Relativistic effect on total energies for determination of correlation energies of atoms from their experimental total energies

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Relativistic effect on total energies for determination of correlation energies of atoms from their experimental total energies

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Relativistic effect E^{rel} upon the total electronic energy of an atom is discussed with particular reference to obtaining the nonrelativistic total energy E^{exact} from the experimental total energy. Numerical values of this effect obtained by various authors by different nonempirical methods are compared for neutral atoms of rare-gas elements. It is shown that methods either of a Hartree–Fock-type or of a Dirac–Hartree–Fock-type give much the same E^{rel} value for He through Ar. It is pointed out that E^{rel} calculated with Hartree–Fock wave functions is not adequate for use in obtaining E^{exact} from the experimental total energy and that the E^{rel} value calculated with wave functions including electron correlation should work well, although an actual demonstration can be done only for two-electron systems for lack of data. A semiempirical formula is therefore proposed, which is useful for least-squares fit of experimental total energies of isoelectronic series of atoms to extract nonrelativistic total energies along with the relativistic effect. From nonrelativistic energies thus derived, semiempirical values of correlation energies of atoms are obtained. The results thus obtained are in reasonable agreement with correlation energies derived by Clementi along somewhat different lines. The power series expansion in Z of the fitted formula for the He series shows that numerical values of expansion coefficients agree reasonably well with the corresponding values obtained by accurate relativistic and nonrelativistic Z expansion-type calculations.

I. INTRODUCTION

The correlation energy E^{corr} is defined as the difference between the Hartree–Fock (HF) total energy E^{HF} and the nonrelativistic exact total energy E^{exact}[1]:

$$E^{\text{corr}} = E^{\text{exact}} - E^{\text{HF}}. \tag{1}$$

Semiempirical value of E^{corr} obtained by Clementi[2] has been used widely.[3-6] In obtaining E^{corr}, Clementi has used E^{exact} obtained from the experimental total energy E^{exptl} as

$$E^{\text{exact}} = E^{\text{exptl}} - E^{\text{"rel"}}, \tag{2}$$

where $E^{\text{"rel"}}$ is supposed to be the relativistic effect. Instead of using E^{rel} values obtained by Clementi himself,[7] which are essentially the same as published later by Fraga,[8] he has adopted semiempirical values estimated by Scherr, Silverman and Matsen,[9] who have taken all effects, not included in nonrelativistic calculations, together into $E^{\text{"rel"}}$. Remembering accurate calculations on helium-like atoms by Pekeris[10] and by Midtdal and Aashamar,[11] one would have to have used

$$E^{\text{exact}} = E^{\text{exptl}} - E^{\text{rel}} - E_M - E_L \tag{3}$$

rather than Eq. (2). In Eq. (3), E_M and E_L stand for the mass polarization and the Lamb shift, respectively. The mass polarization is the effect of the electron correlation upon the nuclear motion and comes mostly from a pair of $1s$

electrons[12]; it changes little with Z for isoelectronic atoms[13(a)] so that it can be ignored as compared with E^{rel} or E_L when $Z > 3$.[13(b)] Equation (2) then becomes

$$E^{\text{exact}} = E^{\text{exptl}} - E^{\text{rel}} - E_L. \tag{4}$$

As will be shown in a separate paper,[14] E^{rel} calculated either with HF wave functions or with correlated wave functions for isoelectronic atoms can be fitted to an equation

$$E^{\text{rel}} = a(Z - s)^4, \tag{5}$$

where a and s are constants, whereas E_L can be fitted to another equation

$$E_L = a'(Z - s')^3, \tag{6}$$

with constants a' and s', rather than Eq. (5). Moreover, E^{rel} for atoms[13(a)] with a constant Z value depends upon the number of electrons, whereas E_L for such atoms are almost independent of the number of electrons in so far as the $1s^2$ core is preserved.[15] It should, therefore, be apparent that E^{rel} and E_L must be treated separately in a semiempirical analysis of electronic energies of atoms.

The value of E^{exptl} can be obtained as the sum of the ionization potentials (IPs) obtained either experimentally or by extrapolation of experimental data,[16,17] so that E^{exact} values can be calculated if E^{rel} suitably chosen are used, since E_L values are known.[11,15] Then, E^{corr} can be calculated with Eq. (1) by using either E^{HF} obtained by Fraga[18] with numerical HF calculations or those obtained by Clementi and Roetti with analytical HF calculations.[19,20] This scheme

