A Study of the Upper and Lower Bounds of the Second-order Perturbation Energy

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A method of calculation for the upper and lower bounds of the second-order perturbation energy is investigated. The expression for the upper bound is based on Hylleraas's variation perturbation condition and is an improved version of that obtained by Goodisman. The lower bound is based on the Temple-type inequality and is an improved version of that by Prager and Hirschfelder. The result is numerically tested for examples of the polarizability of a hydrogen atom and the coefficients (C_6 and C_8) of the dispersion force between two separated hydrogen atoms, yielding fairly good results. Particularly, the results of the upper bound for C_8 are the best so far calculated in a non-empirical way.

The second-order perturbation energy, E_2, is given by:

$$E_2 = -\sum_{i>0}^{\infty}|H_{1i}|^2/\varepsilon_i, \tag{1}$$

where $H_{1i}=\langle\phi_0^{(i)}|H_1|\phi_0^{(0)}\rangle$ and $\varepsilon_i=E_0^{(i)}-E_0^{(0)}$, in which H_1 is the perturbation, and $\phi_0^{(i)}$ and $E_0^{(i)}$ are the i-th eigenfunction and eigenvalue of the unperturbed Hamiltonian H_0 respectively. In the following, we will denote $\phi_0^{(0)}$ and $E_0^{(i)}$ as ϕ_0 and E_0 respectively, since we will deal with only the ground state in this paper.

Generally it is difficult to calculate the summation of Eq. (1); therefore, many approximate methods have been devised. Among them, the most useful method is Hylleraas's variation condition for the second-order perturbation energy:[1]

$$\langle\tilde{\phi}_1|H_0-E_0|\tilde{\phi}_1\rangle+\langle\tilde{\phi}_1|H_1-E_1|\phi_0\rangle+\langle\phi_0|H_1-E_1|\tilde{\phi}_1\rangle\geqq E_2, \tag{2}$$

in which $\tilde{\phi}_1$ is an arbitrary function corresponding to the first-order perturbation function. One of the effective forms which have been applied for $\tilde{\phi}_1$ is that of Goodisman,[2] who, using Eq. (2), obtained the upper bound of the second-order energy for the case in which first n excited states of unperturbed system are known. On the other hand, neglecting energies of a higher order than the second-order, Prager and Hirschfelder[3] found the lower bound of the second-order energy based on the Temple principle:[4]

$$\langle(H-E^{(0)})\tilde{\Psi}|(H-E^{(1)})\tilde{\Psi}\rangle\geqq 0, \tag{3}$$

where $E^{(i)}$ is the i-th eigenvalue associated with i-th eigenfunction, $\Psi^{(i)}$, of the total Hamiltonian, $H=H_0+H_1$, and where $\tilde{\Psi}$ is a variational function for $\Psi^{(0)}$, which may be divided into $\phi_0+\tilde{\phi}_1$.

Other theories estimating the upper and lower bounds were developed by Lindner and Löwdin[5] and subsequently by Miller.[6] They utilized operator techniques in the direction of using a finite arbitrary basis set for $\tilde{\phi}_1$. Especially Miller extended the theory of Lindner and Löwdin, who treated only the second-order energy in the ground state, to a theory which can be adopted to the second-order energy in the arbitrary excited state.

It seems, however, that the form of $\tilde{\phi}_1$ used by Goodisman is rather tractable for performing the calculation. Therefore, in the present paper, we will try to improve both the upper bound of Goodisman and the lower bound of Prager and Hirschfelder by the use of a form of $\tilde{\phi}_1$ similar to that of Goodisman.

Derivation of the Upper Bound

Let us consider the following first-order variational function:

$$\tilde{\phi}_1(n,\lambda,\{\mu_i|i\geqq n+1\}) = -\sum_{i>0}^{n}H_{1i}\phi_0^{(i)}/\varepsilon_i+\lambda\sum_{i=n+1}^{\infty}\mu_iH_{1i}\phi_0^{(i)}, \tag{4}$$

where λ and each μ_i are arbitrary real parameters. Substituting this function into Hylleraas's condition in Eq. (2), one obtains:

$$E_2^{\mathrm{up}}(n,\lambda,\{\mu_i|i\geqq n+1\}) = (\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i)\lambda^2 + 2(\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2)\lambda+A_n, \tag{5}$$

