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Z dependence of the total energy and the electrostatic potential at the nucleus for the isoelectronic atoms with particular reference to the two-electron atoms in their ground state

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Equations expressing the total energy E and the electrostatic potential at the nucleus $V_{0,A}$ for an isoelectronic series of atoms as functions of atomic number Z have been examined. Based upon the $Z - \alpha$ expansion of Fröman and Hall, it has been found that equations $E = (1/2)LZ^2 + KZ + W_2 + W_3'(Z - \alpha)^{-1} + W_4'(Z - \alpha)^{-2}$ and $V_{0,A} = LZ + K - W_3'(Z - \alpha)^{-2} - 2W_4'(Z - \alpha)^{-3}$ work very well in the sense that they can form the basis of constructing very accurate empirical formulas for $E(Z)$ and $V_{0,A}(Z)$ by fitting these equations to the Thakkar–Smith data for the He–like atoms including H^-. Superiority of our approach over Gorunganthu and Bonham's approach based upon the Taylor series expansion is pointed out. Relevance of our formulas with the results of the Z^{-1} perturbation calculations has been pointed out.

I. INTRODUCTION

Various properties of atoms have been studied from the viewpoint of isoelectronic series. Many of the spectroscopic works have been done along such a line.[1] Clementi's compilation[2] of his results of the near Hartree–Fock calculations on a wide range of atoms and ions has also been done from the isoelectronic point of view.

Of the various isoelectronic series of atoms, the two-electron systems or the He isoelectronic series in their ground states have been most extensively studied from the theoretical point of view. Calculations by Pekeris[3] and by Thakkar and Smith[4] are among the most accurate works. Such systems have also been studied by using the perturbation method.[5-7] The most extensive calculation of this kind is due to Midtdal.[7] These sort of calculations have usually been called the Z expansion or Z^{-1} expansion method, since the expression of the total energy $E(Z)$ of the isoelectronic systems is given as a power series in Z^{-1}. The Z^{-1} expansion method may be regarded as the first achievement in obtaining $E(Z)$ of the isoelectronic system based upon theoretical ground. The expression $V_{0,A}(Z)$, the electrostatic potential at the nucleus for the isoelectronic series, can be obtained from $E(Z)$ straightforwardly by applying the Hellmann–Feynman theorem,[8] as was first pointed out by Foldy.[9] Politzer and Daiker[10] have made a least-squares fit of the nonrelativistic energy of the two- to four-electron isoelectron series, by assuming that either the electron–electron interaction energy V_{ee} or the nuclear attraction energy V_{en} can be expanded as a finite power series of Z, including both the positive and the negative powers of Z, and by using the virial and the Hellmann–Feynman theorem. The $E(Z)$ formula of the two-electron system has been constructed by Stillinger[11] based upon a semiempirical analysis of the expansion coefficients in the Z^{-1} expansion method obtained by Midtdal.[7]

There have been reports, however, of convergence problem in such expansions.[12,13] Goruganthu and Bonham[14] (GB) have constructed $E(Z)$ formulas by assuming that $E(Z)$, the nuclear attraction potential $V_{en}(Z)$ or electron–electron interaction energy $V_{ee}(Z)$ for isoelectronic series of atoms can be expanded as Taylor series about $Z = Z_0$ and by using the Hellmann–Feynman and/or the virial theorem if necessary. They have finally adopted such an $E(Z)$ formula [their Eq. (6)] based upon the Taylor series expansion of $V_{en}(Z)$ as a working formula.