in obtaining E^{corr} have been used by Veillard and Clementi[21] and by Sasaki and Yoshimine,[22] although the Lamb shift correction has erroneously been made by Veillard *et al.*[23] No systematic data on E^{corr} covering not only neutral atoms but also isoelectronic positive ions based upon on Eqs. (1) and (4), however, are available. In the present paper, it will be shown that E^{exact} calculated with Eq. (4) for the isoelectronic series do not show the Z dependence expected from the theory, if E^{rel} values calculated with conventional *ab initio* methods are used along with E^{exptl}. This would mean that E^{corr} obtained by Eq. (1) from such E^{exact} should be in error. It will actually be shown that the Z dependence of E^{corr} thus obtained for an isoelectronic series is not in conformity with what one would expect from the theory such as due to Sinanoğlu.[3,4] It is suspected something must be wrong in evaluating E^{rel} with conventional methods, for use in the present context. It will, therefore, be discussed what the relativistic correction is, to be used in Eq. (4), and a semiempirical scheme to obtain adequate values of the relativistic correction will be proposed in the present paper.

II. DISCUSSION ON THE *AB INITIO* CALCULATION OF THE RELATIVISTIC EFFECT

The relativistic effect can formally be defined as the difference between the exact eigenvalues of the relativistic and nonrelativistic Hamiltonian of the system. It is well known that the Hamiltonian can be written down immediately for any system so far as one can ignore the relativistic effect. If the relativistic effect can*not* be ignored in such cases as heavy atoms, the situation becomes different: the Hamiltonian cannot be written out in a closed form if more than one electron is present in the system.[24] If the system involves only one electron, the Dirac theory is sufficient. If more than one electron is present in the system, however, the Hamiltonian taken to be the sum of the one-electron Dirac Hamiltonian plus the electron–electron repulsion must be amended by the magnetic and retardation effect, as has been pointed out by Breit.[25] Such effect as a whole is called the Breit interaction.[24] It is well known, however, that the Hamiltonian including the Breit interaction is not to be taken as the exact Hamiltonian of the system and that the Breit interaction is to be taken as the first-order correction to energy.[24,26] It seems that there are two ways to get the energy corresponding to this approximate Hamiltonian: the first is to do HF-type calculations by using the Hamiltonian which is composed of the Dirac-type Hamiltonian for each of electrons and the interelectron repulsion only. Such HF-type calculations, called Dirac–Hartree–Fock (DHF) calculations, must then be amended by the correction for the Breit-type interaction by using the first-order perturbation theory. The second type is to take the expectation value of the relativistic Hamiltonian composed of the sum of Dirac-type one-electron Hamiltonians and the interaction between electrons where the Breit-type interaction is added, with respect to a nonrelativistic wave function either of a HF type or of more general type including the electron correlation effect. The first type calculations have been performed by Desclaux[27] and by Mann and Johnson.[28] The second type calculations have been done by Hartmann and Clementi[7] as well as by Fraga[8]

by using HF wave functions and by Pekeris[10] as well as by Midtdal and Aashamar[11] by using wave functions including electron correlation effect.

In view of the fact that the nonrelativistic Hamiltonian is "exact" but the relativistic Hamiltonian is correct only to the first order, the connection between DHF type calculations, as amended by the Breit-type interaction,[26,27] and Clementi–Fraga-type calculations[7,8] using nonrelativistic HF wave functions are in order. In Table I, relativistic effects, obtained as differences between "relativistic" total energies derived from DHF-type calculations by Desclaux[27] and by Mann and Johnson[28] with or without the Breit-type correction and nonrelativistic HF total energies, are compared with Clementi's[7] and Fraga's data.[8] It may be seen that Desclaux's calculation[27] has given much the same numerical values as those given by Mann and Johnson's calculation.[28] It may also be seen that these values are nearly in agreement with the results of Clementi–Fraga calculations[7,8] for He through Ar. It may also be seen for Kr, Xe, and Rn that relativistic effects obtained from calculations by Desclaux[27] and by Mann and Johnson[28] get larger in absolute value than the Clementi–Fraga value,[7,8] the difference becoming larger in this order. It might be thought that this phenomenon is due to higher values of Z for Kr, Xe, and Rn as compared with He, Ne, and Ar. One should, however, remember the fact that not only Z but also the number of electrons becomes larger for neutral atoms of Kr, etc. in comparison with He, etc. If results of DHF calculations covering not only neutral atoms but also a wide range of ions were available, one would be able to give an answer to the question whether such disagreement is due to a higher value of Z or to a larger number of electrons. In any case, Fraga's estimate for E^{rel} is fairly accurate so far as the number of electrons is not more than 18 and if $Z \leq 20$ at least to the extent that a DHF calculation as amended by the Breit correction, gives a "true" relativistic correction. Since we confine ourselves to 2–10 electron isoelectronic atoms with $Z \leq 20$ in the present work, we may be able to use Fraga's extensive E^{rel} data without worrying about the difference between the HF value and the DHF value mentioned above.

