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Variational Calculation of Atoms and Molecules by a Modified Hassé Method Using Hulthén Functions. I. Hydrogen and Helium Atoms

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A modification of the Hassé method is presented in an attempt to describe perturbed systems. This method resolves divergence difficulties which are often encountered when the simple Kirkwood-Hassé method or Unsöld approximation is used for the coulombic perturbation problems. The procedure is illustrated for the perturbed hydrogen atom; energy values which are close to the exact ones are thus obtained. The method is also applied to the case of the ground-state helium atom; a closed-form expression of the energy is thus derived. The optimized value is -2.8983 a. u. Some other discussions are given in connection with the perturbation theory.

In the perturbation problems of atoms and molecules, the Unsöld approximation[1] is often employed to calculate the second-order perturbation energy; it is known to be equivalent to the so-called average-energy method,[2] where the operator (H_0-E_0) in the first-order perturbation equation is replaced by an average energy, ε. The approximate first-order wave function, ϕ_1, then becomes:

$$\phi_1 = -\varepsilon^{-1}(H_1 - E_1)\phi_0, \tag{1a}$$

where ϕ_0 is the unperturbed eigenfunction and where H_1 and E_1 are the perturbation and the first-order perturbation energy respectively. This wave function is also employed for the first-order wave function in the variation-perturbation method (VP method). In this case, ε^{-1} is regarded as a scale parameter; Eq. (1a) is, then, usually rewritten in the following form:

$$\phi_1 = A(H_1 - E_1)\phi_0, \tag{1b}$$

where A is a constant. In the variation method, the simple Kirkwood-Hassé form[3] is often used for the perturbative part, χ, of a trial function, $\phi=\phi_0+\chi$:

$$\chi = AH_1\phi_0, \tag{1c}$$

which is not generally orthogonal to ϕ_0. The orthogonalized form corresponds to Eq. (1b).

It has been pointed out by several authors[2,4], however, that these approximations often lead to physically unacceptable wave-functions and, accordingly, unreasonable results for the perturbation energies. For example, consider an atomic hydrogen perturbed by the removal of a small amount (ΔZ) of the nuclear charge. In this case, $H_1=\Delta Z/r$, where r is the distance from the nucleus to the electron. In accordance with the approximation (Eq. (1a)), ϕ_1 is singular at $r=0$; hence, the second- or the third-order perturbation energy will be infinite. Such a result can be essentially attributed to the divergency of the integrals, $\langle\phi_0|r^{-3}|\phi_0\rangle$ and $\langle\phi_0|r^{-4}|\phi_0\rangle$, involved in the energy calculations. Many other examples were given by Kirtman and Benston.[2] They applied the average-energy method to some of these examples and showed that such difficulties could be successfully avoided by making the average-energy infinite only in the neighborhood of singularity and finite elsewhere (the eae method). This method is, however, difficult to use for multidimensional problems, in particular, molecular problems.

The purpose of the present paper is to show that difficulties of divergence can be removed, easily and elegantly, not by the variation of the average energy, but by a slight modification of H_1 in Eq. (1c). In this work, we will use the variation method for energy calculations; this approximation may correspond to an extension of the simple Kirkwood-Hassé form. It will be demonstrated in the first section of this paper that the energy obtained is, besides being an upper bound, in agreement with the results of the extension of the perturbation theory to the third order. The present method is illustrated by this example and then applied to the calculation of the ground-state energy of the helium atom.

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[1] A. Unsöld, *Z. Phys.* **43**, 563 (1927).

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

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

[4] J. O. Hirschfelder, W. B. Brown and S. T. Epstein, *Advan. Quantum Chem.*, **1**, 280 (1964).