where:

$$A_n = -\sum_{i>0}^{\infty}|H_{1i}|^2/\varepsilon_i. \tag{6}$$

$E_2^{\mathrm{up}}(n,\lambda,\{\mu_i|i\geqq n+1\})$ in Eq. (5) is a quadratic formula with regard to λ and takes the minimum value:

$$E_2^{\mathrm{up}}(n,\{\mu_i|i\geqq n+1\}) = A_n-(\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2)^2/(\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i), \tag{7}$$

when λ is:

$$\lambda = -(\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2)/(\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i). \tag{8}$$

After modifying μ_i into some more convenient form, as will be shown below, we can further optimize $E_2^{\mathrm{up}}(n,\{\mu_i|i\geqq n+1\})$ with respect to $\{\mu_i\}$ for each n to get the desired upper bound, $E_2^{\mathrm{up}}(n)$. If the simplest form of μ_i is chosen, *i.e.*, $\mu_i=1$ for any i, the result is just that obtained by Goodisman.

It can easily be proved that the upper bound thus obtained really satisfies the relation that $E_2^{\mathrm{up}}(n-1)\geqq E_2^{\mathrm{up}}(n)$. In order to prove this, let us calculate the following subtraction between $E_2^{\mathrm{up}}(n,\{\mu_i|i\geqq n+1\})$ and $E_2^{\mathrm{up}}(n-1,\{\mu_i|i\geqq n\})$ of Eq. (7), keeping $\{\mu_i\}$ in common for both:

$$E_2^{\mathrm{up}}(n,\{\mu_i|i\geqq n+1\})-E_2^{\mathrm{up}}(n-1,\{\mu_i|i\geqq n\}) = -|H_{1n}|^2/\varepsilon_n-(\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2)^2/(\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i) + (\sum_{i=n}^{\infty}\mu_i|H_{1i}|^2)^2/(\sum_{i=n}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i). \tag{9}$$

The right-hand side in Eq. (9) becomes:

$$-|H_{1n}|^2\{\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2(\mu_i\varepsilon_i-\mu_n\varepsilon_n)\}^2/$$
$$\{\varepsilon_n(\sum_{i=n}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i)(\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i)\}\leqq 0,$$

and is always nonpositive, since all of ε_i values are nonnegative. Consequently, when n becomes infinite, $E_2^{\mathrm{up}}(n,\{\mu_i|i\geqq n+1\})$; hence, $E_2^{\mathrm{up}}(n)$ also approaches to E_2 in Eq. (1) from the upper side.

Next, we set the modified form of μ_i as $\mu_i=1+\mu E_0^{(i)}/E_0$ to get the optimal value, $E_2^{\mathrm{up}}(n)$.[7] Substituting this μ_i into Eq. (7) and optimizing with respect to μ, one gets:

$$\begin{aligned}E_2^{\mathrm{up}}(n) &= A_n-\{\langle\psi_0|H_1^2|\psi_0\rangle+(\mu_{\mathrm{opt}}/E_0)\langle\psi_0|H_1H_0H_1|\psi_0\rangle\\ &\quad-\sum_{i>0}^{n}(1+\mu_{\mathrm{opt}}E_0^{(i)}/E_0)|H_{1i}|^2\}^2/\{\langle\psi_0|H_1(H_0-E_0)H_1|\psi_0\rangle\\ &\quad+(2\mu_{\mathrm{opt}}/E_0)\langle\psi_0|H_1H_0(H_0-E_0)H_1|\varphi_0\rangle\\ &\quad+(\mu_{\mathrm{opt}}^2/E_0^2)\langle\psi_0|H_1H_0(H_0-E_0)H_0H_1|\psi_0\rangle\\ &\quad-\sum_{i>0}^{n}(1+\mu_{\mathrm{opt}}E_0^{(i)}/E_0)^2|H_{1i}|^2\varepsilon_i\},\end{aligned}\tag{10}$$

where:

$$\begin{aligned}\mu_{\mathrm{opt}} &= [-(a^2e-b^2c)-\{(a^2e-b^2c)^2\\ &\quad-(a^2d-2abc)(2abe-b^2d)\}^{1/2}]/(a^2d-2abc)\\ &= (bd-2ae)/(ad-2bc),\end{aligned}\tag{11}*$$