III. CATASTROPHE IN CORRELATION ENERGY

We are now in a position to get E^{exact} from E^{exptl} with Eq. (4) by using Fraga's values[8] of E^{rel}. The value of E^{corr} may then be obtained with Eq. (1). As for experimental values of IPs to be used to get E^{exptl}, data compiled by Moore[16] have been adopted except a few cases. Moore has listed IPs either measured experimentally or calculated rigorously from theory as far as possible. When no such data are available, she has adopted Edlén's value[17] based upon extrapolation formulas. Edlén has, however, given actual numerical values for neutral atoms and positive ions up to $q = +14$. When no data are available even in Edlén's table, Moore has adopted Lotz's[29] estimated values by enclosing in a pair of brackets. In the present work, we have used calculated values based upon Edlén's extrapolation formulas[17] even in such cases for reasons to be described in Sec. IV of this paper, by rounding off at the order of ten kaysers. Such a

TABLE I. Comparison of relativistic effect on total energies of neutral atoms of rare-gas elements calculated by various authors (au).

	Hartmann–[a] Clementi	Fraga[b]	Midtdal[c]	Desclaux[d] With[f]	Desclaux[d] Without[f]	Mann–Johnson[e] With[f]	Mann–Johnson[e] Without[f]
He	− 0.000 071	− 0.000 0708	− 0.000 103 9	− 0.000 05	− 0.000 11	− 0.000 04	− 0.000 103
Ne	− 0.131 293	− 0.128 9864		− 0.126 8	− 0.144 35	− 0.128 06	− 0.144 71
Ar	− 1.766 130	− 1.731 965		− 1.722 2	− 1.865 62	− 1.733 48	− 1.865 84
Kr		− 34.408 79		− 35.226	− 36.804 18	− 35.378 9	− 36.805 7
Xe		− 194.553 8		− 208.319	− 214.759 5	− 208.982	− 214.757
Rn		− 1386.518		− 1702.33	− 1735.207 9	− 1706.287	− 1735.684

[a] Reference 7.
[b] Reference 8.
[c] Reference 11.
[d] Reference 27.
[e] Reference 28.
[f] "With" and "Without" stand for with and without including the Breit interaction, respectively.

value of the IP will be called "Moore's value amended by Edlén's value" to distinguish from Moore's[16] compilation itself. For two-electron systems, Pekeris[10] and Midtdal[11] have published theoretical values of the total energy in the ground state including not only the electron correlation but also the relativistic as well as the radiative effect (Lamb shift). Their values agree almost perfectly with experimental values of helium-like atoms with lower Z values. For helium-like atoms with higher Z values, theoretical values are believed to be more accurate than experimental values, because experimental values involve IPs of higher stages and are subject to experimental error. Therefore, E^{expt1} have been calibrated by using data of two-electron systems.

As for E_L, it has been taken to be equal to those of two-electron systems in their ground states with same Z, on the basis of a work by present authors.[15] Actual numerical values adopted for E_L are those given by Midtdal and Aashamar.[11]

Before getting into the problem of E^{corr}, we are going to see E^{exact} values with Eq. (4) by using various quantities obtained as outlined above. In a previous paper, Anno and Teruya have shown that the nonrelativistic total energy E^{exact} for an isoelectronic series of atoms can be fitted very accurately into an equation[30,31]

$$E^{\text{exact}} = (1/2)LZ^2 + KZ + W_2 + W'_3(Z - \alpha)^{-1}, \quad (7)$$

where L and K are constants characteristic of the isoelectronic series, which can be calculated exactly by using hydrogenic wave functions,[32] while W_2, W'_3, and α are parameters to be determined through a least-squares fit (LSF). From the functional form of Eq. (7), it is expected that the quantity E_2 defined as

$$E_2 = E^{\text{exact}} - (1/2)LZ^2 - KZ \quad (8)$$

should approach an asymptotic value W_2 when $Z \to \infty$. In Fig. 1, this quantity obtained from E^{exact} values mentioned above is plotted against Z for 2–10 isoelectronic series. It may be seen that none of curves bear out our expectation. We suspect that something must be wrong in E^{rel}. It is to be added that E^{exact} thus obtained gives, through Eq. (1) with

E^{HF},[18–20] such $|E^{\text{corr}}|$ vs Z curves for isoelectronic atoms that show minima (and maxima) or decrease monotonically.

