}{r_{a3}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} + \frac{1}{r_{13}}, \tag{8}$$

which is then rearranged into three parts:

$$H_1 = \left[\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}}\right] + \left[\frac{1}{r_{13}} + \frac{1}{R} - \frac{1}{r_{b1}} - \frac{1}{r_{a3}}\right] - \left[\frac{1}{R} - \frac{1}{r_{b1}}\right] \equiv H_1(1,2) + H_1(1,3) - H_1(1). \tag{9}$$

It can easily be seen that the first two terms and the last term furthest to the right correspond to the interactions between H-H and that between H-H⁺ respectively. Using the wavefunction in Eq. (7), $\langle H_1\rangle_{00}$ and $\langle H_1^2\rangle_{00}$ may be rewritten as:

$$\begin{aligned}\langle H_1\rangle_{00} &= \langle H_1(1,2)\rangle_{00} + \langle H_1(1,3)\rangle_{00} - \langle H_1(1)\rangle_{00} \\ &= 2\langle H_1(1,2)\rangle_{00} - \langle H_1(1)\rangle_{00},\end{aligned} \tag{10}$$

and:

$$\begin{aligned}\langle H_1^2\rangle_{00} &= \langle H_1^2(1,2)\rangle_{00} + \langle H_1^2(1,3)\rangle_{00} + \langle H_1^2(1)\rangle_{00} \\ &\quad + 2\langle H_1(1,2)H_1(1,3)\rangle_{00} - 2\langle H_1(1,2)H_1(1)\rangle_{00} \\ &\quad - 2\langle H_1(1,3)H_1(1)\rangle_{00} \\ &= 2\langle H_1^2(1,2)\rangle_{00} + \langle H_1^2(1)\rangle_{00} \\ &\quad + 2\langle H_1(1,2)H_1(1,3)\rangle_{00} \\ &\quad - 4\langle H_1(1,2)H_1(1)\rangle_{00}.\end{aligned} \tag{11}$$

It should be noticed that only the first two terms furthest to the right in Eq. (11) contain non-exponentially decreasing terms and therefore contribute to the origin of the long-range interaction. That is, the first term, $\langle H_1^2(1,2)\rangle_{00}$, corresponds to the second-order interaction energy of H-H with the well-known R^{-6} decay, while the second term, $\langle H_1^2(1)\rangle_{00}$, corresponds to that of H-H⁺ giving the first leading term of R^{-4} in the Unsöld approximation except for the factors of the 'average excitation energy.'

Using Eqs. (10) and (11), Eq. (2) can be rewritten as:

$$\begin{aligned}\bar{E}_2(\text{Unsöld}) = -\frac{1}{\langle \Delta E\rangle_{\text{AV}}}\Bigg[&-\frac{2}{R^2} + \frac{4}{R}\langle H_1(2)\rangle_{00} - \langle H_1^2(1)\rangle_{00} \\ &-2\langle H_1^2(2)\rangle_{00} + 4\left\langle \frac{1}{r_{a2}} W(2,1)\right\rangle_{00} \\ &+2\left\langle \frac{1}{r_{12}^2}\right\rangle_{00} + 2\langle H_1(2)H_1(3)\rangle_{00} \\ &-2\langle H_1(2)W(1,3)\rangle_{00} - 2\langle H_1(3)W(1,2)\rangle_{00} \\ &+2W\langle(1,2)W(1,3)\rangle_{00} - 4\langle H_1(1,2)\rangle_{00}^2 \\ &-\langle H_1(1)\rangle_{00}^2 + 4\langle H_1(1,2)\rangle_{00}\langle H_1(1)\rangle_{00}\Bigg],\end{aligned} \tag{12}$$

where:

$$\left.\begin{aligned} W(1,i) &= \frac{1}{r_{b1}} - \frac{1}{r_{1i}} \quad (i=2,3), \\ W(i,1) &= \frac{1}{r_{ai}} - \frac{1}{r_{1i}} \quad (i=2,3), \end{aligned}\right\} \tag{13}$$