and where:

$$\left.\begin{aligned}a &= \langle\psi_0|H_1H_0H_1|\psi_0\rangle/E_0-\sum_{i=0}^{n}(E_0^{(i)}/E_0)|H_{1i}|^2,\\ b &= \langle\psi_0|H_1^2|\psi_0\rangle-\sum_{i=0}^{n}|H_{1i}|^2,\\ c &= \langle\psi_0|H_1H_0(H_0-E_0)H_0H_1|\psi_0\rangle/E_0^2\\ &\quad-\sum_{i>0}^{n}(E_0^{(i)}/E_0)^2|H_{1i}|^2\varepsilon_i,\\ d &= 2\{\langle\psi_0|H_1H_0(H_0-E_0)H_1|\psi_0\rangle/E_0\\ &\quad-\sum_{i>0}^{n}(E_0^{(i)}/E_0)|H_{1i}|^2\varepsilon_i.\end{aligned}\right\}\tag{11'}$$

and:

$$e=\langle\psi_0|H_1(H_0-E_0)H_1|\psi_0\rangle-\sum_{i>0}^{n}|H_{1i}|^2\varepsilon_i.$$

Derivation of the Lower Bound

If the variational function $\tilde{\Psi}$, which is divided into $\phi_0+\tilde{\phi}_1$, as has previously been mentioned, is orthogonal to the first several excited eigenfunctions of the total Hamiltonian, *i.e.*:

$$\langle\tilde{\Psi}|\Psi^{(k)}\rangle=0\quad(k=1,2,\cdots,n),\tag{12}$$

the following Temple-type inequality:

$$\langle(H-E^{(0)})\tilde{\Psi}|(H-E^{(n+1)})\tilde{\Psi}\rangle\geqq 0,\tag{13}$$

is easily established and can be utilized as the base to get the lower bound. Here we try to employ the same form as in Eq. (4) for $\tilde{\phi}_1$; namely, $\tilde{\Psi}$ is:

$$\tilde{\Psi}=\phi_0+\tilde{\phi}_1=\phi_0-\sum_{i>0}^{n}H_{1i}\phi_0^{(i)}/\varepsilon_i+\lambda\sum_{i=n+1}^{\infty}\mu_iH_{1i}\phi_0^{(i)},\tag{14}$$

which satisfies Eq. (12) as far as the second-order energy is considered.[8] Substituting this $\tilde{\Psi}$ into Eq. (13) and neglecting the energies of a higher order than the second-order one, we obtain a lower bound for the second-order energy:

$$\begin{aligned}E_2 &\geqq \{\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i(1-\varepsilon_i/\varepsilon_{n+1})\}\lambda^2\\ &\quad+2\{\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2(1-\varepsilon_i/\varepsilon_{n+1})\}\lambda\\ &\quad+\{A_n-\sum_{i=n+1}^{\infty}|H_{1i}|^2/\varepsilon_{n+1}\}\\ &\equiv E_2^{\mathrm{low}}(n,\lambda,\{\mu_i|i\geqq n+1\}),\end{aligned}\tag{15}$$

which takes the maximum value:

$$\begin{aligned}E_2^{\mathrm{low}}(n,\{\mu_i|i\geqq n+1\}) &= -\{\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2(1-\varepsilon_i/\varepsilon_{n+1})\}^2/\\ &\{\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i(1-\varepsilon_i/\varepsilon_{n+1})\}+\{A_n-\sum_{i=n+1}^{\infty}|H_{1i}|^2/\varepsilon_{n+1}\},\end{aligned}\tag{16}$$

when:

$$\begin{aligned}\lambda &= -\{\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2(1-\varepsilon_i/\varepsilon_{n+1})\}/\\ &\{\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i(1-\varepsilon_i/\varepsilon_{n+1})\}.\end{aligned}\tag{17}$$

$E_2^{\mathrm{low}}(n,\{\mu_i|i\geqq n+1\})$ can be further optimized with regard to $\{\mu_i\}$ to obtain $E_2^{\mathrm{low}}(n)$ much as in the previous section. If $n=0$ and $\mu_i=1$, the result coincides with that obtained by Prager and Hirschfelder.