As for the He series, accurate nonrelativistic values of the total energy are available,[10,11] so that E^{corr} can be obtained without invoking E^{rel}. The E^{corr} value thus obtained for the He series has been found to increase in its absolute value *monotonically* when $Z \to \infty$. According to Sinanoğlu's many-electron theory,[3,4] the total correlation energy E^{corr} is generally divided into three physically distinct types of correlations: internal E_{int}, semiinternal plus polarization E_F,
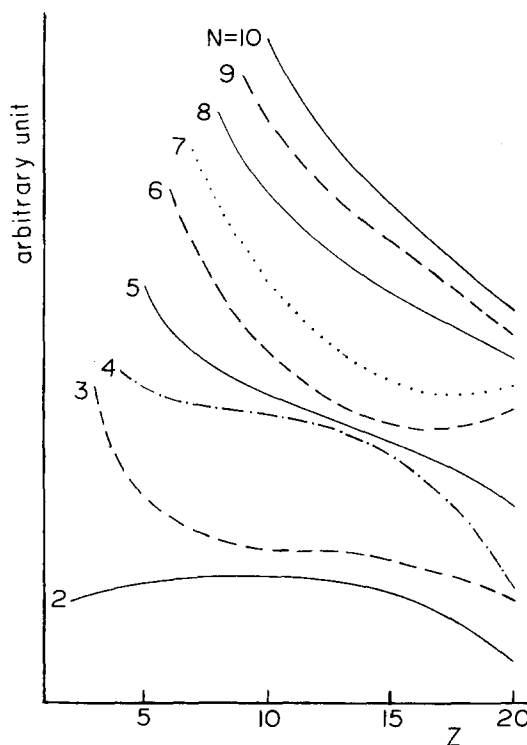

FIG. 1. E_2 defined by Eq. (8) of the text, plotted against atomic number Z for the 2–10 electron isoelectronic series. Note that E_2 is negative, so that ordinate represents the absolute value of this quantity in arbitrary units.

TABLE II. Relativistic effect in He-like atoms as obtained by various methods (au).

Z	Fraga[a]	Calc 1	Calc 2	Midtdal[b]
2	− 0.000 070 8	− 0.000 075 5	− 0.000 105 3	− 0.000 103 9
3	− 0.000 538 6	− 0.000 556 4	− 0.000 629 0	− 0.000 628 8
4	− 0.002 060 1	− 0.002 095 4	− 0.002 222 7	− 0.002 225 6
5	− 0.005 605 1	− 0.005 662 8	− 0.005 851 9	− 0.005 859 2
6	− 0.012 468 6	− 0.012 547 7	− 0.012 801 4	− 0.012 813 9
7	− 0.024 274 3	− 0.024 358 0	− 0.024 675 4	− 0.024 693 7
8	− 0.042 961 1	− 0.043 020 3	− 0.043 397 8	− 0.043 421 9
9	− 0.070 790 5	− 0.070 780 0	− 0.071 211 7	− 0.071 241 4
10	− 0.110 349 0	− 0.110 201 0	− 0.110 680 0	− 0.110 715 0
11	− 0.164 544 0	− 0.164 167 0	− 0.164 684 0	− 0.164 724 0
12	− 0.236 606 0	− 0.235 878 0	− 0.236 425 0	− 0.236 469 0
13	− 0.330 087 0	− 0.328 857 0	− 0.329 426 0	− 0.329 473 0
14	− 0.448 780 0	− 0.446 940 0	− 0.447 525 0	− 0.447 575 0
15	− 0.597 120 0	− 0.594 288 0	− 0.594 883 0	− 0.594 936 0
16	− 0.779 393 0	− 0.775 375 0	− 0.775 979 0	− 0.776 034 0
17	− 1.000 510 0	− 0.994 999 0	− 0.995 612 0	− 0.995 668 0
18	− 1.265 650 0	− 1.258 270 0	− 1.258 900 0	− 1.258 960 0
19	− 1.580 280 0	− 1.570 630 0	− 1.571 280 0	− 1.571 340 0
20	− 1.950 230 0	− 1.937 820 0	− 1.938 510 0	− 1.938 570 0

[a] Reference 8.
[b] Reference 11.

TABLE III. Comparison of the relativistic effect obtained by the present work with those obtained by Hartmann and Clementi and by Fraga (au).[a]

· Z	Hartmann–[b] Clementi	Fraga[c]	Present · work
(N = 2)			
2	− 7.1(− 5)	− 7.08(− 5)	− 7.549 2(− 5)
4	− 2.090(− 3)	− 2.0960(− 3)	− 2.095 4(− 3)
10	− 1.098 90(− 1)	− 1.1035(− 1)	− 1.102 0(− 1)
20	− 1.934 64(0)	− 1.9502(0)	− 1.937 8(0)
(N = 4)			
4	− 2.200(− 3)	− 2.1914(− 3)	− 2.296 1(− 3)
10	− 1.320 01(− 1)	− 1.3192(− 1)	− 1.308 0(− 1)
20	− 2.427 21(0)	− 2.4393(0)	− 2.355 5(0)
(N = 10)			
10	− 1.312 93(− 1)	− 1.2899(− 1)	− 0.967 66(− 1)
20	− 2.728 09(0)	− 2.6792(0)	− 2.457 5(0)