The Variation Method

Assume that a system with a Hamiltonian operator, H_0, is given, and that the function, ψ_0, describing its state and its energy, E_0, in the state are known; then:

$$H_0\psi_0 = E_0\psi_0. \tag{2}$$

When a perturbation is applied to H_0, changing it to H_0+H_1, the energy, E, of this perturbed system, H, is optimized by the variational principle:

$$\langle H\rangle = N^2\int \psi^* H\psi \mathrm{d}\tau \geqq E, \tag{3}$$

where ψ is an arbitrary trial function and where;

$$N = \left[\int \psi^*\psi \mathrm{d}\tau\right]^{-1/2}.$$

In Hassé's method, one may take the following type of function:

$$\psi = \psi_0(1+v), \tag{4}$$

where v is a function to be specified later. As a consequence, Eq. (3) can be rewritten[5] in atomic units:

$$\langle H\rangle = E_0 + N^2\left\{((1+v)^2H_1)_{00} + \frac{1}{2}\sum_i ((\partial v/\partial x_i)^2)_{00}\right\}, \tag{5}$$

where $(\mathrm{F})_{00}$ signifies $\langle\psi_0|F|\psi_0\rangle$; that is, the matrix elements calculated with the ψ_0 function, and where the summation extends over all the Cartesian coordinates of the problem.

Now we need a concrete form of v to calculate the energy of the perturbed system. The simplest and useful form of v is the one proportional to H_1, namely, the simple Kirkwood-Hassé form, Eq. (1c):

$$v = AH_1. \tag{6}$$

As has been pointed out in the introduction,[2,4] however, when one uses this approximation one encounters serious defects in many cases, particularly in the important case of the coulombic-type perturbation problem which we will discuss in this paper. In other words, these defects can be ascribed to the fact that the integrals in Eq. (5) diverge because of the singularities at $r=0$ (except, of course, if ψ_0 vanishes at the nuclei). To remove the difficulties, we replaced the coulomb potential in v by the following function, $\tilde{H}_1$:

$$v = A\tilde{H}_1 = A\{\Delta Z\sum_a\sum_i (1-e^{-\kappa_i R_{ai}})R_{ai}{}^{-1} + \frac{1}{2}\sum_{\substack{i\\(i\neq j)}}\sum_j (1-\mathrm{e}^{-\lambda_{ij}r_{ij}})r_{ij}{}^{-1}\}, \tag{7}$$

where:

ΔZ : the decrease in the nuclear charge,
a : the number of a nucleus,
i, j : the number of an electron,
κ_i, λ_{ij} : variational parameters,
R_{ai}, r_{ij} : the distances between a nucleus, a, and an electron, i, and between the i and j electrons respectively.

The function $\tilde{H}_1$ is the one known as the Hulthén function.[6] When κ and λ are positive, this function behaves like the original coulomb potential at larger distances, but it is finite as r approaches zero. In this case, the main factor underlying the correctness of Eq. (7) is that the v function is finite at $r=0$, which causes even $\langle\psi|r^{-4}|\psi\rangle$ to become finite. This is the essential point of the present method for solving this divergence problem.

The perturbed wave function that we have presented may not be considerably different from the one using the Unsöld approximation or, more generally, the Dirichlet form in the VP method. In order to investigate the relation between our method and the VP method, we will write Eq. (5) with the present $v=A\tilde{H}_1$. The perturbed wave function, ψ, is, then obtained from Eq. (4) as:

$$\psi = \psi_0(1+A\tilde{H}_1). \tag{8}$$

Hence, from Eq. (5):

$$\langle H\rangle = E_0 + E_1 + \frac{2\mathrm{A}\{(H_1\tilde{H}_1)_{00} - E_1(\tilde{H}_1)_{00}\} + A^2\left\{\frac{1}{2}\sum_i ((\partial\tilde{H}_1/\partial x_i)^2)_{00} + (\tilde{H}_1H_1\tilde{H}_1)_{00} - E_1(\tilde{H}_1{}^2)_{00}\right\}}{1 + 2A(\tilde{H}_1)_{00} + A^2(\tilde{H}_1{}^2)_{00}} \geqq E, \tag{9}$$

where $E_1=(H_1)_{00}$. On the other hand, following the VP theory,

$$\tilde{E}_2 = \langle\tilde{\psi}_1|H_0 - E_0|\tilde{\psi}_1\rangle + 2\langle\tilde{\psi}_1|H_1 - E_1|\psi_0\rangle \geqq E_2, \tag{10}$$