In the course of exploring an energy–density equation for isoelectronic changes in atoms, the present authors have found[15,16] that $V_{0,A}(Z)$ for an isoelectronic series of atoms can be expressed very well as

$$V_{0,A}(Z) = LZ + K + a(Z - c)^{-n}, \qquad (1)$$

where L and K are constants characteristic of the series and can be determined exactly from theory, while a, c, and n are parameters to be determined by a least-squares fitting of Eq. (1) to the $V_{0,A}(Z)$ data. Since n turns out to be nearly equal to 2, Eq. (1) explains very well the fact that $V_{0,A}(Z) - LZ$ increases or decrease monotonically with increase in Z along an isoelectronic series in such a way that it approaches a limit characteristic of the series. If the negative ion is included, however, Eq. (1) fails to work. With the Thakkar–Smith data[4] on the He series, for example, $V_{0,A} - LZ$ *decreases* from H^- to He but it starts to *increase* from He with increase in Z toward an asymptotic limit. Such a drawback of Eq. (1) might be improved if another term similar in form to the third term is added to Eq. (1). This suggestion seems, however, to be rather empirical. It is the purpose of the present paper to give theoretical grounds to such a $V_{0,A}(Z)$ function just suggested empirically.

II. COMMENTS ON THE TAYLOR SERIES EXPANSION

Before deriving our $V_{0,A}(Z)$ formula having a theoretical grounds, comments must be made on the Taylor series

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expansion method used by GB[14] in their construction of $E(Z)$ and the other related formulas, although we will see the superiority of our approach over those based upon the Taylor series numerically later in this paper.

The Taylor series expansion of $V_{en}(Z)$ about some charge Z_0 can be rewritten as a power series in Z, without involving any inverse power of Z or $Z - c$, the order of the highest-order term being equal to the order of the highest-order term in $Z - Z_0$ retained in the Taylor series. According both to the Z^{-1} expansion theory and to our semiempirical analysis of $V_{0,A}$,[15] the highest-order term in $V_{en}(Z)$ must be of Z^2. In order to be consistent with this requirement, the Taylor series expansion of V_{en} *must be truncated* at the $(Z - Z_0)^2$ term. It is expected therefore that the Taylor series expansion might work well in dealing with isoelectronic series with fairly narrow range of Z but it might fail to work when the range is not so small. Also it might fail to work when the negative ion is included in the series since the isoelectronic change of $V_{0,A}$ occurring when one goes from the neutral atom to the negative ion is very different from the corresponding changes occurring along the series without including the negative ion as described before. It should also be pointed out that the asymptotic behavior of $\Delta V_{0,A}(Z)$ $= V_{0,A}(Z) - V_{0,A}(Z - 1)$ discovered previously by the present authors[17] cannot be explained from any form of the $V_{0,A}(Z)$ functions obtainable from the Taylor type expansion of $V_{en}(Z)$.

III. THEORY

Relevance of the Z scaling procedure with the Z^{-1} expansion theory is well known.[18] Instead of introducing an artificial charge $\bar{e}$ as $\bar{e} = Z^{1/2}e$, Fröman and Hall[19] have proposed to take $\bar{e}$ as $(Z - \alpha)^{1/2}e$, where α is a parameter to be determined later, and have shown that $E(Z)$ can be expressed as

$$E(Z) = W_0'(Z - \alpha)^2 + W_1'(Z - \alpha) + W_2'$$
$$+ W_3'(Z - \alpha)^{-1} + W_4'(Z - \alpha)^{-2} + \cdots, \quad (2)$$

where W_i' is the ith order energy with the unperturbed wave function constructed as an antisymmetrized product of the hydrogenic orbitals, the perturbation in the Hamiltonian being

$$H_1' = \sum_{i<j}(1/r_{ij}) - \alpha \sum_i (1/r_i). \quad (3)$$

Equations (2) and (3) are to be compared with the $E(Z)$ expression obtained through the usual Z scaling procedure:

$$E(Z) = W_0 Z^2 + W_1 Z + W_2 + W_3 Z^{-1} + W_4 Z^{-2} + \cdots, \quad (4)$$

where $H_1 \equiv \sum_{i<j}(1/r_{ij})$ is taken to be the perturbation in the Hamiltonian. Since Eqs. (2) and (4) express the same thing, the following identities must hold:

$$W_0' = W_0,$$
$$W_1' = W_1 + 2W_0\alpha, \quad (5)$$
$$W_2' = W_2 + W_1\alpha + W_0\alpha^2.$$

