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Relation between the Z^{-1} type expansion of the total energy of isoelectronic atoms and the many-electron theory on the electron correlation by Sinanoğlu

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By applying the economical formula for the total energies of isoelectronic atoms presented by the present authors [J. Chem. Phys. **84**, 6895 (1986)] to both the nonrelativistic exact energy and the Hartree–Fock energy, an expression of the Z^{-1} expansion type for the correlation energy is obtained for isoelectronic series involving the first-row atoms. Based upon the expression obtained, the following conclusions are derived on the relation between the Z^{-1} type expansion theory and Sinanoğlu's many-electron theory (MET): (i) the Z^2 term has nothing to do with the electron correlation; (ii) the term proportional to Z represents the internal correlation energy E_{int} in MET, at least when Z is large in comparison with the number of electrons N; (iii) the constant term in the Z^{-1} type expansion is the limiting value of the sum of the semi-internal and the all-external correlation energy ($E_F + E_u$) when $Z \to \infty$ and its values for the ground-state atoms show a systematic trend when plotted against N; (iv) the sum of the Z^{-1} and the higher order terms in Z^{-1} represents the Z dependence of $E_F + E_u$, although its small amount is attributable to a part of E_{int} when $Z - N \lesssim 1$.

I. INTRODUCTION

In a recent paper,[1] the present authors have shown that

$$E(Z) = W_0 Z^2 + W_1 Z + W_2$$
$$+ W'_3 (Z - \alpha)^{-1} + W'_4 (Z - \alpha)^{-2} \quad (1)$$

is a very economical formula for a least-squares fit of the total energies $E(Z)$ of isoelectronic atoms. In Eq. (1), W_0, W_1, and W_2 are identical to the coefficient of Z^2, Z^1, and Z^0, respectively, in the usual Z^{-1} expansion theory.[2] Of these quantities, W_0 and W_1 can easily be calculated analytically by using products of hydrogenic orbitals (HAO)[1,3] as the zero-order wave functions. Equation (1), therefore, contains only four parameters to be determined but has been found to be very useful in the fit because the reproduction of the input $E(Z)$ data is excellent if the parameters are optimized. The numerical determination of the parameters has been done by using the Thakkar–Smith data[4] on the exact nonrelativistic total energies for He-like atoms and it has been pointed out that the Fröman–Hall $(Z - \alpha)^{-1}$ expansion[5] for the total energy of an isoelectronic series of atoms, which is known to be more rapidly convergent than the Z^{-1} expansion, forms the theoretical basis of our formula. Linderberg and Shull[3] have shown that the Z^{-1} perturbation expansion can be made for the Hartree–Fock (HF) total energies E^{HF} in precisely the same manner as in the case of the nonrelativistic exact total energy E^{exact}. This is tantamount to saying that Eq. (1) can be used as a working formula for the least-squares fit to the E^{HF} data as well as of the E^{exact} data for an isoelectronic series. Such a fit using E^{HF} as well as the examination of the numerical accuracy of the fit have already been done by the present authors for the two to ten electron atoms and have been published elsewhere.[6] Since the correlation energy E^{corr} is defined[7] as the differ-

ence between E^{exact} and E^{HF},[8,9]

$$E^{corr} = E^{exact} - E^{HF}. \quad (2)$$

Therefore, if an $E(Z)$ formula for E^{exact} is established, we should be able to establish an $E^{corr}(Z)$ formula as

$$E^{corr} = (W_1^{exact} - W_1^{HF})Z + W_2^{exact} - W_2^{HF}$$
$$+ W'_3{}^{exact}(Z - \alpha^{exact})^{-1} - W'_3{}^{HF}(Z - \alpha^{HF})^{-1}$$
$$+ W'_4{}^{exact}(Z - \alpha^{exact})^{-2} - W'_4{}^{HF}(Z - \alpha^{HF})^{-2}, \quad (3)$$

since W_0 is exactly the same for both E^{exact} and E^{HF} of a given isoelectronic series.[1]