where E_2 is the second-order perturbation energy and where $\tilde{\psi}_1$ is an arbitrary function; the equality in Eq. (10) holds only when the variation function, $\tilde{\psi}_1$, is the true first-order wave function. Regarding $A\tilde{H}_1\psi_0$ as $\tilde{\psi}_1$, the approximate second and third-order energies are, respectively:

$$\tilde{E}_2 = 2A\{(H_1\tilde{H}_1)_{00} - E_1(\tilde{H}_1)_{00}\} + \frac{1}{2}A^2\sum_i ((\partial\tilde{H}_1/\partial x_i)^2)_{00} \geqq E_2, \tag{11}$$

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5) H. Margenau, *Rev. Mod. Phys.*, **11**, 1 (1939).

6) L. Hulthén, *Arkiv Fys.*, **28A**, 5 (1942).

$$\tilde{E}_3 = -2A\tilde{E}_2(\tilde{H}_1)_{00} + A^2\{(\tilde{H}_1H_1\tilde{H}_1)_{00} - E_1(\tilde{H}_1{}^2)_{00}\}. \tag{12}$$[7]

Then, one obtains from Eq. (9):

$$\langle H\rangle = E_0 + E_1 + \tilde{E}_2 + \tilde{E}_3 + E_{\mathrm{R}} \geqq E, \tag{13}$$

where:

$$E_{\mathrm{R}} = -\frac{\{2A(\tilde{H}_1)_{00} + A^2(\tilde{H}_1{}^2)_{00}\}\tilde{E}_3 + A^2(\tilde{H}_1{}^2)_{00}\tilde{E}_2}{1 + 2A(\tilde{H}_1)_{00} + A^2(\tilde{H}_1{}^2)_{00}} = \mathrm{O}(H_1{}^4). \tag{14}$$

The above results show that the present method is in agreement with the perturbation theory to the third order. More general investigations have been presented by Sinanoğlu.[8]

Finally, it is necessary to consider the effect of the orthogonalization. Corresponding to Eq. (1b) the orthogonalized form is given by:

$$\tilde{\phi} = \phi_0 + \tilde{\chi} \quad \text{and} \quad \tilde{\chi} = A(\tilde{H}_1 - (\tilde{H}_1)_{00})\phi_0,$$

which leads to a slight correction of the energy, $\varDelta E_{\mathrm{corr.}}$:

$$\varDelta E_{\mathrm{corr.}} = \bar{E} - \tilde{E} = \frac{-2A(H_1)_{00}\{\bar{E} - E_0 - E_1 - A(E_0(\tilde{H}_1)_{00} + (H_1\tilde{H}_1)_{00})\} - A^2(\tilde{H}_1)_{00}{}^2(\bar{E} + E_0 + E_1)}{N^{-2} - 2A(\tilde{H}_1)_{00} - A^2(\tilde{H}_1)_{00}{}^2}, \tag{15}$$

where:

$$\bar{E} = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}, \quad \tilde{E} = \frac{\langle\tilde{\phi}|H|\tilde{\phi}\rangle}{\langle\tilde{\phi}|\tilde{\phi}\rangle}.$$

The dependency of $\varDelta E_{\mathrm{corr.}}$ upon the arguments, κ, λ, A, and Z, is not simple. This will be given numerically in the case of the helium atom.

Applications to Hydrogen and Helium Atoms

In the first place, we would like to choose the case of a hydrogen atom merely for the purpose of illustrating our method. Consider the hydrogen atom perturbed by the removal of the $\varDelta Z$ charge from the nucleus. Then, in atomic units,

$$H_0 = -\frac{1}{2}\varDelta - r^{-1}, \quad H_1 = \varDelta Z r^{-1}$$

$$\phi_0 = \pi^{-1/2}e^{-r}, \quad v = A(1 - e^{-\kappa r})r^{-1}. \tag{16a}$$

Hence,

$$\phi = \phi_0\{1 + A(1 - e^{-\kappa r})r^{-1}\} \tag{16b}$$

results from Eq. (4),
where, for convenience, $\varDelta Z$ has been absorbed in A.