In other words, the first three terms in Eq. (2) are no more general than the first three in Eq. (4), but the fourth and the subsequent terms in Eq. (2) are of quite different form. Equation (2) may thus be written as

$$E(Z) = W_0 Z^2 + W_1 Z + W_2 + W_3'(Z - \alpha)^{-1}$$
$$+ W_4'(Z - \alpha)^{-2} + \cdots. \quad (6)$$

If the fifth and the subsequent terms are omitted in Eq. (6), this equation comes out to be identical to Eq. (3) of our recent paper,[16] which has been obtained starting from an empirical analysis of $V_{0,A}(Z)$. Inclusion of the fifth term should of course make the $E(Z)$ formula better. The corresponding $V_{0,A}(Z)$ formula can be obtained through the Hellmann–Feynman theorem[8] as

$$V_{0,A} = \frac{\partial E(Z)}{\partial Z} = 2W_0 Z + W_1 - W_3'(Z - \alpha)^{-2}$$
$$- 2W_4'(Z - \alpha)^{-3}, \quad (7)$$

which has exactly the same form as suggested toward the end of the Introduction. Since W_0 and W_1, which are equal to $\frac{1}{2}L$ and K, respectively, of Eq. (1), can be calculated exactly for any of the isoelectronic series of atoms,[16] independent of whether the electron correlation is considered or not, Eq. (6), if it is truncated at the fifth term, becomes the basis of an empirical formula involving four parameters to be determined through the least-squares fitting to the $E(Z)$ data of an isoelectronic series of atoms. The $V_{0,A}$ value may then be calculated with such parameters by using Eq. (7) and V_{en} may be obtained as $V_{en} = ZV_{0,A}$. Application of the virial theorem then gives V_{ee}, electron–electron interaction energy within an atom, as $V_{ee} = 2E - V_{en}$.

IV. APPLICATION TO He ISOELECTRONIC SERIES

To show the superiority of Eq. (6) as a formula of the least-squares fitting of $E(Z)$ data over the method based upon the Taylor series expansion of $V_{en}(Z)$ as suggested by GB,[14] the nonrelativistic data due to Thakkar and Smith[4] on the He isoelectronic series have been used, since their calculations, having nearly a comparable accuracy to a more accurate calculation by Pekeris,[3] cover a wide range of isoelectronic members of this series including H^- and these authors have given calculated values for various quantities in addition to the total energy.

To see the superiority of one of the equations over the other to be used for a least-squares fitting, the number of the parameters must be kept equal in both the equations. In view of our argument developed in the Introduction, the sixth and the subsequent terms have been omitted in Eq. (6) to be used in the fitting. The resulting equation, which will be called our two-term equation, involves four parameters to be determined. Equation (6) of the GB paper[14] has therefore been truncated at the term involving V_{en},[(2)] leaving four parameters to be determined, and has been used for the least-squares fitting. Unless stated otherwise, the equation thus truncated will simply be called the GB equation. In the least-squares fittings, the energies of He and the available He-like positive ions have been used as a set of data to be fitted first. The results are given in Table I. The energy of the H^- ion has

TABLE I. Calculated values of total energy E, nuclear attraction potential energy V_{en}, and electron–electron interaction energy V_{ee} by using formulas obtained through a least-squares fitting of E for the He series (the H^- data are excluded) (a. u.).[a,b]