[a] − 7.1(− 5), for example, stands for − 7.1×10⁻⁵.
[b] See Ref. 7.
[c] See Ref. 8.

and all external E_u. In atoms and ions of rare-gas-type electronic structures, E^{corr} consists only of E_u. Therefore, $|E^{corr}|$ vs Z curve of the Ne series should behave in much the same way as that of the He series, contrary to its behavior mentioned before. This is another reason why we suspect that E^{rel} values from Fraga's work[8] are inappropriate to be used in the present context.

So far as the He series is concerned, the different feature of the $|E^{corr}|$ vs Z curve for this series obtained by using Fraga's E^{rel} as compared with the correct curve comes essentially from the difference between Fraga's[8] E^{rel} and Midtdal's.[11] In Table II, Fraga's E^{rel} values are compared with Midtdal's values. It may be seen that they agree with each other for around $Z = 10$ but there is a subtle difference when Z gets larger or smaller. The difference between these two calculations lies only in the difference of the wave function used: a HF wave function or a wave function including electron correlation. The difference between the two sets of numerical values given in Table II may therefore be regarded as the effect of the correlation within a pair of 1s electrons. If this is the case, Fraga's E^{rel} values for all atoms with 1$s^2$2s^m2p^n configuration must be corrected at least for the correlation within the 1s-electron pair.

From this point of view, the "corrected" relativistic effect, denoted as E_C^{rel}, within an atom has been obtained as

$$E_C^{rel} = E_{Fraga}^{rel} - [E_{Fraga}^{rel}(2) - E_{Midtdal}^{rel}(2)] \qquad (9)$$

and has been used to get E^{corr}. In Eq. (9), $E_{Fraga}^{rel}(2)$ and $E_{Midtdal}^{rel}(2)$ stand for the Fraga and Midtdal E^{rel} value, respectively, of the He-like atom having the same Z value as the atom under consideration. The E^{corr} values thus obtained for the Li series have been found to show a proper Z dependence. However, $|E^{corr}|$ vs Z curves for 4–10 electron systems still do not behave properly. Perhaps, correlation effect upon E^{rel} among 2s and/or 2p electrons may have to

be taken into account, although the 1s–2s correlation is not important in just the same way as in the case of determining E^{corr} itself.[4] Unfortunately, however, there are no accurate calculations including correlation effect except for the He series. We must, therefore, look for some semiempirical methods to get relativistic corrections.

IV. SEMIEMPIRICAL ESTIMATE OF RELATIVISTIC CORRECTIONS AND EXACT NONRELATIVISTIC ENERGIES

As was discussed before, E^{rel} for an isoelectronic series of atoms can be fitted to an equation of the type Eq. (5). Since $E^{exptl} - E_L$ must equal to $E^{exact} + E^{rel}$, the following equation, which is the combination of Eqs. (5) and (7), may be regarded as an appropriate equation for the $E^{exptl} - E_L$ data of an isoelectronic series of atoms to be fitted:

$$E^{exptl} - E_L = (1/2)LZ^2 + KZ + W_2$$
$$+ W'_3(Z - \alpha)^{-1} + a(Z - s)^4. \qquad (10)$$

By using resulting values of parameters, E^{rel} can be obtained as the last term of Eq. (10), while E^{exact} can be obtained as the rest.

· In actual numerical calculations, two sets of LSF of Eq. (10) have been tried: one based upon E^{exptl} values obtained as described in Sec. III, and the other based upon E^{exptl} obtained as the sum of IPs compiled by Moore,[16] *without* amendments using Edlén's formulas. In the latter case, convergence has, however, not been obtained except for the 10-electron series.[33] It is believed therefore that such amendments are essential. Table III compares semiempirical values of E^{rel} obtained in the present work with Clementi's and Fraga's values.[7,8] It may be seen that our semiempirical value of E^{rel} agrees fairly well with the Clementi–Fraga value, although the agreement is only qualitative when the number of electrons characteristic of the series gets larger especially for a lower Z value. As will be described in the next section, E^{exact} extracted from experimental total energy as described above in this section gives such E^{corr} value that

shows a Z dependence expected from the Sinanoğlu theory.[3,4] This would mean that the Z dependence of E^{corr} for an isoelectronic series of atoms depends upon a subtle difference in the Z dependence of E^{rel}.