Furthermore, the relation that $E_2^{\mathrm{low}}(n)\geqq E_2^{\mathrm{low}}(n-1)$ can be proved by calculating the following subtraction with the use of Eq. (15), keeping λ and $\{\mu_i\}$ in common for both $E_2^{\mathrm{low}}(n,\lambda,\{\mu_i|i\geqq n+1\})$ and $E_2^{\mathrm{low}}(n-1,\lambda,\{\mu_i|i\geqq n\})$:

$$\begin{aligned}&E_2^{\mathrm{low}}(n,\lambda,\{\mu_i|i\geqq n+1\})-E_2^{\mathrm{low}}(n-1,\lambda,\{\mu_i|i\geqq n\})\\ &\quad=\{(\varepsilon_{n+1}-\varepsilon_n)\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i^2/\varepsilon_n\varepsilon_{n+1}\}\lambda^2\\ &\qquad+2\{(\varepsilon_{n+1}-\varepsilon_n)\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2\varepsilon_i/\varepsilon_n\varepsilon_{n+1}\}\lambda\\ &\qquad+\{(\varepsilon_{n+1}-\varepsilon_n)\sum_{i=n+1}^{\infty}|H_{1i}|^2/\varepsilon_n\varepsilon_{n+1}\}.\end{aligned}\tag{18}$$

Equation (18) is a quadratic formula of λ and is always positive, since the coefficient of λ^2 is positive and since the discriminant of Eq. (18):

$$\begin{aligned}D &= (\varepsilon_{n+1}-\varepsilon_n)^2\{(\sum_{i=n+1}^{\infty}\mu_i|H_{1i}|^2\varepsilon_i)^2\\ &\quad-(\sum_{i=n+1}^{\infty}\mu_i^2|H_{1i}|^2\varepsilon_i^2)(\sum_{i=n+1}^{\infty}|H_{1i}|^2)\}/(\varepsilon_{n+1}^2\varepsilon_n^2),\end{aligned}$$

is always negative, which is ensured by the Schwartz inequality. Therefore, when n becomes infinite, $E_2^{\mathrm{low}}(n,\lambda,\{\mu_i|i\geqq n+1\})$; hence, $E_2^{\mathrm{low}}(n)$ also approaches to the true E_2 value from the lower side.

As a special case, by substituting $\mu_i=1$[7] into Eq. (16) one gets the lower bound, $E_2^{\mathrm{low}}(n)$:

$$\begin{aligned}E_2^{\mathrm{low}}(n) &= -\{\sum_{i=n+1}^{\infty}|H_{1i}|^2(1-\varepsilon_i/\varepsilon_{n+1})\}^2/\\ &\{\sum_{i=n+1}^{\infty}|H_{1i}|^2\varepsilon_i(1-\varepsilon_i/\varepsilon_{n+1})\}+\{A_n-\sum_{i=n+1}^{\infty}|H_{1i}|^2/\varepsilon_{n+1}\},\end{aligned}\tag{19}$$

which can then be rewritten by using the a, b, d, and e defined in the previous section:

$$\begin{aligned}E_2^{\mathrm{low}}(n) &= -[b-(a-b)E_0/\varepsilon_{n+1}]^2/\\ &\quad[(a-b)E_0-(d/2-2e+aE_0-bE_0)E_0/\varepsilon_{n+1}]\\ &\quad+(A_n-b/\varepsilon_{n+1}).\end{aligned}\tag{20}$$

* We are indebted to the referee for the final result of Eq. (11).