In order to avoid complexity arising from the presence of many terms, we will introduce some further notations. For any hermitian operator, F, the expectation value, $\langle F\rangle_{00}$, in which 0 stands for the function defined as in Eq. (7), is decomposed into three parts:

$$\langle F\rangle_{00} = \frac{1}{2(1+s^2)}[\{F|R,z,z'\} + \{F|R,z',z\} + 2s^2\{F|R,z'',z''\}], \tag{14}$$

where s is defined as in Eq. (6), where $z''=(z+z')/2$, and where:

$$\left.\begin{aligned} \{F|R,z,z'\} &= \langle \Psi_a^*(1)\Psi_b^*(2)\Psi_b'^*(3) \\ &\qquad |F|\Psi_a(1)\Psi_b(2)\Psi_b'(3)\rangle, \\ \{F|R,z',z\} &= \langle \Psi_a^*(1)\Psi_b'^*(2)\Psi_b^*(3) \\ &\qquad |F|\Psi_a(1)\Psi_b'(2)\Psi_b(3)\rangle, \\ \text{and} \\ \{F|R,z'',z''\} &= \langle \Psi_a^*(1)\Psi_b''^*(2)\Psi_b''^*(3) \\ &\qquad |F|\Psi_a(1)\Psi_b''(2)\Psi_b''(3)\rangle. \end{aligned}\right\} \tag{15}$$

In Eq. (15), the asterisk indicates the hermitian conjugate, $\Psi_b(i)$ and $\Psi_b'(j)$ are defined by Eqs. (5-a) and (5-b), and

$$\Psi_b''(k) = \frac{z''^{3/2}}{\sqrt{\pi}} \exp[-z''r_k]. \tag{5-c}$$

All the integrals used in Eq. (12) are shown in the Appendix. Thus, Eq. (12) may be evaluated exactly without resorting to a series expansion and can be given in a closed analytical form applicable to an arbitrary internuclear distance, R, and orbital exponents, z and z'.

Results and Discussion

In the calculation of $\bar{E}_2$ (Unsöld), we adopt the values of the orbital exponents following Fischer-Hjalmars[10] that is, $z=1.00$, $z'=0.30$, and hence $z''=(z+z')/2=0.65$. As to $\langle \Delta E\rangle_{\text{AV}}$, we can consider three kinds of values: 1) the sum of the first ionization potentials of H and H⁻, 0.52775*, which is

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* Pekeris has obtained, by concentrated numerical efforts, the ground state energy of H⁻ as −0.52775 (*Phys. Rev.*, **126**, 1470 (1962)). He has also thought that H⁻ has no more than one bound state; that is, the first ionization potential of H⁻ is 0.02775 to make the H+e⁻ system. Power and Somorjai have tried to prove the above fact (*ibid.*, **A5**, 2401 (1972)), but in vain (*ibid.*, **A6**, 1996 (1972)). It is very likely, however, that H⁻ has no more than one bound state (Ref. 2-b); hence, we assume that the first ionization potential is 0.02775.

TABLE 1. LONG-RANGE INTERACTION ENERGY ΔW BETWEEN H AND H^- IN 10^{-3} a.u.

R (a. u.)	$-E_1$	$-\overline{E}_2$ (Unsöld)[a]			$\Delta W = -E_1 - \overline{E}_2$ (Unsöld)[a]			CI[b] (D)	Modified CI[c] (E)
		(A)	(B)	(C)	(A)	(B)	(C)		
4.0	5.8912	17.749	34.565	45.293	23.640	40.456	51.184	13.3	6.25
5.0	2.6218	8.4450	16.446	21.550	11.067	19.068	24.172	11.3	4.25
6.0	1.2900	4.3092	8.3919	10.996	5.5992	9.6819	12.286	9.3	2.25
7.0	0.67434	2.3220	4.5219	5.9253	2.9963	5.1962	6.5996	8.3	1.25
8.0	0.36306	1.2996	2.5309	3.3164	1.6627	2.8940	3.6795	—	—
9.0	0.19804	0.74726	1.4552	1.9069	0.94530	1.6532	2.1049	—	—
10.0	0.10863	0.43891	0.85473	1.1200	0.54754	0.96336	1.2287	—	—
11.0	0.059717	0.26288	0.51195	0.67084	0.32260	0.57167	0.73056	—	—
12.0	0.032853	0.16068	0.31292	0.41004	0.19353	0.34577	0.44289	—	—

a) $\langle \Delta E \rangle_{AV} = 1.02775$, 0.52775, and 0.402775 in the cases (A), (B), and (C), respectively. b) Ref. 11. c) At $R = \infty$, $E = -1.02775$.