Z	Goruganthu–Bonham	This work
$-E$		
2	2.903 736 019 (1.164×10^{-5})	2.903 724 434 (5.688×10^{-8})
4	13.655 559 2 (-5.767×10^{-6})	13.655 565 8 (8.359×10^{-7})
6	32.406 260 8 (1.536×10^{-5})	32.406 245 5 (6.063×10^{-8})
8	59.156 592 4 (-1.427×10^{-6})	59.156 592 8 (-9.858×10^{-7})
10	93.906 789 7 (-1.272×10^{-5})	93.906 803 2 (7.634×10^{-7})
12	136.656 958 (1.361×10^{-5})	136.656 944 (1.038×10^{-7})
	1.543×10^{-10}	5.227×10^{-13}
$-V_{en}$		
2	6.753 105 361 (-1.618×10^{-4})	6.753 257 629 (-9.555×10^{-6})
4	29.502 088 40 (8.596×10^{-5})	29.502 003 28 (8.371×10^{-7})
6	68.251 374 0 (-9.648×10^{-6})	68.251 380 5 (-3.094×10^{-6})
8	123.000 962 0 (-9.077×10^{-5})	123.001 048 3 (-4.456×10^{-6})
10	193.750 852 6 (-3.628×10^{-6})	193.750 844 0 (-4.987×10^{-6})
12	280.501 045 7 (-3.366×10^{-4})	280.500 706 0 (-3.177×10^{-6})
	1.697×10^{-8}	1.993×10^{-11}
V_{ee}		
2	0.945 633 324 (-1.851×10^{-4})	0.945 808 761 (-9.690×10^{-6})
4	2.190 969 9 (9.743×10^{-5})	2.190 871 6 (-8.947×10^{-7})
6	3.438 852 4 (-4.065×10^{-5})	3.438 889 6 (-3.495×10^{-6})
8	4.687 777 3 (-87.772×10^{-5})	4.687 862 7 (-2.285×10^{-6})
10	5.937 273 3 (2.948×10^{-5})	5.937 237 7 (-6.114×10^{-6})
12	7.187 130 5 (3.099×10^{-4})	7.186 817 8 (-2.785×10^{-6})
	1.697×10^{-8}	2.046×10^{-11}

[a] Number in parentheses is the difference from the exact value (Ref. 4) defined as $Q(\text{calc}) - Q(\text{exact})$, where Q represents either one of $-E$, $-V_{en}$, or V_{ee}.
[b] Number given at the bottom of each of the items is the variance defined as described in Ref. 20 of the text.

TABLE II. Calculated values of total energy E, nuclear attraction potential energy V_{en}, and electron–electron interaction energy V_{ee} by using formulas obtained through a least-squares fitting of E for the He series (the H^- data are included) (a. u.).[a,b]

Z	Goruganthu–Bonham	This work
$-E$		
1	0.527 646 492 (-1.045×10^{-4})	0.527 751 006 (-9.646×10^{-9})
2	2.904 021 475 (2.971×10^{-4})	2.903 724 876 (4.986×10^{-7})
4	13.655 435 4 (-1.296×10^{-4})	13.655 565 9 (8.951×10^{-7})
6	32.406 210 7 (-3.468×10^{-5})	32.406 246 1 (7.408×10^{-7})
8	59.156 652 6 (5.882×10^{-5})	59.156 593 1 (-6.762×10^{-7})
10	93.906 785 7 (5.427×10^{-5})	93.906 803 0 (5.712×10^{-7})
12	136.656 865 (-7.855×10^{-5})	136.656 943 (-5.506×10^{-7})
	1.237×10^{-8}	8.195×10^{-13}
$-V_{en}$		
1	1.376 941 21 (1.042×10^{-2})	1.369 343 12 (2.819×10^{-3})
2	6.752 025 851 (-1.241×10^{-3})	6.753 226 623 (-4.056×10^{-4})
4	29.502 012 18 (9.740×10^{-6})	29.502 007 09 (4.647×10^{-6})
6	68.251 754 6 (3.710×10^{-4})	68.251 380 1 (-3.513×10^{-6})
8	123.000 125 3 (2.002×10^{-4})	123.001 046 4 (-6.415×10^{-6})
10	193.750 507 5 (-3.415×10^{-4})	193.750 841 6 (-7.446×10^{-6})
12	280.499 518 1 (-1.191×10^{-3})	280.500 703 4 (-5.753×10^{-6})
	9.395×10^{-6}	6.625×10^{-7}
V_{ee}		
1	0.321 648 23 (1.063×10^{-2})	0.313 841 11 (2.819×10^{-3})
2	0.943 982 901 (-1.836×10^{-3})	0.945 776 871 (-4.158×10^{-5})
4	2.191 141 5 (2.690×10^{-4})	2.190 875 3 (2.797×10^{-6})
6	3.439 333 1 (4.400×10^{-4})	3.438 887 8 (-5.274×10^{-6})
8	4.687 947 8 (8.278×10^{-5})	4.687 860 1 (-4.862×10^{-6})
10	5.936 794 2 (-4.496×10^{-4})	5.937 235 6 (-8.189×10^{-6})
12	7.185 787 2 (-1.033×10^{-3})	7.186 816 5 (-4.052×10^{-6})
	9.904×10^{-6}	6.625×10^{-7}