Correlation energies for atoms and ions have been examined from a theoretical point of view most systematically by Sinanoğlu and his co-workers. We refer here only three of their papers.[10–12] Other papers may be found as references cited in these papers. It is the purpose of the present paper to establish an $E(Z)$ formula for E^{exact} and to get an E^{corr} formula of the form of Eq. (3), from the $E(Z)$ formula thus established, by combining it with a similar formula for E^{HF} obtained previously.[6] Based upon such an E^{corr} formula, the relation between the Z^{-1} types expansion theory[2,5] and the many-electron theory by Sinanoğlu[10–12] will be discussed.

II. DETERMINATION OF PARAMETERS

To establish a semiempirical $E(Z)$ formula along the line described before,[1] we must have E^{exact}, the exact nonrelativistic value of the total energy. Except for two-electron atoms, however, such data based upon *ab initio* calculations are available only for limited cases. There are several attempts in the literature to get E^{exact} semiempirically.[13–15] As is well known, it holds that $E = E^{HF} + E^{corr} + E^{rel}$, where E^{rel} stands for the relativistic effect on the total energy and E is the total energy to be compared with the experimental value. In the semiempirical estimation of E^{exact}, it has been

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TABLE I. Numerical value of parameters in Eq. (1) as fitted to the exact nonrelativistic total energies of various isoelectronic series in their ground configurations.[a]

Series	Multiplet	α	W_1[b]	W_2	W_3'	W_4'	Variance[c]
He	^1S	0.326 84	0.625 00	− 0.157 66	0.008 595 6	− 0.003 3760	5.227×10^{-13}
Li	^2S	1.117 5	1.022 8	− 0.408 85	− 0.015 155	− 0.016 077	8.017×10^{-10}
Be	^1S	1.107 2	1.559 3	− 0.879 78	− 0.034 367	− 0.108 31	3.554×10^{-8}
B	^2P	2.367 9	2.327 5	− 1.842 5	− 0.195 18	− 2.122 1 $\times 10^{-6}$	8.012×10^{-8}
C	^3P	0.581 31	3.528 9	− 3.254 7	− 0.383 52	− 2.178 9	7.236×10^{-8}
	^1D	− 3.407 2	3.280 0	− 3.536 2	4.720 0	− 39.462	3.686×10^{-6}
	^1S	− 11.059	3.302 7	− 3.536 2	38.657	− 440.14	2.341×10^{-5}
N	^4S	0.452 90	4.353 5	− 5.200 8	− 0.814 39	− 4.857 7	5.009×10^{-8}
	^2D	− 2.377 2	4.385 2	− 5.497 1	3.551 0	− 40.161	1.699×10^{-7}
	^2P	1.480 6	4.400 8	− 5.413 3	− 0.576 21	− 3.745 1	6.145×10^{-7}
O	^3P	2.362 7	5.661 9	− 8.061 0	− 0.946 16	− 4.240 7	2.569×10^{-7}
	^1D	1.442 4	5.683 0	− 8.163 7	− 0.609 90	− 8.813 7	5.467×10^{-7}
	^1S	3.697 7	5.707 2	− 8.218 7	− 1.530 3	− 2.467 8 $\times 10^{-7}$	7.243×10^{-7}
F	^2P	2.939 4	7.134 3	− 11.650	− 1.612 1	− 5.555 9	2.683×10^{-7}
Ne	^1S	2.875 6	8.770 8	− 16.102	− 1.961 2	− 13.746	4.853×10^{-8}

[a] "Exact" nonrelativistic total energies can only be obtained from a semiempirical analysis of experimental total energies, except for He. As for He series, see Ref. 1 and the references cited therein.

[b] Discussion on the theoretical determination of W_1 may be found in text, while $W_0 = -\frac{1}{2}\Sigma_i (1/n_i^2)$, where n_i is the principal quantum number of the orbital containing the ith electron.