Now we are ready to obtain $\langle H\rangle$ by substituting Eqs. (16a) and (16b) into Eq. (5). In this calculation, however, there appear several well-known integrals which diverge, namely, in general forms.

$$\int_0^\infty \frac{e^{-sr}}{r}dr = -\lim_{\varepsilon\to 0} Ei(-s\varepsilon) \tag{17}$$

and:

$$\int_0^\infty \frac{e^{-tr}}{r^2}dr = \lim_{\varepsilon\to 0}\left[\frac{1}{\varepsilon} - t + tEi(-t\varepsilon)\right]. \tag{18}$$

Fortunately, however, these integrals cancel each other out in $(\tilde{H}_1H_1\tilde{H}_1)_{00}$ and $\sum_i((\partial\tilde{H}_1/\partial x_i)^2)_{00}$ respectively when our modification is used. Thus, one gets the perturbed energy in the following closed form:

$$\varDelta E = \frac{2A\varDelta Z(1 - 2\alpha)^2 + A^2\{4(1 - \varDelta Z)\log(4\alpha^2/\beta) + \kappa^2\beta(1 - 2\alpha\varDelta Z)\}}{1 + 2A(1 - 4\alpha^2) + 2A^2\kappa^2\alpha\beta}, \tag{19}$$

where:

$$\varDelta E = \langle H\rangle - E_0 - E_1,$$
$$\alpha = (2 + \kappa)^{-1}, \quad \beta = (1 + \kappa)^{-1}.$$

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[7] H. A. Bethe and E. E. Salpeter, "Encyclopedia of Physics, Vol. 35", ed. by S. Flügge Springer-Verlag, Berlin (1957).

[8] O. Sinanoğlu, *J. Chem. Phys.*, **34**, 1237 (1961).

Determining the optimum values of κ and A variationally, one obtains the minimum energy for a given ΔZ. The results listed in Table 1 are almost equal to the correct value ($\Delta E/(\Delta Z)^2=-0.5000$).

Table 1. The energy $\Delta E/(\Delta Z)^2$ for various perturbation ΔZ

ΔZ	κ	A	$\Delta E/(\Delta Z)^2$
0.0	0.000	∞	−0.5000
0.1	−0.146	25.20	−0.4999
0.2	−0.285	11.93	−0.4999
0.3	−0.415	7.39	−0.4999
0.4	−0.537	5.12	−0.4998
0.5	−0.650	3.74	−0.4997
0.6	−0.753	2.81	−0.4993
0.7	−0.843	2.13	−0.4987
0.8	−0.918	1.63	−0.4981
0.9	−0.977	1.26	−0.4982
1.0	−1.000	1.00	−0.5000

In the calculations, the value of A giving the minimum of the energy for a given κ is, of course, determined by a simple quadrature satisfying $\partial\Delta E/\partial A=0$. Figure 1 shows the relationships between the energy and κ. For large positive values of κ, where the present treatment approaches the average-energy method, the energy converges to zero, as has often been pointed out.[2)] It should be noticed here that the κ giving the lowest energy is always negative in the present case. The negative κ value is not unexpected, considering that the function of Eq. (16b) is a kind of trial function. In this connection, it seems adequate to regard the present method, not as a modification of the simple Kirkwood-Hassé or Unsöld procedure, but as a method using the wave-function in which the effect of the mixing of the Os function is taken into account.[9)] This can easily be understood by rewriting Eq. (16b) so that:

$$\psi=\pi^{-1/2}\mathrm{e}^{-r}+A\pi^{-1/2}\{\mathrm{e}^{-r}-\mathrm{e}^{-(1+\kappa)r}\}r^{-1}. \qquad (20)$$

The inclusion of the Os function into ψ seems not to be strange, considering the discussion presented by Robinson.[10)] A parallelism is found between κ and ΔZ. This result is reasonable in view of Eq. (20).