[a] Number in parentheses is the difference from the exact value (Ref. 4) defined as $Q(\text{calc}) - Q(\text{exact})$, where Q represents either one of $-E$, $-V_{en}$, or V_{ee}.
[b] Number given at the bottom of each of the items is the variance defined as described in Ref. 20 of the text.

then been added to the set of the data. The results of such a fitting are given in Table II.

As may be seen in Tables I and II, it should be apparent that the fittings based upon our two-term equation is superior to the fittings based upon the GB equation, since the variance[20] turns out to be smaller by a factor of 10^3 if our equation is used.[21]

V. DISCUSSION

As was shown in the preceding section, our two-term equation may be regarded as superior to the GB equation to be used for the least-squares fitting of the energies of the He-like atoms. Although the superiority of our equation is already apparent for the fittings of the energies, the superiority becomes more apparent when V_{en} or V_{ee} are calculated from the resulting energy formula by way of the Hellmann–Feynman theorem as can also be seen in Tables I and II. This is understandable because the calculation of V_{en} and V_{ee} along the line mentioned above involves the calculation of $\partial E(Z)/\partial Z$, which is more affected by the subtle functional form of $E(Z)$ than the energy itself is affected.

The reason why our two-term equation works better than the GB equation will now be discussed. As was described above in this paper, W_0 and W_1 in Eq. (3) can be determined exactly from the theory. Let us therefore consider the quantity of E_2 defined as

$$E_2 = E - W_0 Z^2 - W_1 Z. \tag{8}$$

In Fig. 1, the quantity ΔE_2, the difference in E_2 between two successive members of the He isoelectronic series is plotted against Z. It may be seen that ΔE_2 asymptotically approaches zero when $Z \to \infty$. This sort of behavior may be seen for any of the isoelectronic series of atoms by using the Clementi data,[2] where the necessary data are available for a wide variety of isoelectronic series although the electron correlation is not included in the calculations. With Eq. (6) of the GB paper, it can easily be shown that ΔE_2 diverges when $Z \to \infty$, unless it is truncated at $V_{en}^{(2)}$ term. Even if it is truncated at $V_{en}^{(2)}$ term as was done in the present paper for comparative purpose, ΔE_2 turns out to diverge when $Z \to \infty$ unless the following equalities hold exactly:

$$V_{en}^{(1)} = W_1,$$
$$V_{en}^{(2)} = 4W_0. \tag{9}$$

TABLE III. Extrapolated values of several quantities for H^- by using various $E(Z)$ formulas (a. u.).

Formula[a]	$-E$	$-V_{en}$	V_{ee}
One term[b]	0.525 679 8	1.380 370	0.329 010 8
Two term[b]	0.527 337 5	1.371 832	0.317 157 1
GB(2)[c]	0.527 982 3	1.376 700	0.320 735 7
GB(4)[c]	0.526 347 6	1.378 727	0.326 032
Exact[d]	0.527 751 0	1.366 523 85	0.311 021 97