[c] Variance here is defined as $\Sigma_{i=1}^n [E_i^{calc} - E_i^{input}]^2/n$, where n is the number of the data used for the fitting.

customary to get it from the empirical value of E, to be obtained as an appropriate sum of experimental ionization potentials, by subtracting E^{rel} properly estimated. Clementi[15] has used this technique to obtain E^{exact}, from which he has obtained E^{corr} for a wide variety of atoms by using his own value[16] of E^{HF}. In view of a successful analysis of Clementi's E^{corr} in terms of the pair correlation energies by Anno and

Sakai,[17] Clementi's E^{corr} is believed to be fairly reliable. Therefore, the E^{exact} value Clementi has estimated is believed to be fairly reliable, although the numerical value is not given in his paper. It has therefore been decided to obtain E^{exact} as the sum of Clementi's E^{HF} [16] and E^{corr}.[15] It is to be noted that this is just to reproduce Clementi's estimation of E^{exact}.[18] The E data used for the actual least-squares fit have

TABLE II. Numerical value of parameters in Eq. (1) as fitted to the approximate Hartree–Fock total energies of various isoelectronic series in their ground configurations.[a]

Series	Multiplet	α	W_1[b]	W_2	W_3'	W_4'	Variance[c]
He	^1S	0.354 96	0.625 00	− 0.111 00	− 1.042 3 $\times 10^{-3}$	− 1.1555 $\times 10^{-4}$	5.215×10^{-12}
Li	^2S	1.118 5	1.022 8	− 0.354 57	− 0.040 556	8.4370 $\times 10^{-10}$	2.120×10^{-10}
Be	^1S	1.410 1	1.571 0	− 0.805 45	− 0.133 49	− 5.7956 $\times 10^{-8}$	1.087×10^{-9}
B	^2P	1.637 1	2.334 4	− 1.707 6	− 0.399 05	− 2.9671 $\times 10^{-8}$	2.488×10^{-9}
C	^3P	1.825 7	3.262 0	− 3.061 7	− 0.828 64	6.8032 $\times 10^{-9}$	5.358×10^{-9}
	^1D	1.887 6	3.283 1	− 3.122 7	− 0.850 24	1.6542 $\times 10^{-7}$	1.325×10^{-8}
	^1S	1.999 6	3.314 7	− 3.217 3	− 0.880 90	− 3.1410 $\times 10^{-7}$	3.373×10^{-8}
N	^4S	2.044 4	4.353 5	− 4.956 3	− 1.458 0	− 4.2239 $\times 10^{-8}$	1.071×10^{-8}
	^2D	2.121 3	4.385 2	− 5.060 9	− 1.494 2	7.1984 $\times 10^{-8}$	2.202×10^{-8}
	^2P	2.177 8	4.406 3	− 5.132 0	− 1.517 6	1.3806 $\times 10^{-7}$	3.3805×10^{-8}
O	^3P	2.413 4	5.661 9	− 7.676 1	− 2.391 8	2.3221 $\times 10^{-7}$	4.727×10^{-8}
	^1D	2.461 7	5.683 0	− 7.756 2	− 2.418 3	1.3701 $\times 10^{-7}$	6.116×10^{-8}
	^1S	2.536 4	5.714 6	− 7.877 7	− 2.458 1	− 1.7560 $\times 10^{-8}$	8.823×10^{-8}
F	^2P	2.814 6	7.134 3	− 11.160	− 3.604 5	− 5.8444 $\times 10^{-7}$	1.055×10^{-7}
Ne	^1S	3.250 4	8.770 8	− 15.495	− 5.124 8	− 5.9938 $\times 10^{-7}$	1.740×10^{-7}

[a] Approximate Hartree–Fock total energy have been taken from Clementi's tables published in 1974 (Ref. 16).

[b] See footnote b to Table I.