Results and Discussion

Polarizability of a Hydrogen Atom in the Ground State. The value of the polarizability, α, is twice the absolute value of E_2 caused by the perturbation, H_1, which, in this case, is z (in a.u.), the coordinate of the direction of the electric field (we will always use the atomic unit hereafter). Then,

$$\alpha = -2E_2 = 2\sum_{i>0}^{\infty}|\langle\psi_0^{(i)}|z|\psi_0\rangle|^2/(E_0^{(i)}-E_0). \quad (21)$$

In order to examine the usefulness of the present theory for the upper and lower bounds, we must calculate Eqs. (10), (11), and (20). In the calculation, the following values of integrals are required:

$$\left.\begin{aligned}&\langle\psi_0|z|\psi_0\rangle = 0,\\ &\langle\psi_0|z^2|\psi_0\rangle = 1,\\ &\langle\psi_0|zH_0z|\psi_0\rangle = 0,\\ &\langle\psi_0|zH_0^2z|\psi_0\rangle = 1/12,\\ &\text{and}\\ &\langle\psi_0|zH_0^3z|\psi_0\rangle = 5/12,\end{aligned}\right\} \quad (22)$$

in which ψ_0 is the 1s-function of a hydrogen atom and in which E_0 is $-1/2$.

In Table 1, the results for $n=0$, 1, 2, 3, and 4 are shown. The values of λ and μ are also shown, since they are the parameters corresponding to $1/E_0$ and $E_0/(E_0-E_0^{(i)})$ respectively.[7] Compared with the results of the lower bounds of α reported by Goodisman ($\mu_i=1$), the present lower bounds are fairly well improved because of the existence of the μ_i parameter; the upper bounds are also better than that reported by Prager and Hirschfelder. For both the upper and lower bounds, the improvement from $n=0$ to $n=1$ is meaningful, but for $n\geqq 2$ the improvement does not seem to be substantial.

The Dispersion Force between Two Hydrogen Atoms. When the internuclear distance, R, between two hydrogen atoms in the ground state is large enough, the overlap and, hence, the exchange are insignificant; we can take $\psi_0=\psi_A(1)\psi_B(2)$ as the unperturbed wavefunction for this system, where $\psi_A(1)$ and $\psi_B(2)$ are the isolated atomic wavefunctions of the two hydrogen atoms. Besides, the perturbation, H_1, in usual notations:[9]

$$H_1 = -1/r_{B1} - 1/r_{A2} + 1/R + 1/r_{12}, \quad (23)$$

can be expanded in an inverse power series of R, and the second-order energy is generally represented by:

$$-E_2 = C_6/R^6 + C_8/R^8 + \cdots, \quad (24)$$

where:

$$C_6 = \sum_{i>0}^{\infty}|\langle\psi_0^{(i)}|H_{dd}|\psi_0\rangle|^2/(E_0^{(i)}-E_0),$$
$$H_{dd} = x_1x_2 + y_1y_2 - 2z_1z_2, \quad (25)$$

and

$$C_8 = \sum_{i>0}^{\infty}|\langle\psi_0^{(i)}|H_{qd}|\psi_0\rangle|^2/(E_0^{(i)}-E_0),$$
$$H_{qd} = (3/2)\{r_1^2z_2 - r_2^2z_1 + (2x_1x_2+2y_1y_2-3z_1z_2)(z_1-z_2)\}. \quad (26)$$

In the calculation of the bounds for C_6, we need various kinds of integrals, which are evaluated as follows:

$$\left.\begin{aligned}&\langle\psi_0|H_{dd}|\psi_0\rangle = 0,\\ &\langle\psi_0|H_{dd}^2|\psi_0\rangle = 6,\\ &\langle\psi_0|H_{dd}H_0H_{dd}|\psi_0\rangle = 0,\\ &\langle\psi_0|H_{dd}H_0^2H_{dd}|\psi_0\rangle = 1,\\ &\text{and}\\ &\langle\psi_0|H_{dd}H_0^3H_{dd}|\psi_0\rangle = 5.\end{aligned}\right\} \quad (27)$$

In Table 2, the results for C_6 using $n=0$, 1, 2, 3, 4, 5, 6, and 7 are shown. As in the case of polarizability, the improvement from $n=0$ to $n=1$ is remarkable, but for $n\geqq 2$ the effect is not so large.