V. CALCULATION OF CORRELATION ENERGY

Now that we have been able to extract E^{exact} from E^{exptl} as well as E^{rel}, we should be able to get E^{corr} with Eq. (1) by

TABLE IV. Comparison of the correlation energies obtained in the present work (lower row) with Clementi's value (upper row) (au). All in negative. The probable error of our semiempirical estimate is given in parentheses.

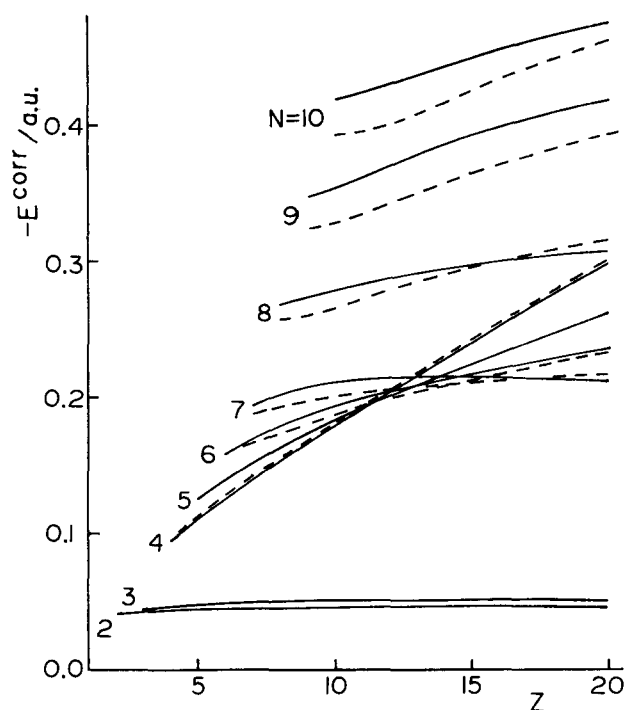| Z	He	Li	Be	B	C	N	O	F	Ne
2	0.0421								
	0.0418								
	(0.28D-03)								
3	0.0435	0.0453							
	0.0435	0.0454							
	(0.20D-03)	(0.16D-02)							
4	0.0443	0.0475	0.0944						
	0.0444	0.0476	0.0944						
	(0.16D-03)	(0.91D-03)	(0.31D-02)						
5	0.0448	0.0489	0.1123	0.125					
	0.0449	0.0488	0.1111	0.1258					
	(0.14D-03)	(0.67D-03)	(0.19D-02)	(0.57D-02)					
6	0.0451	0.0498	0.1268	0.139	0.158				
	0.0453	0.0496	0.1263	0.1402	0.1593				
	(0.12D-03)	(0.56D-03)	(0.15D-02)	(0.41D-02)	(0.18D-01)				
7	0.0453	0.0505	0.1412	0.151	0.167	0.188			
	0.0456	0.0501	0.1404	0.1525	0.1718	0.1948			
	(0.11D-03)	(0.50D-03)	(0.13D-02)	(0.33D-02)	(0.15D-01)	(0.44D-01)			
8	0.0455	0.051	0.1551	0.162	0.175	0.193	0.258		
	0.0458	0.0505	0.1539	0.1634	0.1808	0.2046	0.2686		
	(0.10D-03)	(0.46D-03)	(0.11D-02)	(0.29D-02)	(0.12D-01)	(0.38D-01)	(0.35D-01)		
9	0.0456	0.0513	0.1684	0.173	0.182	0.197	0.26	0.324	
	0.0460	0.0508	0.1669	0.1733	0.1880	0.2095	0.2744	0.3477	
	(0.98D-04)	(0.43D-03)	(0.10D-02)	(0.26D-02)	(0.11D-01)	(0.34D-01)	(0.29D-01)	(0.59D-01)	
10	0.0457	0.0516	0.1814	0.182	0.188	0.2	0.267	0.328	0.393
	0.0462	0.0511	0.1797	0.1827	0.1942	0.2121	0.2795	0.3551	0.4193
	(0.94D-04)	(0.41D-03)	(0.97D-03)	(0.24D-02)	(0.10D-01)	(0.31D-01)	(0.26D-01)	(0.49D-01)	(0.79D-01)
11	0.0458	0.0519	0.1941	0.191	0.193	0.203	0.274	0.336	0.396
	0.0463	0.0512	0.1923	0.1916	0.1997	0.2136	0.2841	0.3633	0.4247
	(0.90D-04)	(0.40D-03)	(0.93D-03)	(0.22D-02)	(0.93D-02)	(0.28D-01)	(0.23D-01)	(0.43D-01)	(0.68D-01)
12	0.0459	0.0521	0.2066	0.2	0.199	0.205	0.279	0.344	0.402
	0.0464	0.0514	0.2047	0.2001	0.2047	0.2144	0.2882	0.3717	0.4309
	(0.87D-04)	(0.39D-03)	(0.90D-03)	(0.21D-02)	(0.88D-02)	(0.27D-01)	(0.21D-01)	(0.39D-01)	(0.61D-01)
13	0.0459	0.0523	0.219	0.208	0.204	0.207	0.285	0.35	0.409
	0.0465	0.0515	0.2170	0.2084	0.2094	0.2147	0.2919	0.3797	0.4374
	(0.85D-04)	(0.38D-03)	(0.88D-03)	(0.21D-02)	(0.84D-02)	(0.25D-01)	(0.20D-01)	(0.36D-01)	(0.56D-01)
14	0.046	0.0524	0.2313	0.216	0.209	0.209	0.291	0.358	0.417
	0.0465	0.0517	0.2292	0.2165	0.2138	0.2149	0.2952	0.3871	0.4439
	(0.83D-04)	(0.37D-03)	(0.86D-03)	(0.20D-02)	(0.81D-02)	(0.24D-01)	(0.19D-01)	(0.34D-01)	(0.52D-01)
15	0.0461	0.0525	0.2435	0.225	0.214	0.211	0.296	0.366	0.426
	0.0466	0.0516	0.2413	0.2243	0.2180	0.2148	0.2981	0.3938	0.4502
	(0.82D-04)	(0.37D-03)	(0.84D-03)	(0.19D-02)	(0.78D-02)	(0.23D-01)	(0.18D-01)	(0.33D-01)	(0.49D-01)
16	0.0461	0.0527	0.2556	0.232	0.218	0.213	0.301	0.372	0.434
	0.0467	0.0518	0.2534	0.2321	0.2221	0.2147	0.3007	0.4000	0.4561
	(0.80D-04)	(0.36D-03)	(0.83D-03)	(0.19D-02)	(0.76D-02)	(0.23D-01)	(0.18D-01)	(0.31D-01)	(0.47D-01)
17	0.0462	0.0528	0.2677	0.24	0.222	0.214	0.305	0.379	0.442
	0.0467	0.0519	0.2655	0.2398	0.2260	0.2145	0.3032	0.4056	0.4617
	(0.79D-04)	(0.36D-03)	(0.82D-03)	(0.19D-02)	(0.75D-02)	(0.22D-01)	(0.17D-01)	(0.30D-01)	(0.45D-01)
18	0.0463	0.0529	0.2797	0.248	0.227	0.215	0.309	0.384	0.449
	0.0468	0.0520	0.2775	0.2474	0.2298	0.2143	0.3053	0.4107	0.4670
	(0.78D-04)	(0.36D-03)	(0.82D-03)	(0.19D-02)	(0.73D-02)	(0.21D-01)	(0.17D-01)	(0.30D-01)	(0.44D-01)
19	0.0463	0.0529	0.2917	0.255	0.231	0.217	0.313	0.389	0.456
	0.0468	0.0520	0.2894	0.2549	0.2335	0.2140	0.3072	0.4153	0.4717
	(0.78D-04)	(0.36D-03)	(0.81D-03)	(0.18D-02)	(0.72D-02)	(0.21D-01)	(0.16D-01)	(0.29D-01)	(0.43D-01)
20	0.0463	0.053	0.3037	0.263	0.235	0.218	0.317	0.394	0.463
	0.0468	0.0521	0.3014	0.2624	0.2372	0.2137	0.3090	0.4195	0.4761
	(0.77D-04)	(0.35D-03)	(0.80D-03)	(0.18D-02)	(0.71D-02)	(0.21D-01)	(0.16D-01)	(0.28D-01)	(0.42D-01)