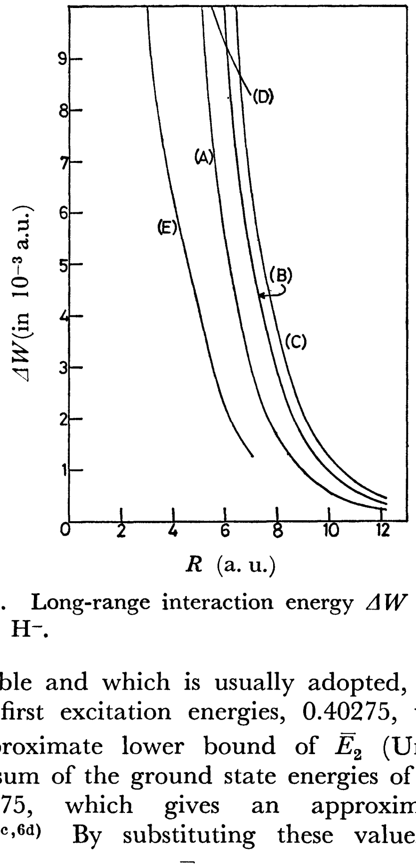

Fig. 2. Long-range interaction energy ΔW between H and H^-.

reasonable and which is usually adopted, 2) the sum of the first excitation energies, 0.40275, which gives an approximate lower bound of $\overline{E}_2$ (Unsöld), and 3) the sum of the ground state energies of H and H^-, -1.02775, which gives an approximate upper bound.[6c,6d] By substituting these values into Eq. (12), three kinds of $\overline{E}_2$ (Unsöld) values for various R values are obtained, as is shown in Table 1. The first-order perturbation energy, E_1, is equal to the expectation value, $\langle H_1 \rangle_{00}$; it is also shown in Table 1 for each R.

On the other hand, Taylor and Harris have previously obtained a potential curve for the ${}^2\Sigma_u^+$ state of the H_2^- system using a CI method until $R=7.0$;[11] this seems to be the most reliable value at present. In Fig. 2, three kinds of total interaction energy curves, (A), (B), and (C) taken as far as the second-order between the H and H^- obtained by means of the above criterion, are compared with the results of the variational calculation done by Taylor and Harris and also with the version modified here using the exact sum of the ground state energies of H and H^-, -1.02775, as the standard of the separated system. This modified version can afford a strict lower bound of the total interaction energy.** The potential curve (A) represents almost the lower bound of the interaction energy taken up to the second-order term, and (C), almost the upper bound. The exact one would lie in the zone between (A) and (C). The result of the original variational calculation, (D), lies above the zone obtained here. However, the modified version, (E), lies below.

Now, discarding the terms attenuating exponentially with an increase in R in Eq. (12), we obtain this reduced formula:

$$\overline{E}_2(\text{Unsöld}) \simeq -\frac{1}{\langle \Delta E \rangle_{AV}} \cdot \frac{1}{2(1+s^2)} [V(R,z) + V(R,z') + 2s^2 V(R,z'')], \tag{16}$$

where:

