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Ground-state correlation energies for two- to ten-electron atomic ions

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Improved estimates of the nonrelativistic stationary nucleus correlation energies of the ground-state atomic ions with three to ten electrons and Z up to 20 are derived by combining experimental data and improved *ab initio* calculations. Unlike previous work in this area, we focus on the correlation contribution to individual ionization energies, computed by comparing experimental data with relativistic complete-valence-space Hartree-Fock energies.

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INTRODUCTION

The exact ground-state eigenvalues $E(N,Z)$ of the nonrelativistic, stationary nucleus, Coulomb field Hamiltonian for atomic ions in Hartree units,

$$H=\sum_{i=1}^{N}\left[-\tfrac{1}{2}\nabla_i^2-Z/r_i+\sum_{j(<i)}1/r_{ij}\right], \qquad (1)$$

where N is the number of electrons and Z is the nuclear charge, are of considerable interest as calibration points for *ab initio* and density-functional calculations of atoms and molecules. Estimates for E can be obtained from spectroscopic data corrected for relativistic effects. Scherr, Silverman, and Matsen [1] were the first to use the tabulations of Moore [2(a)] to obtain values of the relativistic corrections for the ground-state energies of 3- to 10-electron atomic ions. Their results are surprisingly accurate, considering that their analysis was entirely empirical. Clementi [3] estimated correlation energies of atoms by subtracting from the experimental ground-state energies obtained from Moore's tabulations [2(a)] the values of the corresponding Hartree-Fock energy E_{HF} and relativistic corrections [4] from Breit-Pauli perturbation theory. Even though the HF energies were calculated with adequate accuracy, the relativistic corrections, especially the radiative terms, were not available with sufficient accuracy. Recently, Anno and Teruya [5] have suggested a semiempirical refinement of relativistic energies for Z up to 20, and they have computed nonrelativistic energies and correlation energies using Moore's revised tables [2(b)]. With the advent of accurate relativistic corrections [4,6,7] and fully relativistic numerical Dirac-Fock computations, reasonably accurate estimations of all higher-order radiative corrections have become possible [8–12]. In this paper, we have examined the problem of estimating an accurate correlation energy E_c, where

$$E_c(N,Z)=E(N,Z)-E_{\mathrm{HF}}(N,Z) \qquad (2)$$

following an approach somewhat different from Anno and Teruya.

THE NONRELATIVISTIC TOTAL ENERGY

One approach to finding E would be just to solve the Schrödinger equation to the desired accuracy. This can be done exactly for $N=1$ and to more accuracy than needed for our purposes [13] for $N=2$ for all Z. In Table I, we list the total energies for $N=1$ and 2 along with $E_{\mathrm{HF}}(2,Z)$ and $E_c(2,Z)$. Beyond $N=2$, the accuracy obtainable is less than is desired and decreases with increasing N. Also little work of any kind has been published for $Z \gg N$.

Another related approach is based on extending the results to high Z based on the formal Laurent series in Z^{-1}, where E/Z^2 has a power series [1,14,15] in Z^{-1}. For closed-shell systems where a single configuration is an adequate zeroth-order approximation to the wave function, E_c has a series in Z^{-1} beginning with a constant term. For other systems the Hartree-Fock approximation is not a good zero-order approximation due to the inherent multiconfiguration nature of the ground-state configuration, e.g., the $2s^2$-$2p^2$ near degeneracy mixing in a Be atom [16]. In hydrogenlike atoms, the $2s$ and $2p$ orbitals are degenerate; in many-electron systems this exact degeneracy is lifted due to electron-electron repulsion. The effect on the energy of the near degeneracy of atomic configurations in many-electron systems has been calculated for a number of atoms of the first and second period by Clementi and Veillard [17]. For example, the Be atom has two important configurations, viz., $1s^22s^2$ and $1s^22p^2$, which are nearly degenerate and therefore need to be treated as equally important in deriving a zeroth-order approximation to the wave function and total energy [18]. The Laurent series of E_c for such systems begins with a linear term in Z. This problem is circumvented with the use of a modified correlation energy E_c'

$$E_c'(N,Z)=E(N,Z)-E_{\mathrm{CAS}}(N,Z), \qquad (3)$$

where E_{CAS} is the complete-active-space (CAS) self-consistent-field energy, viz., a multiconfiguration calculation including all possible valence-electron–valence-orbital configurations.