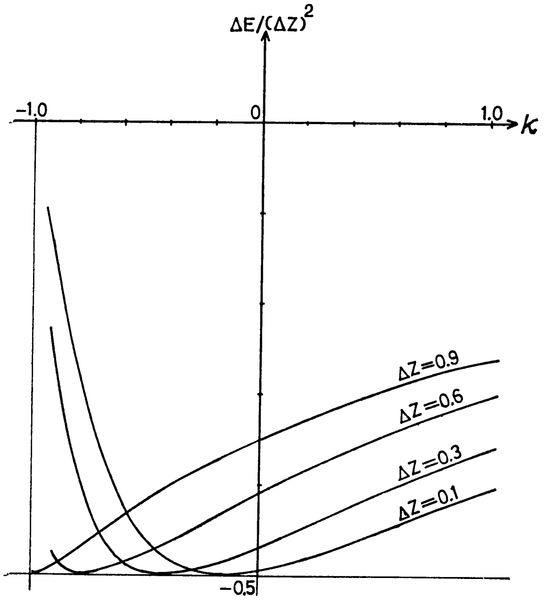

Fig. 1. $\Delta E/(\Delta Z)^2$ *vs.* κ.

Kirtman and Benston showed that, by their eae method, the difficulty of the divergency can also be avoided. They gave the exact first-order wave function for the same problem. Their way around this difficulty is to let the average energy be infinite in the neighborhood of the singularity, while the present method is to let H_1 in χ be finite; it also gives almost the exact energy, though the wave function is of a variational type.

Secondly, let us apply the present method to the ground state of the helium atom. Let the perturbed Hamiltonian, H, be split as H_0+H_1:

$$H_0=-\frac{1}{2}(\Delta_1+\Delta_2)-Z(r_1{}^{-1}+r_2{}^{-1})$$

$$H_1=-\Delta Z(r_1{}^{-1}+r_2{}^{-1})+r_{12}{}^{-1},$$

$$\psi_0=\pi^{-1}Z^3\mathrm{e}^{-Z(r_1+r_2)}, \qquad (21\mathrm{a})$$

where: $Z+\Delta Z=2$.

According to the present method, the perturbed wave function, ψ, is given from Eq. (4) by:

$$\psi=\psi_0(1+A[-\Delta Z\{(1-\mathrm{e}^{-\kappa r_1})r_1{}^{-1}+(1-\mathrm{e}^{-\kappa r_2})r_2{}^{-1}\}+(1-\mathrm{e}^{-\lambda r_{12}})r_{12}{}^{-1}]) \qquad (21\mathrm{b})$$

for the four parameters κ, λ, A, and Z. From Eqs. (5), (21a), and (21b), one easily obtains the energy expression in a closed form (shown in the Appendix). Our result is given in Table 2, along with those calculated by other researchers. Sur-

Table 2. The energy of He atom (in a. u.)

Method	Energy
Experimental[a)]	−2.9033
Hartree-Fock[b)]	−2.8617
Parr and Weare[c)]	−2.8911
Snyder[d)]	−2.8979
Present result[e)]	−2.8983
Weare, Weber, and Parr[f)]	−2.9002
Pekeris[g)]	−2.9037

a) From Ref. 12. b) From Ref. 13. c) From Ref. 14. d) From Ref. 15. e) Here, $\kappa=0.891$, $\lambda=0.591$, $A=-1.1324$ and $Z=1.6108$, respectively. f) From Ref. 11. g) From Ref. 16.

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9) R. McWeeny and C. A. Coulson, *Proc. Phys. Soc.* (London), *A*, **62**, 509 (1949); R. McWeeny *ibid.*, *A* **62**, 519 (1949); J. T. Zung and R. G. Parr, *J. Chem. Phys.*, **41**, 2888 (1964).

10) P. D. Robinson, *ibid.*, **45**, 1858 (1966).

prisingly, in view of the result obtained, Eq. (21b) is a very good approximation of the perturbed wave function in spite of its simple form. Orthogonalization leads no better result, *i.e.*, $\Delta E_{\mathrm{corr.}} = -0.0006$ in the present case.