When calculating the bounds for C_8, the following integrals are required:

$$\left.\begin{aligned}&\langle\psi_0|H_{qd}|\psi_0\rangle = 0,\\ &\langle\psi_0|H_{qd}^2|\psi_0\rangle = 135,\\ &\langle\psi_0|H_{qd}H_0H_{qd}|\psi_0\rangle = 45/2,\\ &\langle\psi_0|H_{qd}H_0^2H_{qd}|\psi_0\rangle = 207/8,\\ &\text{and}\\ &\langle\psi_0|H_{qd}H_0^3H_{qd}|\psi_0\rangle = 12501/160.\end{aligned}\right\} \quad (28)$$

In Table 3, the results for C_8 are presented in the case of $n=0$ and 1. It can also be seen that the improvement of the lower bound is remarkable when variable parameters, μ_i, are used in comparison with that obtained by using a constant $\mu_i=1(\mu=0)$; moreover, the improvement for both bounds from $n=0$ to $n=1$ is appreciable. The present result for the upper bound for C_8 is the best so far calculated in a non-empirical way.

From the above numerical results, it is clear that the present treatment is very tractable because of the convenient form of the variational function used. Although the numerical results are rather inferior to those in Refs. 5 and 10, the average of the both bounds for each n gives good approximations to the exact values as may be seen in Tables 1, 2, and 3. Hence, the

TABLE 1. THE UPPER AND LOWER BOUNDS FOR POLARIZABILITY OF A HYDROGEN ATOM IN THE GROUND STATE (Exact=4.5)

n	$\alpha^{low}(n)=-2E_2^{up}(n)$ a)	λ	μ	$\alpha^{low}(n)$ b) ($\mu_i=1$)	$\alpha^{up}(n)=-2E_2^{low}(n)$ a)	λ	$\{\alpha^{low}(n)+\alpha^{up}(n)\}/2$
0	4.125	−2.063	0.09091	4.0000	4.762*	−0.8571	4.444
1	4.363	−1.611	0.07286	4.3162	4.646	−0.7495	4.505
2	4.391	−1.499	0.06644	4.3636	4.623	−0.7156	4.507
3	4.415	−1.457	0.06638	4.3800	4.612	−0.7007	4.514
4	4.420	−1.435	0.06525	—	4.607	−0.6929	4.514

a) Present work (*; Ref. 3). b) Ref. 2.

Table 2. The upper and lower bounds for dispersion force constant C_6 between two hydrogen atoms in the ground state (Reliable value=6.4990267[c])

n	$C_6^{low}(n)=-E_2^{up}(n)$ [a]	λ	μ	$C_6^{low}(n)$ [b] ($\mu_i=1$)	$C_6^{up}(n)=-E_2^{low}(n)$ [a]	λ	$\{C_6^{low}(n)+C_6^{up}(n)\}/2$
0	6.171	−1.029	0.1667	6.000	6.800	−0.6000	6.486
1	6.302	−0.9393	0.1445	6.201	6.709	−0.5560	6.506
2	6.339	−0.9049	0.1365	6.256	6.684	−0.5412	6.512
3	6.345	−0.8917	0.1335	6.269	6.674	−0.5345	6.510
4	6.357	−0.8853	0.1321	6.284	6.668	−0.5310	6.513
5	6.360	−0.8817	0.1313	6.289	6.665	−0.5288	6.513
6	6.362	−0.8794	0.1308	—	6.663	−0.5274	6.513
7	6.364	−0.8779	0.1304	—	6.662	−0.5264	6.513

a) Present work. b) Ref. 2. The values are recalculated by us. c) Ref. 5.

Table 3. The upper and lower bounds for dispersion force constant C_8 between two hydrogen atoms in the ground state (Reliable value=124.3991[c])

n	$C_8^{low}(n)=-E_2^{up}(n)$ [a]	λ	μ	$C_8^{low}(n)$ [b] ($\mu_1=1$)	$C_8^{up}(n)=-E_2^{low}(n)$ [a]	λ	$\{C_8^{low}(n)+C_8^{up}(n)\}/2$
0	119.749	−0.9225	0.2306	115.714	129.837	−0.6103	124.793
1	120.035	−0.9136	0.2262	—	127.368	−0.5552	123.702

a) Present work. b) The value obtained by us. c) Ref. 10.

present treatment may be expected to be effective for larger molecular systems.