TABLE I. Total energies for $N=1$ and 2, along with $E_{\mathrm{HF}}(2,Z)$ and $E_c(2,Z)$. All values are in hartrees.

Z	$-E(1,Z)$	$-E(2,Z)$	$-E_{\mathrm{HF}}(2,Z)$	$-E_c(2,Z)$
2	2.00	2.903 724	2.861 680	0.042 044
3	4.50	7.279 913	7.236 415	0.043 498
4	8.00	13.655 566	13.611 299	0.044 267
5	12.50	22.030 972	21.986 234	0.044 737
6	18.00	32.406 247	32.361 193	0.045 054
7	24.50	44.781 445	44.736 164	0.045 281
8	32.00	59.156 595	59.111 143	0.045 452
9	40.50	75.531 712	75.486 126	0.045 586
10	50.00	93.906 807	93.861 113	0.045 693
11	60.50	114.281 884	114.236 103	0.045 781
12	72.00	136.656 948	136.611 094	0.045 854
13	84.50	161.032 003	160.986 087	0.045 916
14	98.00	187.407 050	187.361 081	0.045 969
15	112.50	215.782 091	215.736 075	0.046 015
16	128.00	246.157 126	246.111 071	0.046 056
17	144.50	278.532 158	278.486 067	0.046 091
18	162.00	312.907 186	312.861 063	0.046 123
19	180.50	349.282 211	349.236 060	0.046 151
20	200.00	387.657 234	387.611 057	0.046 177

We now define a few quantities that will be used in our subsequent analysis and calculations. The energy increment $\Delta E(N,Z)$ is the difference of the N-electron energy and its $N-1$-electron counterpart, i.e., the negative of the ionization potential $-I(N,Z)$,

$$\Delta E(N,Z)=-I(N,Z)=E(N,Z)-E(N-1,Z)\ . \quad (4)$$

Thus, the Hartree-Fock $\Delta E_{\mathrm{HF}}(N,Z)$ is

$$\Delta E_{\mathrm{HF}}(N,Z)=-I_{\mathrm{HF}}(N,Z)=E_{\mathrm{HF}}(N,Z)-E_{\mathrm{HF}}(N-1,Z)\ , \quad (5)$$

the CAS ΔE is

$$\begin{aligned}\Delta E_{\mathrm{CAS}}(N,Z)&=-I_{\mathrm{CAS}}(N,Z)\\&=E_{\mathrm{CAS}}(N,Z)-E_{\mathrm{CAS}}(N-1,Z)\ ,\end{aligned} \quad (6)$$

and the modified correlation contribution to the energy increment is

$$\Delta E_c'(N,Z)=E_c'(N,Z)-E_c'(N-1,Z)\ . \quad (7)$$

Since E_c' has a series expansion in Z^{-1} beginning with a constant term, so does $\Delta E_c'$. In this study, we focus on $\Delta E_c'$ as the primary quantity to be estimated by examining its dependence on Z^{-1}. This correlation contribution to the ionization energy is also the theoretical quantity most directly related to the experimental data. As we will see, careful attention to trends in this quantity make discrepancies in the experimental data very apparent. With the determination of this primary quantity, $\Delta E_c'(N,Z)$ the other quantities of interest, viz., $E_c(N,Z)$ and $E(N,Z)$, are easily obtained. However, it is essential that $\Delta E_c'(N,Z)$ be known for $n=2$–N in order to determine $E(N,Z)$, since

$$E(N,Z)=E_{\mathrm{CAS}}(N,Z)+\sum_{n=2}^{N}\Delta E_c'(n,Z)\ . \quad (8)$$

EXPERIMENTAL IONIZATION ENERGIES AND RELATIVISTIC CORRECTIONS

In order to obtain the nonrelativistic ionization energy $I(N,Z)$ from the experimental atomic spectra, we use the table of experimental energies [2(b)], $I_{\mathrm{expt}}(N,Z)$, in cm^{-1} obtained by extrapolating Rydberg series for the atoms to the ionization limit. Moore has also estimated the uncertainties for these limits. For $Z \gg N$, both the ionization energy and the uncertainty in its magnitude become large. In some of the past works [3,5] on this subject, the ionization energies were summed to give an estimate of $-E$, which was then deperturbed by correcting for relativistic effects, nuclear motion and quantum electrodynamics. The value of E_{HF} was then subtracted to obtain E_c. Scherr, Silverman, and Matsen [1] instead deperturbed each ionization energy and then fit $I(N,Z)$ to a series in Z for each N. We also deperturb each ionization energy individually, but then subtract E_{CAS} to obtain $\Delta E_c'(N,Z)$, the correlation contribution to the ionization energy before fitting to a series. From Eq. (8), the relation between $\Delta E_c'$ and I is

$$\Delta E_c'(N,Z)=-\Delta E_{\mathrm{CAS}}(N,Z)-I(N,Z)\ . \quad (9)$$

Since $\Delta E_c'$ is a very small part of the total ionization energy, its dependence on Z provides a sensitive test of the experimental data and of the deperturbation procedure.