$$\begin{aligned} V(R,z) = {} & \exp[-2R]\widetilde{Ei}[2R] \\ & \times \left\{-1 + \frac{2z^4}{(1-z^2)^2} + \left(-\frac{1}{2} + \frac{z^4(5-z^2)}{(1-z^2)^3}\right)\frac{1}{R}\right\} \\ & + \exp[2R]Ei[-2R] \\ & \times \left\{-1 + \frac{2z^4}{(1-z^2)^2} + \left(\frac{1}{2} - \frac{z^4(5-z^2)}{(1-z^2)^3}\right)\frac{1}{R}\right\} \\ & + \exp[-2zR]\widetilde{Ei}[2zR] \\ & \times \left\{-2z^2 + \frac{2z^2}{(1-z^2)^2} + \left(-z + \frac{z(1-5z^2)}{(1-z^2)^3}\right)\frac{1}{R}\right\} \\ & + \exp[2zR]Ei[-2zR] \\ & \times \left\{-2z^2 + \frac{2z^2}{(1-z^2)^2} + \left(z - \frac{z(1-5z^2)}{(1-z^2)^3}\right)\frac{1}{R}\right\}. \end{aligned} \tag{17}$$

In Eq. (17), $\widetilde{Ei}[x]$ is the usual exponential integral, defined as:

$$\widetilde{Ei}[x] = -\int_{-x}^{\infty} \frac{\exp[-t]}{t} dt,$$

and

$$Ei[-x] = -\int_{x}^{\infty} \frac{\exp[-t]}{t} dt.$$

** It should be noticed that the lower and the upper bound alternate in the case of the interaction energy, since it is defined as a positive quantity.

Using the well-known asymptotic expansion,

$$\exp[-x]\widetilde{Ei}[x] \simeq \sum_{n=1}^{\infty}\frac{(n-1)!}{x^n},$$

and

$$\exp[x]Ei[-x] \simeq \sum_{n=1}^{\infty}\frac{(-1)^n(n-1)!}{x^n},$$

we obtain:

$$\begin{aligned} V(R,z) = {} & \frac{1}{R^4}+\frac{3(8+3z^2)}{2z^2}\cdot\frac{1}{R^6}+\frac{45(3+3z^2+z^4)}{z^4}\cdot\frac{1}{R^8} \\ & +\frac{315(16+18z^2+16z^4+5z^6)}{2z^6}\cdot\frac{1}{R^{10}} \\ & +\frac{14175(3z^8+10z^6+12z^4+12z^2+10)}{2z^8}\cdot\frac{1}{R^{12}}\cdots\cdots \end{aligned} \tag{18}$$

Using Eqs. (16) and (18), and substituting $z=1.00$, $z'=0.30$, and $z''=0.65$, we obtain a form of series expansion with respect to the inverse powers of R, which can be compared with Davison's result using Eq. (1), as follows:

$$\begin{aligned} \overline{E}_2(\text{Unsöld}) = {} & -\frac{1}{\langle \Delta E\rangle_{\text{AV}}}\Big(\frac{1}{R^4}+\frac{65.497}{R^6}+\frac{7116.8}{R^8} \\ & +\frac{1.4302\cdot 10^6}{R^{10}}+\frac{4.4604\cdot 10^8}{R^{12}}+\cdots\cdots\Big). \end{aligned} \tag{19}$$

In this series, at $R=18$, 14, and 10, the R^{-12} term is comparable with the R^{-10} term, the R^{-10} term with the R^{-8} term, and the R^{-8} term with the R^{-6} term. Adopting $\langle \Delta E\rangle_{\text{AV}}=0.52775$, which gives the potential (B) in Fig. 2, we obtain:

$$\begin{aligned} \overline{E}_2(\text{Unsöld}) = {} & -\Big(\frac{1.8948}{R^4}+\frac{1.2411\cdot 10^2}{R^6}+\frac{1.3485\cdot 10^4}{\mathrm{R}^8} \\ & +\frac{2.7100\cdot 10^6}{R^{10}}+\frac{8.4517\cdot 10^8}{R^{12}}+\cdots\cdots\Big). \end{aligned} \tag{20}$$

The results definitely show the divergent nature of the sequence C_{2n} ($n=2$, 3, 4, 5, 6, and so on). On the contrary, the use of the closed form obtained in this paper easily affords the value of $\overline{E}_2$ (Unsöld) at any given R. It can easily be seen that the R^{-4} term comes from the first term of the induction force in the H–H⁺ system:[12)]

$$\begin{aligned} \overline{E}_2 = {} & -\Big(\frac{2.25}{R^4}+\frac{7.50}{R^6}+\frac{65.625}{R^8}+\frac{1063.125}{R^{10}} \\ & +\frac{27286.875}{R^{12}}+\cdots\cdots\Big). \end{aligned} \tag{21}$$