[c] See footnote c to Table I.

been confined to those for $Z < 20$, since the E^{corr} data of Clementi (i.e., his estimation of E^{exact}) are less reliable when $Z > 20$. In Tables I and II, the numerical values of the parameters thus obtained are given along with the theoretical values of W_1. Table I refers to the E^{exact} data while Table II to the E^{HF} data. In the last column of each row of both Tables I and II, the variance is given to show how reasonable our least-squares fit of Eq. (1) is. It is to be noted that the parameters for the He series given in Table I are just the reproduction of the results of the previous work,[1] since there is no reason why one has to use "E^{exact}" based upon Clementi's approximate data when genuine E^{exact} values are available.[1,4]

III. COMPARISON WITH SINANOĞLU'S MANY-ELECTRON THEORY

Now that we have determined all the parameters involved in Eq. (3), we can calculate E^{corr} for each of the isoelectronic series systematically. W_0, W_1, and W_2 in Eq. (1) are identical to those in the usual Z^{-1} expansion theory.[2] Both of the last two terms of Eq. (1), on the other hand, can be expanded into infinite series in Z^{-1}. It would be tempting therefore to regard the last two terms as representing the first and the higher order terms in Z^{-1} in the usual Z^{-1} expansion theory.[2] As is well known, the first three terms in the Z^{-1} expansion expression of $E(Z)$ represent the zero-, first-, and second-order terms in the language of the nonrelativistic perturbation theory as applied to the electronic structure of atoms, by regarding the interelectronic repulsion as the perturbation. Then, the last two terms in Eq. (1) represent the third and the higher order terms in such a language. With these facts in mind, it would be evident that the first term in Eq. (3) comes from the first-order perturbation, while W_2 terms are due to the second-order perturbation. The other terms in Eq. (3) are then attributable to the third- and the higher order perturbation. For convenience of the following discussion, let us call such three kinds of terms in Eq. (3) $E^{corr(1)}$, $E^{corr(2)}$, and $E^{corr(3)}$, respectively:

$$E^{corr(1)} = (W_1^{exact} - W_1^{HF})Z,$$

$$E^{corr(2)} = W_2^{exact} - W_2^{HF},$$

$$E^{corr(3)} = W_3'^{exact}(Z - \alpha^{exact})^{-1} - W_3'^{HF}(Z - \alpha^{HF})^{-1}$$
$$+ W_4'^{exact}(Z - \alpha^{exact})^{-2}$$
$$- W_4'^{HF}(Z - \alpha^{HF})^{-2}. \qquad (4)$$

According to the Sinanoğlu theory,[10,11] E^{corr} is divided into three categories:

$$E^{corr} = E_{int} + E_F + E_u, \qquad (5)$$

where E_{int}, E_F, and E_u are called the internal, semi-internal (plus polarization), and the all-external correlation, respectively. Of the three kinds of correlation energy, E_{int} is such a correlation effect that can be described in the CI language as the interaction among the configurations arising from various ways of assigning electrons to $1s$, $2s$, and $2p$ spin-orbitals. Because of the large energy gap, configurations corresponding to virtual transition from the K shell to the L shell do not make appreciable contributions to E_{int}. Configurations arising from single-electron excitations $2s \to 2p$ cannot

TABLE III. Comparison among internal correlation energy of Öksüz and Sinanoğlu, degeneracy effect of Clementi and Veillard, and $E^{corr(1)}$ of the present work for the B-like ($1s^2 2s^2 2p, {}^2P$) atoms (in eV).

Z	Clementi–Veillard[a]	Öksüz–Sinanoğlu[b]	$E^{corr(1)}$
5	− 0.846	− 0.802	− 0.942
6	− 1.112	− 1.088	− 1.130
7	− 1.335	− 1.313	− 1.318
8	− 1.543	− 1.522	− 1.507
9	− 1.743	− 1.723	− 1.695
10	− 1.941	− 1.920	− 1.883

[a] See Ref. 19.
[b] See Ref. 10.