FIG. 2. The correlation energy obtained with Eq. (1) by using E^{exact} obtained through the least-squares fit of Eq. (10) to the experimental total energy, as plotted against the atomic number Z for the 2–10 electron isoelectronic series. Similar plots of Clementi's correlation energy are also given in dashed curves. For the 2 and 3 electron series Clementi's E^{corr} is so close to our value that dashed curves cannot be distinguished from full curves for these series. Note that the general feature of the two sets of correlation energies are similar to each other.

using Fraga's numerical HF energy.[18] The results are given in Table IV. The probable error is also given in parentheses. Clementi's values[2] are also given for comparison. It may be seen that our E^{corr} agrees essentially with Clementi's value. In Fig. 2, our $|E^{corr}|$ is plotted against Z for 2–10 electron atoms. Clementi's[2] $|E^{corr}|$ is also plotted in dashed curves. It may be seen that general feature of these two sets of $|E^{corr}|$ vs Z curves are essentially the same and "anomaly" mentioned in Sec. III may be seen to have disappeared. In view of the fact that Clementi's E^{corr} values have been successfully used for analyses of atomic correlation energies,[3–6] it may be claimed that our E^{corr} values are also reasonable. It is true that whether or not our set of E^{corr} is preferable numerically

to the Clementi set is not clear at this moment for lack of accurate calculations on atoms with more than two electrons, having comparable accuracy to those on the He isoelectronic series, but it may be claimed that our scheme of semiempirical determination of E^{corr} is logically preferable to the Scherr–Clementi scheme. Accurate *ab initio* calculations are, therefore, needed also for obtaining E^{rel}.