The other terms in Eq. (21) contribute little to Eq. (20). In order to clarify this, we have calculated another series expansion with regard to the perturbation H_1:

$$H_1 = H_1(1,2) + H_1(1,3), \tag{22}$$

which involves no H–H⁺ interaction, in contrast with Eq. (9). The results of expansion are as follows:

$$\begin{aligned} \overline{E}_2(\text{Unsöld}) = {} & -\frac{1}{\langle \Delta E\rangle_{\text{AV}}}\Big(\frac{60.998}{R^6}+\frac{7071.8}{R^8} \\ & +\frac{1.4294\cdot 10^6}{R^{10}}+\frac{4.4601\cdot 10^8}{R^{12}}+\cdots\cdots\Big). \end{aligned} \tag{23}$$

In this case, $V(R, z)$ as defined in Eq. (16) becomes:

$$\begin{aligned} V(R,z) = {} & \frac{12}{z^2}\cdot\frac{1}{R^6}+\frac{135(1+z^2)}{z^4}\cdot\frac{1}{R^8} \\ & +\frac{2520(1+z^4)+2835z^2}{z^6}\cdot\frac{1}{R^{10}} \\ & +\frac{70875(1+z^6)+85050(z^4+z^2)}{z^8}\cdot\frac{1}{R^{12}}+\cdots\cdots. \end{aligned} \tag{24}$$

If we subsitute unity into z, this $V(R, z)$ is clearly reduced to twice the values of the well-known H–H long-range interaction previously obtained by Dalgarno and Lewis.[13)] When we compare Eq. (19) with Eq. (23), the terms of higher-order than R^{-4}, therefore, prove to be mainly due to the dispersion force.

In Fig. 3, we show some $\overline{E}_2$ (Unsöld) curves obtained by the partial summation of the series in Eq. (20), along with Davison's series expansion in Eq. (1). It should be noticed that his expansion may be rather near to our closed form at R values less than 6.0, while at larger R values there appears an underestimating tendency. On the other hand, the series expansion until the R^{-10} or R^{-12} term leads to an overestimation of the interaction energy at R values less than *ca.* 9.0.

In conclusion, it turns out that the closed form obtained above is effective for describing the long-range interaction for the H–H⁻ system. Although the values of the second-order interaction energy predicted here have some ambiguousness because of the arbitrariness of the 'average excitation energy,' the upper and lower bounds obtained are reliable to a considerable extent. The series expansion described here shows that the dispersion force contributes to the nature of the interaction: when R is much larger, the R^{-4} term comes to be dominant, and hence

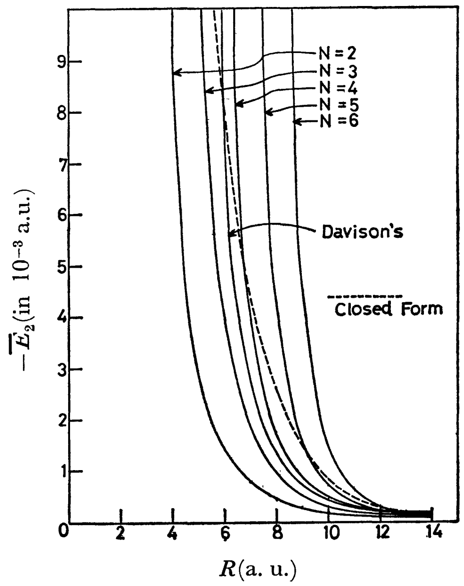

Fig. 3. Various curves of the second-order perturbation energy in the H–H⁻ system obtained by partial summations, $-\overline{E}_2(\text{Unsöld})=\sum_{n=2}^{N}\frac{C_{2n}}{R^{2n}}$ in Eq. (20). The closed form curve corresponds to (B) in Table 1, and Davison's curve is based on the result in Ref. 5.

the induction force begins to prevail over the dispersion. The former extraordinary large magnitude of the dispersion force mainly comes from the quantity of z' in Eq. (7)—namely, the orbital exponent of the outer orbital in H$^-$. In other words, the weakly bound electron plays an important role in the origin of the large dispersion force in the system. Generally speaking, a weakly bound electron, which exists also in such anions as F$^-$ or Cl$^-$, or the electron in frontier orbital with a similar physical nature, will maintain its importance when the system interacts with other distant species.