mix with the ground state because of the difference in parity. Therefore for the first-row atoms the only important contribution to E_{int} comes from $1s^2 2s^2 2p^n \leftrightarrow 1s^2 2p^{n+2}$ interaction. Öksüz and Sinanoğlu[10] have thus calculated E_{int} as $1s^2 2s^2 2p^n \leftrightarrow 1s^2 2p^{n+2}$ interaction based upon an assumption on the form of the virtual $2p$ orbitals, while Clementi and Veillard[19] have calculated the same quantity by a two-configuration SCF method. In Table III, E_{int} value thus calculated are compared with $E^{corr(1)}$ for the B-like atoms as examples. As may be seen, our $E^{corr(1)}$ is roughly in agreement with the result of Öksüz and Sinanoğlu[10] as well as with the result of Clementi and Veillard.[19] To be more exact, however, our $E^{corr(1)}$ is larger (in absolute value) than both the Clementi–Veillard and the Öksüz–Sinanoğlu value for the neutral atoms and positive ions of lower stages of ionization. It becomes, however, a little smaller (in absolute value) than the values given by these authors for ions of higher stages of ionization. Such a trend can be explained as follows. Our $E^{corr(1)}$ would be identically equal to E_{int} if atomic orbitals were HAO with nuclear charge Z, since $E^{corr(1)}$ is exactly equal to the degeneracy effect existing in the infinite limit of Z as pointed out earlier by Linderberg and Shull,[3] which is nothing but the $1s^2 2s^2 2p^n \leftrightarrow 1s^2 2p^{n+2}$ interaction in this limit. In the calculations of both Clementi and Sinanoğlu, on the other hand, the HF type AO's are used. It is true that an HF AO approaches an HAO when $Z \to \infty$ but the screening effect has to be introduced if one wants to approximate an HF AO by an HAO for ions of