[a] Various formulas have been obtained by fitting the energy data of the He isoelectronic series as described in Secs. IV and V of the text.
[b] Equations used for the fitting is Eq. (6) truncated at the fourth and the fifth term, respectively.
[c] GB(2) and GB(4) stand for the two- and the four-parameter formula obtained by fitting the Goruganthu–Bonham equation (see the text for detail).
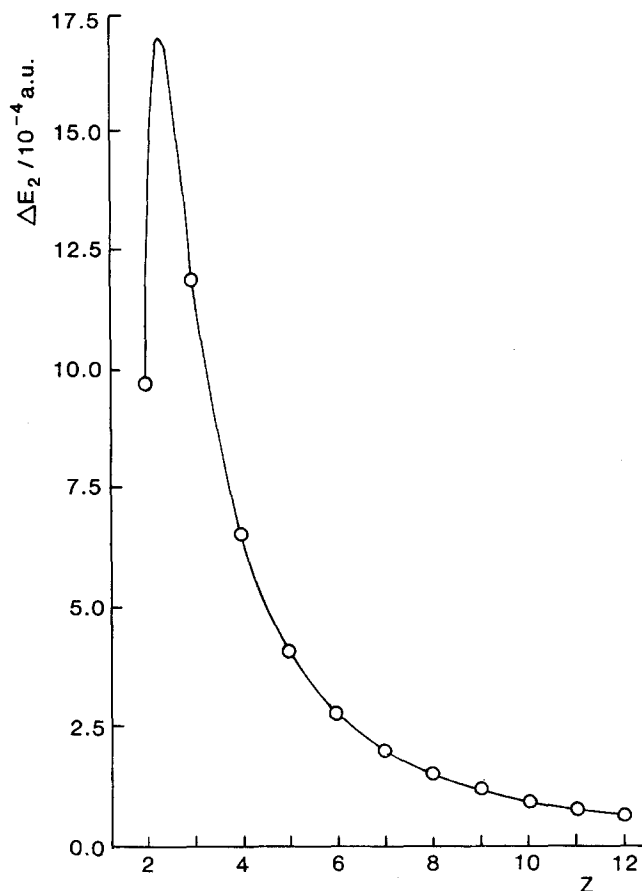[d] Reference 4.

FIG. 1. $\Delta E_2 \equiv E_2(Z) - E_2(Z-1)$ plotted against atomic number Z for the He isoelectronic series. As for the definition of E_2, see Eq. (8) of the text.

With $V_{en}^{(1)}$ and $V_{en}^{(2)}$ values determined by a least-squares fitting of the GB equation, equalities (9) hold with a reasonable accuracy but not exactly. One could fit the GB equation in such a way that equalities (9) hold exactly. In this fitting, the variance increases by a factor of hundreds, reflecting the fact that the number of adjustable parameter decreases to two. With our equation, two-parameter calculation cannot be done, because the fourth term in Eq. (6) must at least be retained in order to ensure the asymptotic behavior of ΔE_2 described above and three parameters must then be determined. The variance for energy increases by a factor of a hundred as a result of dropping the fifth term in Eq. (6) to be used in the fitting, but remains still smaller than the four parameter GB equation. The quality of equations, to be used in the fitting, becomes more apparent if the ability to predict the various quantities of H^- is examined for $E(Z)$ formulas obtained through least-squares fittings without including the energy data of H^- in the set of the data to be fitted. Table III shows the results. It may be seen that our two-term equation gives the best overall reproduction of various quantities of the H^- ion. It is true that the two-parameter GB equation gives a very good extrapolated value for H^- so far as the energy is concerned. Judging from a rather large value of variance, however, it should be regarded as fortuitous.