Appendix A

In deriving the upper bounds, we considered the following form of $\tilde{\phi}_1$:

$$\tilde{\phi}_1(n,\lambda,\mu) = -\sum_{i>0}^{n}(H_{1i}/\varepsilon_i)\phi_0^{(i)} + \lambda\sum_{i=n+1}^{\infty}(1+\mu E_0^{(i)}/E_0)H_{1i}\phi_0^{(i)}. \quad \text{(A-1)}$$

Now, let us refer to the first-order function derived by Lennard-Jones in order to compare it with the $\tilde{\phi}_1$ of Eq. (A-1). The function derived by Lennard-Jones is:[11]

$$\phi_1 = (H_1-E_1)\phi_0/E_0 + \sum_{i>0}^{\infty}E_0^{(i)}H_{1i}\phi_0^{(i)}/\{E_0(E_0-E_0^{(i)})\}, \quad \text{(A-2)}$$

which is reduced to:

$$\phi_1 = -\sum_{i>0}^{n}(H_{1i}/\varepsilon_i)\phi_0^{(i)} + (1/E_0)\sum_{i=n+1}^{\infty}\{1+E_0^{(i)}/(E_0-E_0^{(i)})\}H_{1i}\phi_0^{(i)}. \quad \text{(A-3)}$$

When we compare Eq. (A-1) with Eq. (A-3), it may be seen that λ and μ are taken to correspond to $1/E_0$ and the average of $E_0/(E_0-E_0^{(i)})$ respectively. If we also choose $\mu_i=1+\mu E_0^{(i)}/E_0$ for the derivation of lower bounds, there appears an integral such as $\langle\phi_0|zH_0^4z|\phi_0\rangle$ which diverges. Hence, the simplest form, $\mu_i=1$, is adopted for any i.

Appendix B

The inequality in Eq. (13) can be established not for a completely arbitrary function, but for a restricted one, under the conditions of Eq. (12). Since our variational function satisfies Eq. (12) only approximately, there remains the necessity of estimating the resulting error.

Using an arbitrary $\tilde{\Phi}$ function, Θ, which strictly satisfies the next relation:

$$\langle\Theta|\Psi^{(k)}\rangle = 0 \quad (k=1,2,\cdots,n), \quad \text{(B-1)}$$

may be rewritten as follows:

$$\Theta = \tilde{\Phi} - \sum_{i>0}^{n}\langle\Psi^{(i)}|\tilde{\Phi}\rangle\Psi^{(i)}. \quad \text{(B-2)}$$

Then, instead of Eq. (13), the inequality;

$$\langle(H-E^{(0)})\tilde{\Phi}|(H-E^{(n+1)})\tilde{\Phi}\rangle \geqq \sum_{i>0}^{n}|\langle\Psi^{(i)}|\tilde{\Phi}\rangle|^2(E^{(i)}-E^{(0)})(E^{(i)}-E^{(n+1)}), \quad \text{(B-3)}$$

may easily be obtained. Setting the exact $\Psi^{(i)}$ as:

$$\Psi^{(i)} = \phi_0^{(i)} + \phi_1^{(i)} + \cdots = \phi_0^{(i)} + \sum_{j\neq i}^{\infty}\{\langle\phi_0^{(j)}|H_1|\phi_0^{(i)}\rangle/(E_0^{(i)}-E_0^{(j)})\}\phi_0^{(j)} + \cdots, \quad \text{(B-4)}$$

ans setting $\tilde{\Phi}$ as $\tilde{\Psi}$ in Eq. (14), we obtain:

$$\langle\tilde{\Phi}|\tilde{\Psi}^{(k)}\rangle = \langle\tilde{\Psi}|\Psi^{(k)}\rangle = \langle\phi_0|\phi_0^{(k)}\rangle + \langle\phi_0|\phi_1^{(k)}\rangle + \langle\tilde{\phi}_1|\phi_0^{(k)}\rangle + \langle\tilde{\phi}_1|\phi_1^{(k)}\rangle + \cdots \quad (k=1,2,\cdots,n). \quad \text{(B-5)}$$

It can be easily seen that the first term on the right-hand side of Eq. (B-5) vanishes, and that the second and the third terms cancel each other out when we use the form of $\tilde{\phi}_1$ in Eq. (14) and that of $\phi_1^{(i)}$ in Eq. (B-4). As a result, the first non-vanishing term in Eq. (B-5) is of the second-order of the perturbation. Therefore, the value of the right-hand side of Eq. (B-3) is of the fourth-order of the perturbation and can be neglected as long as we consider the second-order energy.

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