lower stages of ionization $q (= Z - N, N$ being the number of electrons of that atom or ion). This is tantamount to saying that our $E^{corr(1)}$ is expected to overestimate E_{int} (in absolute value) for the neutral atom and ions of lower q values. The data in Table III bear out this expectation. When Z increases, our $E^{corr(1)}$ should approach true E_{int} because HF AO's then approach HAO's and $1s^2 2s^2 2p^n \leftrightarrow 1s^2 2p^{n+2}$ interaction becomes the only source of E_{int} for the first-row atoms. Both the Clementi and the Sinanoğlu values given in Table III have, however, turned out to exceed (in absolute value) our values as mentioned above. Perhaps, their wave functions are more flexible and can give lowering in the energy through either the CI or the MC SCF procedure unless Z is very large. It may be concluded that $E^{corr(1)}$ explains most part of E_{int} unless q is small although the remainder of E_{int} must be attributed to $E^{corr(3)}$. When $Z \to \infty$, $E^{corr(3)}$ becomes zero and $E^{corr(1)}$ then becomes the only contribution to E_{int}.
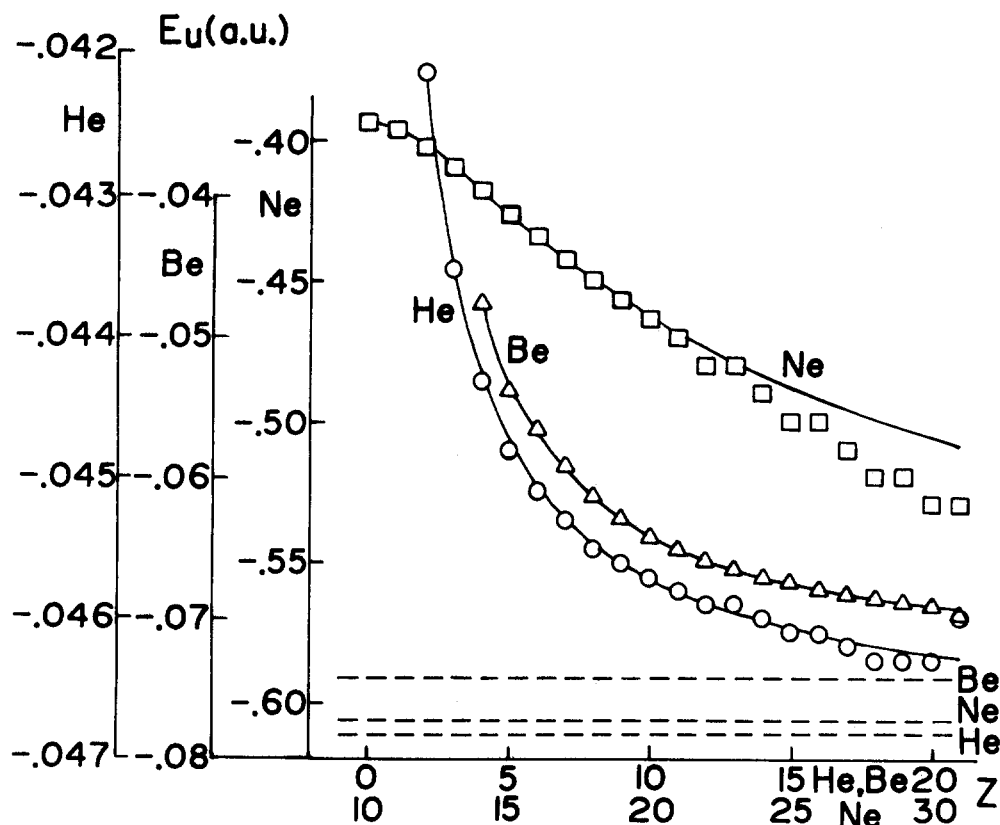
FIG. 1. Semiempirical values of the all-external correlation energy E_u plotted against the atomic number Z for the He-, Be-, and the Ne-like atoms. Notice that a separate ordinate with a different scale is used for each of the He, Be, and the Ne series so that the figure comes into a compact form. Curves drawn are $E^{corr(2)} + E^{corr(3)}$, which equal to E_u for these series, based upon the semiempirical formula of the present paper. Horizontal dashed lines represent $E^{corr(2)}$, which are supposed to be the asymptotic values of E_u for respective series. See the text for detail.
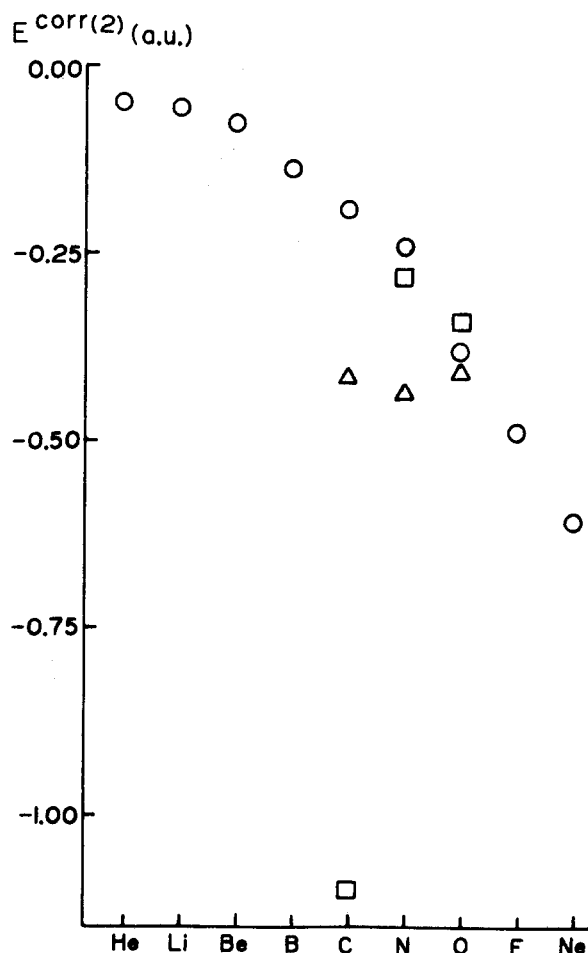