Superiority of our two-term equation over the GB equation with four parameters becomes apparent further when

TABLE IV. Calculated values of total energy E, nuclear attraction potential energy V_{en}, and electron–electron interaction energy V_{ee} by using formulas, based upon our two-term equations, obtained through a least-squares fitting of E and $V_{0,A}$ simultaneously for the He series including H^- (a. u.).[a,b]

Z	$-E$		$-V_{en}$		V_{ee}	
1	0.527 786 430	(3.541×10^{-5})	1.366 528 66	(4.814×10^{-6})	0.310 955 80	(-6.617×10^{-5})
2	2.903 693 962	(-3.042×10^{-5})	6.753 452 316	(1.851×10^{-4})	0.946 064 392	(2.459×10^{-4})
4	13.655 586 8	(2.179×10^{-5})	29.501 199 07	(-1.178×10^{-5})	2.190 817 1	(-5.541×10^{-5})
6	32.406 253 7	(8.341×10^{-6})	68.251 338 0	(-4.557×10^{-5})	3.438 830 6	(-6.253×10^{-5})
8	59.156 588 3	(-5.482×10^{-6})	123.001 003 55	(-4.925×10^{-5})	4.687 826 9	(-3.809×10^{-5})
10	93.906 788 93	(-1.347×10^{-5})	193.750 802 0	(-4.701×10^{-5})	5.937 224 1	(-1.968×10^{-5})
12	136.656 922	(-2.147×10^{-5})	280.500 667 6	(-4.162×10^{-5})	7.186 822 5	(1.926×10^{-6})
	3.616×10^{-10}		4.436×10^{-9}		6.829×10^{-9}	

[a] Number in parentheses is the difference from the exact value (Ref. 4) defined as $Q(\text{calc}) - Q(\text{exact})$, where Q represents either one of $-E$, V_{en}, or V_{ee}.
[b] Number given at the bottom of each of the items is the variance defined as described in Ref. 20 of the text.

the energy of the H^- ion is included in the set of the energy data to be fitted, since inclusion of H^- makes the variance larger by a factor of 10^2 or so with the GB equation while it remains much the same with our two-term equation as may be seen in Tables I and II.

Now that it has been shown that our two-term equation is very adequate to be fitted to the energy data of the whole members of the He series including H^- so far as the data are available, we are in a position to see the accuracy of V_{en} and V_{ee} to be calculated from the $E(Z)$ formula thus obtained by using the Hellmann–Feynman and the virial theorem. Although our two-term equation gives much the same variance independent of whether the H^- ion is included or not so far as the energy is concerned as was mentioned before, the calculated value of V_{en} for the member having the lowest Z value becomes rather poor if the H^- ion is included in the fitting. This may be due to the fact that behavior of $E(Z)$ curve in the region where $Z < 2$ is a bit different from that in the region where $Z > 2$ as revealed by the behavior of ΔE_2 (see Fig. 1). It is expected therefore that the behavior of $\partial E / \partial Z$ at $Z = 1$, which determines V_{en} for H^-, depends upon a subtle behavior of $E(Z)$ curve in the region $Z < 2$, which is not necessarily well represented even by our two-term $E(Z)$ formula.

One could, of course, improve our two-term $E(Z)$ formula in such a way that it reproduces not only the energy but also V_{en} and V_{ee} for all members of the He series so far as the Thakkar–Smith data are available for comparison. The idea is to fit our $E(Z)$ equation and its derivative $\partial E(Z)/\partial Z$ to two sets of the data of the He series, one being energy and the

other $V_{0,A}$. Table IV gives the results in much the same way as used for Tables I and II. It is to be noted that the Hellmann–Feynman theorem is now used during the course of the fitting, contrary to the cases obtaining the data given in Tables I and II. As may be seen, the variance for V_{en} and V_{ee} decreases substantially compared with Table II, although the variance for energy gets a little larger.

VI. CONCLUDING REMARKS AND FURTHER PROSPECT

Now that we have shown that our two-term formulas for $E(Z)$ and $V_{0,A}(Z)$ not only have a theoretical basis but also work very well, we are in a position to show their theoretical implications. In Table V, numerical values of parameters in our two-term formula obtained through least-squares fitting the data on He series including H^- are listed.

