

Relation between the numerical values of parameters appearing in an empirical formula for $V_0 A(Z)$ with the theoretical value of a coefficient in the Z expansion of the total energy of an atom

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TABLE II. Authors presenting measurements comparable with those reported here, together with their temperature ranges and highest pressures.

Authors	Reference	Temperature range (°C)	Highest pressure (MPa)
Michels <i>et al.</i> (1949)	3	0/150	290
Robertson <i>et al.</i> (1969)	4	35/400	1000
Liebenberg <i>et al.</i> (1974)	5	22	1300
Cheng (1972)	6	− 68/37	1025
Stishov <i>et al.</i> (1972)	7	− 73/77	1700

those given by Eq. (1). Also plotted is the departure at 0 °C of the equation of state which represents our earlier results; similar plots for other temperatures are almost coincident with this. The average difference between the present equation of state and the earlier one is 0.017%.

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Relation between the numerical values of parameters appearing in an empirical formula for $V_{0,A}(Z)$ with the theoretical value of a coefficient in the Z expansion of the total energy of an atom

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In a recent paper¹ (hereafter referred to as I), the authors have shown that the total electrostatic potential $V_{0,A}$ at the nucleus A for an isoelectronic series of atoms can be fitted to the formula $V_{0,A}(Z) = V_{0,A}(N) + L(Z - N) + \int_N^Z a(Z' - c)^{-n} dZ'$, where Z and N stand for the atomic number and the number of the electrons characteristic of the series, respectively, while a , c , n , and $V_{0,A}(N)$ are parameters to be determined by a least-squares method. Another quantity L can be expressed as $L = -\sum_i (1/n_i^2)$, where n_i is the principal quantum number of the atomic orbital in which the i th electron is embedded, the sum being to be taken over all the electrons in an atom belonging to the series.^{1,2} The equation described above can be rearranged as

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

where K is a constant defined by

$$K = V_{0,A}(N) - LN - a(N - c)^{1-n}(1 - n)^{-1}. \quad (2)$$

Now, by using the Hellmann–Feynman theorem,³ our $V_{0,A}(Z)$ formula gives that

$$E(Z) = \frac{1}{2}LZ^2 + KZ + E_2 + a(Z - c)^{2-n} \times (1 - n)^{-1}(2 - n)^{-1},$$

where

$$E_2 = E(N) - \frac{1}{2}LN^2 - KN - a(N - c)^{2-n} \times (1 - n)^{-1}(2 - n)^{-1}.$$

In I, all the parameters involved in Eqs. (1) and (2) have been determined for the He through Ne series using the results of the near Hartree–Fock calculations of Clementi⁴ and others.⁵ For the He series, such a calculation has also been done using the accurate results including electron correlation of Thakkar and Smith.⁶ It has been found that n is roughly equal to 3 for all cases treated, although the numerical values of the other parameters depend upon the series. So, if n were exactly equal to 3, this $E(Z)$ formula would become

$$E(Z) = \frac{1}{2}LZ^2 + KZ + E_2 + (a/2)(Z - c)^{-1}, \quad (3)$$

which can be expanded into a power series having an identical form with the energy expression in the Z expansion theory as was pointed out also in I. In the Z expansion theory, the coefficient of Z in the energy expression, which equals K in Eq. (3), is determined by first-order perturbation theory^{7–10}:

$$K = \sum_i \sum_{j>i} (i, j)_{\text{HAO}}, \quad (4)$$

where $(i, j)_{\text{HAO}}$ stands for such a value of the pairwise average interaction energy between the i th and the j th electron within the atom if the AO's involved were hydrogenic with $Z = 1$. It will be shown that the K values determined from our empirical parameters obtained previously with Eq. (2) agree very well with such theoretical values. It will also be shown that Eq. (4) may be derived, without invoking perturbation theory, if the arguments given previously^{1,2} are used. These findings may be regarded as justification of our empirical formula of $V_{0,A}$ and related quantities.

Now, as has been shown previously,² ΔV_{ee} the difference in the electron-electron interaction energy between two successive members of an isoelectronic series of atoms, has the same functional form as $\Delta V_{0,A}$. From an analogy with the argument developed in I,¹ it would therefore be apparent that V_{ee} can be expressed by the following equation:

$$V_{ee}(Z) = L'Z + K' + a'(Z - c')^{1-n'}(1 - n')^{-1}, \quad (5)$$

which is analogous in form to the $V_{0,A}(Z)$ formula. In Eq. (5) K' is a constant defined by

$$K' = V_{ee}(N) - L'N - a'(N - c')^{1-n'}(1 - n')^{-1}. \quad (6)$$

Although all the notations used for various quantities appearing in Eqs. (5) and (6) are self-explanatory, it is worth mentioning that L' stands for the limiting value of ΔV_{ee} when $Z \rightarrow \infty$; i.e., $L' = \sum_i \sum_{j>i} (i, j)_{\text{HAO}}$ as was shown previously.²

It can be obtained that

$$\begin{aligned} E(Z) &= \frac{1}{2}V(Z) = \frac{1}{2}[V_{ee}(Z) + ZV_{0,A}(Z)] \\ &= \frac{1}{2}LZ^2 + \frac{1}{2}(K + L')Z + \frac{1}{2}K' \\ &\quad + \frac{1}{2}[aZ(Z - c)^{1-n}(1 - n)^{-1} \\ &\quad + a'(Z - c')^{1-n'}(1 - n')^{-1}], \end{aligned} \quad (7)$$

from Eqs. (1) and (5) using the virial theorem. Since the coefficient of the first-order terms in Z must be equal in Eq. (7) and our $E(Z)$ formula, it follows that $\frac{1}{2}(K + L') = K$, which means that $K = \sum_i \sum_{j>i} (i, j)_{\text{HAO}}$, in view of the theoretical

TABLE I. Comparison of the K values calculated by Eq. (2) with those calculated by Eq. (4).^a

	Eq. (2) ^b	Eq. (4) ^c
He	0.625 006	0.625 000
	0.624 984	0.625 000
Li	1.022 935	1.022 805
Be	1.570 864	1.571 001
B	2.334 217	2.334 449
C	3.272 002	3.272 506
N	4.384 652	4.385 173
O	5.671 731	5.672 449
F	7.133 336	7.134 335
Ne	8.768 893	8.770 830

^a All the isoelectronic series of atoms are in their average energy of the ground configurations.

^b Calculated with Eq. (2) by using the $V_{0,A}(N)$, a , c , and n values determined from the $V_{0,A}(Z)$ data (Ref. 1).

^c Calculated with Eq. (4) by using the average interaction energy of a pair of electrons embedded in hydrogenic orbitals with $Z = 1$ (see Ref. 2).

value of L' mentioned above. In Table I, the K values calculated with Eq. (4) are compared with the corresponding values calculated with Eq. (2) by using the numerical values of parameters obtained in I.¹ It may be seen that the agreement is excellent.

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