Appendix

The miscellaneous integrals used in Eq. (12) are shown in the form of $\{F|R,z,z'\}$ in Eq. (15).

$$\{H_1(1)\,|\,R,z,z'\} = \int_{-\infty}^{\infty}\frac{1}{\pi}\exp[-2r_1]\left(\frac{1}{R}-\frac{1}{r_{b1}}\right)\mathrm{d}\tau(1)$$
$$=\left(1+\frac{1}{R}\right)\exp[-2R]. \tag{A-1}$$

$$\{H_1(2)\,|\,R,z,z'\} = \int_{-\infty}^{\infty}\frac{z^3}{\pi}\exp[-2zr_2]\left(\frac{1}{R}-\frac{1}{r_{a2}}\right)\mathrm{d}\tau(2)$$
$$=\left(z+\frac{1}{R}\right)\exp[-2zR]. \tag{A-2}$$

$$\{H_1(1,2)\,|\,R,z,z'\} = \int_{-\infty}^{\infty}\frac{z^3}{\pi^2}\exp[-2(r_1+zr_2)]$$
$$\times\left(\frac{1}{R}+\frac{1}{r_{12}}-\frac{1}{r_{b1}}-\frac{1}{r_{a2}}\right)\mathrm{d}\tau(1)\mathrm{d}\tau(2)$$
$$=\frac{1}{(1-z^2)^3}\exp[-2R]$$
$$\times\left\{(2z^4-3z^2+1)+\frac{1}{R}(-3z^2+1)\right\}$$
$$+\frac{z^3}{(1-z^2)^3}\exp[-2zR]$$
$$\times\left\{(-z^4+3z^2-2)+\frac{z}{R}(-z^2+3)\right\},\quad (z\neq 1)$$
$$\tag{A-3}$$

if $z=1$,

$$\{H_1(1,2)\,|\,R,1,z'\} = \exp[-2R]\left(\frac{1}{R}+\frac{5}{8}-\frac{3R}{4}-\frac{R^2}{6}\right). \tag{A-3'}$$

$$\{H_1^2(1)\,|\,R,z,z'\} = \int_{-\infty}^{\infty}\frac{1}{\pi}\exp[-2r_1]$$
$$\times\left(\frac{1}{R^2}-\frac{2}{r_{b1}R}+\frac{1}{r_{b1}^2}\right)\mathrm{d}\tau(1)$$
$$=-\frac{1}{R^2}+\frac{2}{R}\left(1+\frac{1}{R}\right)\exp[-2R]$$
$$+\left(1+\frac{1}{2R}\right)\exp[-2R]\widetilde{Ei}[2R]$$
$$+\left(1-\frac{1}{2R}\right)\exp[2R]Ei[-2R]. \tag{A-4}$$

$$\{H_1^2(2)\,|\,R,z,z'\} = \int_{-\infty}^{\infty}\frac{z^3}{\pi}\exp[-2zr_2]$$
$$\times\left(\frac{1}{R^2}-\frac{2}{r_{a2}R}+\frac{1}{r_{a2}^2}\right)\mathrm{d}\tau(2)$$
$$=-\frac{1}{R^2}+\frac{2}{R}\left(z+\frac{1}{R}\right)\exp[-2zR]$$
$$+\left(z^2+\frac{z}{2R}\right)\exp[-2zR]\widetilde{Ei}[2zR]$$
$$+\left(z^2-\frac{z}{2R}\right)\exp[2zR]Ei[-2zR]. \tag{A-5}$$