Kirtman and Benston also obtained an approximate first-order wavefunction by their eae method and computed the energies to the third order numerically. They indeed avoided the difficulties of divergency, but one will scarcely be able to find a physical meaning in the form of their wave-function. Moreover, the energy obtained is not satisfactory, namely, $E_2^{\mathrm{eae}} = -0.135$ a.u. ($\gtrsim E_2$) and $E_3^{\mathrm{eae}} = 0.01194$ a.u.[*1]

Recently, Weare *et al.*[11] showed that, in correlated trial wave-functions of the $\psi = \phi(r_1)\phi(r_2)(1+v(r_{12}))$ form for helium-like atoms, the Os function, when used for ϕ and/or v, gave excellent results. As one of several expected Os trial wave-functions, they proposed $\psi = 1s_\zeta(r_1)1s_\zeta(r_2)[1+A\,Os_{\gamma\delta}(r_{12})]$, which partly resembles the present function (Eq. (21b)) in its apparent form. It should be stressed, however, that our treatment has quite a different basis than theirs, which is due to the correlated Hartree-Fock orbital approximation. In fact, our method is easily connected to the perturbation method, as has already been discussed. From Eqs. (11) and (12), we can estimate the respective energy terms from E_0 to E_R for the best variational result. As is shown in Table 3, these terms descend monotonously, disclosing the relation of the present method to the perturbational treatment. Additionally, it is worth emphasizing that the present method gives a closed form for the energy expression, whereas Weare *et al.* were unable to obtain such an expression.[11] The extension to isoelectronic atoms is trivial; further applications of this method, in particular, to the important problems of the long-range force between atoms will be presented elsewhere.

TABLE 3. THE VALUES OF RESPECTIVE ENERGY TERMS

The energy term	The value (in a. u.)
E_0	-2.59468
E_1	-0.24710
$\tilde{E}_2$	-0.06270
$\tilde{E}_3$	$+0.00626$
E_R	-0.00008

Appendix

The integrals used in calculating the energy for the helium atom from Eq. (5) are as follows;

$$(H_1)_{00} = Z\left(\frac{5}{8} - 2\Delta Z\right),$$

$$\begin{aligned}(\tilde{H}_1)_{00} = Z\Bigl[&\Bigl(\frac{5}{8} - 2\Delta Z\Bigr) + 8\Delta Z b^2 \\ &+ \frac{1}{2}df - 4df^4(\lambda + 6)\Bigr],\end{aligned}$$

$$\begin{aligned}(\tilde{H}_1{}^2)_{00} = Z^2\Bigl[&\frac{2}{3} - 8\Bigl\{\frac{1}{16}d - \frac{1}{4}df + \frac{3}{16}f + \frac{1}{4}f^2 \\ &+ \frac{1}{3}f^3\Bigr\} + \frac{1}{2}e\Bigl\{\frac{1}{2} + \frac{1}{2}e + \frac{1}{3}e^2\Bigr\} \\ &- 4\Delta Z\Bigl\{\frac{3}{4} - 4b^2(1 - 4c^2) + df(1 - 16c^2) \\ &+ 16d^2f^2(1 - 4c - 4f + 4g)\Bigr\} \\ &+ 2(\Delta Z)^2\{3 + 2a - 8b - 8b^2 + 16b^4\}\Bigr],\end{aligned}$$

$$\begin{aligned}(H_1\tilde{H}_1)_{00} = Z^2\Bigl[&\frac{2}{3} - 4\Bigl\{\frac{1}{16}d - \frac{1}{4}df + \frac{3}{16}f + \frac{1}{4}f^2 \\ &+ \frac{1}{3}f^3\Bigr\} - 4\Delta Z\Bigl\{\frac{3}{4} - 2b^2(1 - 4c^2) \\ &+ df(1 - 16f^2)\Bigr\} + 2(\Delta Z)^2\{1 + 2\kappa b - 4b^2\}\Bigr],\end{aligned}$$