FIG. 2. $E^{corr(2)}$ plotted against the number of electrons characteristic of the isoelectronic series. O indicates the ground states, while $\triangle$ and $\square$ represent the second and the third lowest states, respectively.

For closed-shell atoms, such as the He-, Be-, and the Ne-like atoms, $E_F = 0$.[10,11] Moreover, $E_{int} = 0$ and $E^{corr(1)} = 0$ for the He- and the Ne-like atoms. It holds, therefore, that

$$E^{corr} = E_u = E^{corr(2)} + E^{corr(3)} \qquad (6)$$

for such atoms. For the Be-like atoms, $E_{int} \neq 0$ but E_u can be obtained approximately as

$$E^{corr} - E^{corr(1)} = E^{corr(2)} + E^{corr(3)} \doteq E_u, \qquad (7)$$

since $E_{int} \doteq E^{corr(1)}$ unless q is very low ($q \lesssim 1$) as mentioned before. Based upon Eqs. (6) and (7), E_u, taken to be directly equal to E^{corr} of Clementi's paper[15] for the He- and the Ne-like atoms and taken to be approximately equal to $E^{corr} - E^{corr(1)}$ ($= E^{corr(2)} + E^{corr(3)}$) for the Be-like atoms, is plotted in Fig. 1. $E^{corr(2)} + E^{corr(3)}$ vs Z curves based upon our formula, Eq. (4), with the optimum set of parameters are also given. Discrepancy of Clementi's data from our curve for the Ne series at higher Z values may be due to the error involved in his estimation of E^{corr}. It may be seen that E_u increases in absolute value asymptotically to $E^{corr(2)}$, although such an increase is very slight in the He case and appreciable in the Be and the Ne cases, if we consider a long series of isoelectric atoms. To look into more about $E^{corr(2)}$, this quantity is plotted against the number of electrons characteristic of the series in Fig. 2. So far as the ground states are concerned, $E^{corr(2)}$ of every series from He through Ne lie on a fairly smooth curve passing He–Be–Ne points. As for $E^{corr(2)}$ of excited states belonging to the ground configuration of the C-, N-, or the O-like atoms, they deviate from this curve in such a way that no regularity may be found. We shall not get further into the excited-state problems, because the E^{exact} data are less reliable due to the uncertainties in the excitation energies within an atom as commented in Moore's

TABLE IV. Examination of the relation between Sinanoğlu's E_F–E_u set and our $E^{corr(2)}$–$E^{corr(3)}$ set (in eV).

Z	E_F	E_u	$E_F + E_u$	$E^{corr(2)}$[a]	$E^{corr(3)}$	$E^{corr(2)} + E^{corr(3)}$
$1s^2 2s^2 2p(^2P)$						
11	−0.804	−2.28	−3.084	−3.674	0.546	−3.128
10	−0.789	−2.24	−3.029		0.604	−3.070
9	−0.771	−2.22	−2.991		0.676	−2.998
8	−0.747	−2.14	−2.886		0.765	−2.909
7	−0.714	−2.08	−2.794		0.880	−2.794
6	−0.662	−2.03	−2.692		1.029	−2.845
5	−0.586	−2.01	−2.596		1.213	−2.461
$1s^2 2s^2 2p^2(^3P)$						
11	−1.305	−3.00	−4.305	−5.255	0.913	−4.342
10	−1.281	−2.98	−4.261		0.986	−4.269
9	−1.249	−2.93	−4.179		1.070	−4.185
8	−1.204	−2.88	−4.084		1.172	−4.083
7	−1.135	−2.83	−3.965		1.297	−3.958
6	−1.014	−2.82	−3.834		1.461	−3.794
$1s^2 2s^2 2p^3(^4S)$						
11	−1.549	−3.97	−5.519	−6.654	1.138	−5.516
10	−1.515	−3.93	−5.445		1.213	−5.441
9	−1.465	−3.90	−5.365		1.300	−5.354
8	−1.397	−3.85	−5.247		1.403	−5.251
7	−1.278	−3.84	−5.118		1.537	−5.117
$1s^2 2s^2 2p^3(^2D)$						
11	−1.629	−4.55	−6.179	−11.867	5.691	−6.176
10	−1.587	−4.45	−6.037		5.830	−6.037
9	−1.530	−4.37	−5.900		5.957	−5.910
8	−1.446	−4.35	−5.796		6.076	−5.791
7	−1.314	−4.35	−5.664		6.208	−5.659
$1s^2 2s^2 2p^4(^3P)$						
11	−1.227	−6.23	−7.457	−10.459	3.036	−7.423
10	−1.186	−6.08	−7.266		3.213	−7.246
9	−1.127	−5.94	−7.067		3.368	−7.091
8	−1.036	−5.98	−7.016		3.440	−7.019
$1s^2 2s^2 2p^4(^1D)$						
11	−1.284	−6.50	−7.784	−11.082	3.331	−7.751
10	−1.242	−6.35	−7.592		3.502	−7.580
9	−1.181	−6.22	−7.401		3.658	−7.424
8	−1.091	−6.23	−7.321		3.767	−7.315
$1s^2 2s^2 2p^5(2P)$						
11	−0.702	−8.44	−9.142	−13.314	4.199	−9.115
10	−0.672	−8.25	−8.922		4.390	−8.924
9	−0.625	−8.20	−8.825		4.491	−8.823