$$\left\{\frac{1}{r_{a2}}W(2,1)\,|\,R,z,z'\right\} = \iint_{-\infty}^{\infty}\frac{z^3}{\pi^2}\exp[-2(r_1+zr_2)]$$
$$\times\left(\frac{1}{r_{a2}^2}-\frac{1}{r_{a2}r_{12}}\right)\mathrm{d}\tau(1)\mathrm{d}\tau(2)$$
$$=\exp[-2zR]\left[-z^2\log\left|\frac{z-1}{z+1}\right|+\frac{z^3}{1-z^2}\right.$$
$$\left.+\frac{1}{R}\left(\frac{-z^2}{(1-z^2)^2}-\frac{z}{2}\log\left|\frac{z-1}{z+1}\right|\right)\right]$$
$$+\frac{z^2}{(1-z^2)^2R}\exp[-2R]$$
$$+\left(z^2+\frac{z}{2R}\right)\exp[-2zR]Ei[-2(1-z)R]$$
$$+\left(z^2-\frac{z}{2R}\right)\exp[2zR]Ei[-2(1+z)R],$$
$$(z\neq 1) \tag{A-6}$$

if $z=1$,

$$\left\{\frac{1}{r_{a2}}W(2,1)\,|\,R,1,z'\right\} = \exp[-2R]$$
$$\times\left[-\frac{3}{4}+\frac{R}{2}+\left(1+\frac{1}{2R}\right)(\gamma+\log 4R)\right]$$
$$+\exp[2R]Ei[-4R]\left(1-\frac{1}{2R}\right), \tag{A-6'}$$

where γ is Euler's constant, 0.5772156649…….

$$\left\{\frac{1}{r_{12}^2}\,|\,R,z,z'\right\} = \iint_{-\infty}^{\infty}\frac{z^3}{\pi^2}\exp[-2(r_1+zr_2)]\frac{1}{r_{12}^2}\mathrm{d}\tau(1)\mathrm{d}\tau(2)$$
$$=\left[\frac{z^4}{(1-z^2)^2}+\frac{z^4(5-z^2)}{2(1-z^2)^3R}\right]\exp[-2R]\widetilde{Ei}[2R]$$
$$+\left[\frac{z^4}{(1-z^2)^2}-\frac{z^4(5-z^2)}{2(1-z^2)^3R}\right]\exp[2R]Ei[-2R]$$
$$+\left[\frac{z^2}{(1-z^2)^2}+\frac{z(1-5z^2)}{2(1-z^2)^3R}\right]\exp[-2zR]\widetilde{Ei}[2zR]$$
$$+\left[\frac{z^2}{(1-z^2)^2}-\frac{z(1-5z^2)}{2(1-z^2)^3R}\right]\exp[2zR]Ei[-2zR],$$
$$(z\neq 1) \tag{A-7}$$

if $z=1$,

$$\left\{\frac{1}{r_{12}^2}\,|\,R,1,z'\right\} = -\frac{7}{12}$$
$$+\left(\frac{5}{16R}+\frac{5}{8}+\frac{R}{2}+\frac{R^2}{6}\right)\exp[-2R]\widetilde{Ei}[2R]$$
$$+\left(-\frac{5}{16R}+\frac{5}{8}-\frac{R}{2}+\frac{R^2}{6}\right)\exp[2R]Ei[-2R]. \tag{A-7'}$$

$$\{H_1(2)H_1(3)\,|\,R,z,z'\} = \iint_{-\infty}^{\infty}\frac{z^3z'^3}{\pi^2}\exp[-2(zr_2+z'r_3)]$$

$$\times\left(\frac{1}{R^2}-\frac{1}{r_{a2}R}-\frac{1}{r_{a3}R}+\frac{1}{r_{a2}r_{a3}}\right)\mathrm{d}\tau(2)\mathrm{d}\tau(3)$$

$$=\left(\frac{1}{R^2}+\frac{z}{R}+\frac{z'}{R}+zz'\right)\exp\left[-2(z+z')R\right]. \qquad \text{(A-8)}$$