$$\begin{aligned}(\tilde{H}_1H_1\tilde{H}_1)_{00} = Z^3\Bigl[&\frac{1}{6}\lambda^2(12 + 15\lambda + 4\lambda^2)e^2f^2 \\ &+ \frac{1}{2}\log(e/4f^2) - 4\Delta Z\Bigl\{1 - d - 2(1 + f)f \\ &- 4(bc - cd + cf - df - cg + dg - fg) \\ &+ \frac{1}{4}\lambda^2(8 + 9\lambda + 2\lambda^2)e^2f^2 - \frac{4}{\kappa}(b - g) \\ &+ 2\Bigl(\frac{2}{\kappa^2} - \frac{1}{\kappa} + c + 2c^2\Bigr)\log(g/2bf)\Bigr\} \\ &+ 4(\Delta Z)^2\{1 - b + 4c - 16bc + 4b^3 - 4f^2 \\ &+ 16cfg + 2\log(2ac^2/b^3) + \kappa\lambda^2cdf - 4\log 2b \\ &- 4\lambda^2(8 - \lambda^2)d^2f^2\log 4c - 64d^2f^2\log(f/g)\} \\ &- 4(\Delta Z)^3\{3 + a - 8b - 8b^2 + 16b^3 \\ &+ 2\log(a/4b^2)\}\Bigr],\end{aligned}$$

$$\begin{aligned}\left(\sum_i\left(\frac{\partial\tilde{H}_1}{\partial x_i}\right)^2\right)_{00} = Z^4\Bigl[&\frac{1}{6}\lambda^4(3 + \lambda)(4 + 3\lambda)e^3f^2 \\ &+ 16\Delta Z\Bigl\{\kappa^2(6 + \kappa)c^2df - 16\kappa\lambda d^2f^2g \\ &+ \frac{1}{2}\kappa\lambda^2(20 - \lambda^2)cd^2f^2 - 2\log 2b \\ &+ 2(1 + \lambda^2(8 - \lambda^2)d^2f^2 - (64 + 16\lambda^2 \\ &- 12\lambda^4 + \lambda^6)d^3f^3)\log 4c\end{aligned}$$

[*1] The total energy calculated to the third order is -2.879.

11) J. H. Weare, T. A. Weber, and R. G. Parr, *J. Chem. Phys.*, **50**, 4393 (1969).

12) G. Herzberg, *Proc. Roy. Soc.* (London), **A 248**, 309 (1958).

13) C. C. J. Roothaan, L. M. Sachs and A. W. Weiss, *Rev. Mod. Phys.*, **32**, 186 (1960).

14) R. G. Parr and J. H. Weare, *Progr. Theoret. Phys.* (Kyoto), **36**, 854 (1966).

15) L. C. Snyder, *J. Chem. Phys.*, **33**, 1711 (1960).

16) C. L. Pekeris, *Phys. Rev.*, **115**, 1216 (1959).

$$- \left(1 + \frac{1}{2}\lambda - 16\lambda d^2 f^2 + \left(64 + 32\lambda + 16\lambda^2 + 8\lambda^3 \right.\right.$$

$$\left.\left. - 12\lambda^4 - 6\lambda^5 + \lambda^6 + \frac{\lambda^7}{2}\right) d^3 f^3\right) \log (f/g)\Big\}$$

$$+ 4(\Delta Z)^2 \{\kappa^2 a + 4 \log (4b^2/a)\}\Big],$$

where

$$a = (1 + \kappa)^{-1} \quad b = (2 + \kappa)^{-1}, \quad c = (4 + \kappa)^{-1},$$
$$d = (2 - \lambda)^{-1}, \quad e = (1 + \lambda)^{-1}, \quad f = (2 + \lambda)^{-1}$$
$$\text{and} \quad g = (2 + \kappa + \lambda)^{-1}.$$

The procedure of integration including $e^{-\eta r_{12}}/r_{12}{}^n$ is referred to the method presented by Page.17)

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17) C. H. Page, *Phys. Rev.*, **53**, 426 (1938).