[a] Constant characteristic of the isoelectronic series.

table,[20] which forms the very basis of Clementi's estimation of E^{exact}.

Turning back to the ground states of the Li, B, C, N, O, and the F series, the trend shown by the plot of $E^{corr(2)}$ values given in Fig. 2 would indicate that $E^{corr(2)}$ might be the asymptotic value of E_u when $Z \to \infty$. In Table IV, the E_F and the E_u values given by Öksüz and Sinanoğlu[10] are compared with our $E^{corr(2)}$ and $E^{corr(3)}$ for the B, C, N, O, and F series in their ground states so far as the data are available in the paper of Öksüz and Sinanoğlu. It may be seen that both E_F and E_u increase in absolute value when Z increases. It may, therefore, be concluded that our $E^{corr(2)}$ should be regarded as the limiting value of $E_F + E_u$ when $Z \to \infty$ and $E^{corr(3)}$ represents the Z dependent part of $E_F + E_u$ within the approximation that $E^{corr(1)} \doteq E_{int}$ if there is any E_{int}.

IV. CONCLUSIONS

Arguments given in the preceding section can be summarized as follows.

(i) Z^2 term in the Z^{-1}-type expansion theory has nothing to do with the electron correlation.

(ii) The term proportional to Z or $E^{corr(1)}$ represents E_{int} in MET at least when Z is large as compared with the number of electrons N. If $Z - N \lesssim 1$, however, $E^{corr(1)}$ is only roughly equal to E_{int}.

(iii) The constant term in the Z^{-1}-type expansion or $E^{corr(2)}$ is the limiting value of $E_F + E_u$ when $Z \to \infty$ and the sum of the Z^{-1} and higher order terms in Z^{-1} represents the Z depenence of $E_F + E_u$, although a small contamination from E_{int} is involved when $Z - N \lesssim 1$.

(iv) From the data on the He, Be, and the Ne series, where E_F is absent, it has been shown that E_u of an isoelectronic series of atoms *does* increase (in absolute value) toward its asymptotic limit $E^{corr(2)}$ when Z increases.

Before concluding the present paper, it should be admitted that (i) and (ii) in the abovementioned summary are not new. Both have been involved in the paper of Linderberg and Shull[3] and Sinanoğlu himself[10,11] has related his E_{int} as (ii). What is important in the present paper is the observations (iii) and (iv). In a subsequent paper, where the electron correlation effect upon the nuclear–electron interaction energy V_{en} and the electron–electron interaction energy V_{ee} will be discussed, it will be shown that the constant term in the Z^{-1} type expansion has nothing to do with the correlation effect upon V_{en} but it plays a major role in determining the correlation effect upon V_{ee}. Thus, the analysis given in the present paper may be regarded as a basis for the analysis of the electron correlation effect upon V_{en} and V_{ee}, which is important in the x-ray scattering theory.

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