Judging from the functional form of Eq. (6), the first thing which comes to mind would be to compare our two-term formula with the result of the Z^{-1} perturbation[7] calculation, since the fourth and fifth term in Eq. (6) can be expanded as power series in Z^{-1}. It turns out, however, that the coefficients for $Z^{-n}(n > 2)$ terms are made up of more than two terms including the parameters W'_3, W'_4, and α of Eq. (6) and are liable to uncertainty due to uncertainties in the values of parameters. The fact that $W_0 = 2L$ and $W_1 = K$ can be determined exactly from the theory have already been mentioned. It has therefore been decided to compare our W_2 and W'_3 with Midtdal's λ_2 and λ'_3 by using the relations that $W_2 = \lambda_2$ and $W'_3 = \lambda_3$. Table V shows such a comparison. It may be seen that the parameters obtained through fittings using the energy data only compare more favorably with Midtdal's λ_2 and λ_3. Another point worth commenting is the value of α. As Fröman and Hall pointed out earlier,[19] α may be regarded as a screening effect seen by a $1s$ electron due to the presence of another $1s$ electron in He-like atoms. The numerical value of such a screening effect has been known to be in the range $0.3 \sim 0.4$, depending upon the way in which that effect has been determined and the charge of the ion. The α value obtained in the present work is roughly in this range.[21]

As for the further prospect of the present paper, it would naturally be interesting to apply the present scheme to the isoelectronic series of atoms containing more than two electrons. The calculations along this line have been done but the

TABLE V. Numerical values of the parameters of our two-term formula for $E(Z)$ and $V_{0,A}(Z)$ compared with the results of the Z^{-1} expansion perturbation calculation.[a,b]

	Fitting using E data only	Fitting using E and $V_{0,A}$ data	Z^{-1} perturbation[c]
α	0.363 504 68	0.445 246 18	...
W_2	$-0.157\ 651\ 013$	$-0.157\ 587\ 238$	$-0.157\ 666\ 428$
W'_3	0.008 529 547	0.007 933 602	0.008 699 029
W'_4	$-0.003\ 443\ 895$	$-0.002\ 923\ 738\ 8$	...

[a] In a. u. except α, which is dimensionless.
[b] As for the definition of the parameters, see Eqs. (6) and (7).
[c] From Ref. 7, by using the relations between our parameters and Midtdal's λ_i that $W_2 = \lambda_2$ and $W'_3 = \lambda_3$.

results will be published as a separate paper. This is because of the fact that "exact" nonrelativistic energies to be used in such calculations are inevitably not so accurate as in the case of the two-electron atoms and that the essential purpose of the present work is to establish an $E(Z)$ formula, which is compact but accurate enough not only to reproduce the $E(Z)$ data but also to predict the $V_{en}(Z)$ or the $V_{ee}(Z)$ data through the Hellmann–Feynman and/or the virial theorem. It is, however, just to be added that the degeneracy for the zero-order wavefunction, pointed out by Linderberg and Shull,[22] must be taken into account, for example, in the case of Be series in its $1s^2 2s^2 {}^1S$ state in obtaining the theoretical value of W_1.

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[20]Variance here is defined as $\Sigma_{i=1}^{N} [Q_i(\text{calc}) - Q_i(\text{input})]^2/N$, where Q stands either one of E, V_{en}, or V_{ee} and N is the number of the data used for the fitting.
[21]The referee has pointed out that our formula involves a nonlinear least-squares parameter α and one must be careful whether or not other solutions that are better than or even similar to the one obtained exist. In fact, we have obtained various other solutions in addition to our optimum α value (0.363 492 293). The variance has, however, been found to be much larger with each of the α values corresponding to such other solutions than the variance with our optimum α value. For further assurance of the fact that what we call the optimum α value is really optimum, we have obtained the variance for the least-squares fitting of Eq. (6) as a function of α, which is now fixed in each of the least-squares fit, within a range of $\alpha = 0 \sim 10\,000$. It has been found that the variance is the lowest for optimum α value, the variance with our optimum α value being smaller than for any of the local minimum by at least a factor of 10^4.
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