$$\{H_1(2)W(1,3)\,|\,R,z,z'\}$$

$$=\{H_1(2)\,|\,R,z,z'\}\{W(1,3)\,|\,R,z,z'\}$$

$$=\frac{1}{(1-z'^2)^2}\left(z+\frac{1}{R}\right)\left[\frac{1}{R}(-1+3z'^2)+(-1+2z'^2)\right]$$
$$\times\exp\left[-2(1+z)R\right]$$
$$+\frac{1}{(1-z'^2)^2}\left(z+\frac{1}{R}\right)\left[z'+\frac{1-3z'^2}{(1-z'^2)R}\right]$$
$$\times\exp\left[-2(z+z')R\right], \quad (z'\neq 1) \qquad \text{(A-9)}$$

if $z'=1$,

$$\{H_1(2)W(1,3)\,|\,R,z,1\}$$

$$=\exp\left[-2(1+z)R\right]\left(z+\frac{1}{R}\right)\left(\frac{R^2}{6}+\frac{3R}{4}+\frac{3}{8}\right). \qquad \text{(A-9}'\text{)}$$

$$\{H_1(3)W(1,2)\,|\,R,z,z'\}$$

$$=\{H_1(3)\,|\,R,z,z'\}\{W(1,2)\,|\,R,z,z'\}$$

$$=\frac{1}{(1-z^2)^2}\left(z'+\frac{1}{R}\right)\left[\frac{1}{R}(-1+3z^2)+(-1+2z^2)\right]$$
$$\times\exp\left[-2(1+z')R\right]$$
$$+\frac{1}{(1-z^2)^2}\left(z'+\frac{1}{R}\right)\left[z+\frac{1-3z^2}{(1-z^2)R}\right]$$
$$\times\exp\left[-2(z+z')R\right], \quad (z\neq 1) \qquad \text{(A-10)}$$

if $z=1$,

$$\{H_1(3)W(1,2)\,|\,R,1,z'\}$$

$$=\exp\left[-2(1+z')R\right]\left(z'+\frac{1}{R}\right)\left(\frac{R^2}{6}+\frac{3R}{4}+\frac{3}{8}\right). \qquad \text{(A-10}'\text{)}$$

$$\{W(1,2)W(1,3)\,|\,R,z,z'\}$$

$$=\iiint_{-\infty}^{\infty}\frac{z^3z'^3}{\pi^3}\exp\left[-2(r_1+zr_2+z'r_3)\right]$$
$$\times\left(\frac{1}{r_{b1}}-\frac{1}{r_{12}}\right)\left(\frac{1}{r_{b1}}-\frac{1}{r_{13}}\right)\mathrm{d}\tau(1)\mathrm{d}\tau(2)\mathrm{d}\tau(3)$$

$$=\exp\left[-2R\right]\Bigg[\left[-\log\left|\frac{z+z'-1}{z+z'+1}\right|\right.$$
$$+\frac{(z+z')\{(z+z')^2+zz'-1\}}{\{1-(z+z')^2\}^2}+\frac{1}{R}\left[-\frac{1}{2}\log\left|\frac{z+z'-1}{z+z'+1}\right|\right.$$
$$\left.\left.+\frac{(z+z')\{(z+z')^4-(z+z')^2+zz'(z+z')^2+zz'\}}{\{1-(z+z')^2\}^3}\right]\right]$$
$$+\exp\left[-2(z+z')R\right]\left[\frac{-zz'}{\{1-(z+z')^2\}^2}\right.$$
$$-\frac{z+z'}{\{1-(z+z')^2\}^3}\{R(z+z')^3-(z+z')^2$$
$$\left.-2(z+z')-2zz'+1\}\right]$$
$$+\exp\left[2R\right]Ei\left[-2(z+z'+1)R\right]\left(1-\frac{1}{2R}\right)$$
$$+\exp\left[-2R\right]Ei\left[-2(z+z'-1)R\right]\left(1+\frac{1}{2R}\right).$$
$$(|z+z'|\neq 1) \qquad \text{(A-11)}$$

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