VI. FURTHER REFINEMENT OF SEMIEMPIRICAL ESTIMATE OF RELATIVISTIC CORRECTION

As has been described in Sec. IV, we have been able to extract very useful information on E^{rel} by fitting semiempirical formula Eq. (10) to E^{exptl} data for isoelectronic atoms. Closer examination of the data of Table III reveals that Z dependence of our semiempirical E^{rel} for an isoelectronic atoms is different from that of Fraga's E^{rel}. Although we are *not* claiming that our E^{rel} values are more correct than Fraga's[8] for all atoms and ions, especially in view of the uncertainty of IPs used in our scheme, the difference between Fraga's E^{rel} and more accurate values of E^{rel} obtained with correlated wave function[11] for the He-like atoms, pointed out in Sec. III, must now be recalled. In Table II, where such more accurate E^{rel} values are compared with Fraga's[8] values, our semiempirical E^{rel} values are also included for comparison under the heading of Calc 1. It is true that E^{rel} of the three kinds agree very well with each other for around $Z = 10$ but there is a subtle difference when Z gets larger or smaller. This would again imply that Eq. (5) is yet to be improved for it to be able to represent the E^{rel} more adequately. It may require at least another term to represent the Z dependence correctly. It has therefore been tried to fit

$$E^{exptl} - E_L = (1/2)LZ^2 + KZ + W_2$$
$$+ W'_3(Z - \alpha)^{-1} + a(Z - s)^4 + bZ^4, \quad (11)$$

corresponding to

$$E^{rel} = a(Z - s)^4 + bZ^4, \quad (12)$$

by using Midtdal's[11] E^{theor} as E^{exptl} for the He series. Note that both Eqs. (10) and (11) can be expanded as power series in Z. The quality of LSFs may be assessed by comparing the results of such expansions, using the numerical values of parameters obtained through respective least-squares fit, with Midtdal's exact estimate of the expansion coeffi-

TABLE V. Comparison of numerical values of coefficients of various powers of Z obtained by expanding semiempirical formulas Eqs. (10) and (11) for experimental total energies of isoelectronic atoms corrected for the Lamb shift in the same case of He isoelectronic series.

Powers	Eq. (10)	Eq. (11)	Ab initio calculation
Z^4	$1.328\ 17 \times 10^{-5}$	$1.331\ 00 \times 10^{-5}$	$1.331\ 28 \times 10^{-5}$ [a]
Z^3	-2.4223×10^{-5}	-2.544×10^{-5}	$-2.556\ 77 \times 10^{-5}$ [a]
Z^0	$0.158\ 658$	$0.157\ 734$	$0.157\ 666$ [b]
Z^{-1}	-17.23×10^{-3}	$-9.611\ 34 \times 10^{-3}$	$-8.699\ 03 \times 10^{-3}$ [b]

[a] See Ref. 35.
[b] See Ref. 34.

cients based upon a very accurate Z^{-1} expansion-type non-relativistic calculation[34] and the Dalgarno–Stewart relativistic calculation[35] using the Kinoshita wave function. Table V gives such a comparison. It may be seen that the agreement of the coefficients are better for those obtained from the LSF based upon Eq. (11) rather than upon Eq. (10). The E^{rel} values calculated with Eq. (12), which represents the relativistic part of Eq. (11), by using the parameters just obtained, are included in Table II under the heading of Calc2. The results are in almost complete agreement with Midtdal's accurate E^{rel} values.[11] It may therefore be concluded that Eq. (11) is expected to work very well to extract E^{exact} and E^{rel} properly by fitting $E^{\text{exptl}} - E_L$ data for an isoelectronic atoms, so far as such a set of data is reliable. A LSF of the $E^{\text{exptl}} - E_L$ data to Eq. (11), therefore, has also been tried for each of 3–10 electron series. A convergence has, however, not been obtained. Perhaps, E^{exptl} data are not accurate enough for this purpose due to inaccuracy involved in the experimental data on IPs.

ACKNOWLEDGMENT

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