We will correct for nuclear motion by multiplying the experimental ionization energy by a factor of

$$1+m_e/M_Z=m_e/\mu\ .$$

This correction is needed because the energy from the experimental Hamiltonian with nonstationary nucleus includes a reduced-mass factor μ/m_e. The nuclear mass was obtained for the most common isotope of each Z by subtracting Zm_e from the atomic masses given in Ref. [19]. No corrections for other mass-polarization effects were made. This scaled ionization energy can then be converted to Hartree units by dividing by $2R_\infty$. We note that this procedure is numerically equivalent to dividing the unscaled ionization energies by $2R_Z$.

The relativistic correction was estimated from a CAS Dirac Fock including the Breit correction and Lamb shift using Grant's multiconfiguration Dirac-Fock program GRASP [10]. All configurations contributing to the ground J level were included from all arrangements of the valence electrons among the valence orbitals. Table II gives the resulting relativistic corrections to the ionization energy from the CASDF energy, E_{CASDF}

$$\begin{aligned}\Delta E_{\mathrm{rel}}(N,Z)=&[E_{\mathrm{CASDF}}(N,Z)-E_{\mathrm{CAS}}(N,Z)]\\&-[E_{\mathrm{CASDF}}(N-1,Z)-E_{\mathrm{CAS}}(N-1,Z)]\ .\end{aligned} \quad (10)$$

TABLE II. Relativistic corrections to ionization energies for $N=3$ through $N=10$. See Eq. (10) of text. All values are in hartrees. These values include the Breit correction and quantum electrodynamic corrections with a nucleus of finite radius.

Z	$E_{\rm rel}(3,Z)$	$E_{\rm rel}(4,Z)$	$E_{\rm rel}(5,Z)$	$E_{\rm rel}(6,Z)$	$E_{\rm rel}(7,Z)$	$E_{\rm rel}(8,Z)$	$E_{\rm rel}(9,Z)$	$E_{\rm rel}(10,Z)$
3	−0.000 011							
4	−0.000 092	−0.000 024						
5	−0.000 348	−0.000 154	0.000 034					
6	−0.000 937	−0.000 514	−0.000 047	0.000 200				
7	−0.002 061	−0.001 274	−0.000 366	0.000 356	0.000 647			
8	−0.003 975	−0.002 654	−0.001 112	0.000 483	0.001 320	−0.000 094		
9	−0.006 984	−0.004 922	−0.002 526	0.000 497	0.002 325	−0.000 394	0.000 741	
10	−0.011 441	−0.008 393	−0.004 897	0.000 280	0.003 747	−0.001 070	0.001 104	0.001 988
11	−0.017 753	−0.013 430	−0.008 568	−0.000 325	0.005 678	−0.002 311	0.001 414	0.003 176
12	−0.026 379	−0.020 448	−0.013 933	−0.001 519	0.008 226	−0.004 342	0.001 594	0.004 641
13	−0.037 820	−0.029 911	−0.021 437	−0.003 559	0.011 515	−0.007 424	0.001 556	0.006 388
14	−0.052 648	−0.042 331	−0.031 577	−0.006 762	0.015 694	−0.011 855	0.001 204	0.008 409
15	−0.071 462	−0.058 274	−0.044 903	−0.011 519	0.020 934	−0.017 966	0.000 440	0.010 683
16	−0.094 946	−0.078 360	−0.062 015	−0.018 302	0.027 433	−0.026 118	−0.000 833	0.013 182
17	−0.123 798	−0.103 260	−0.083 568	−0.027 673	0.035 412	−0.036 694	−0.002 702	0.015 865
18	−0.158 808	−0.133 699	−0.110 270	−0.040 287	0.045 107	−0.050 095	−0.005 244	0.018 683
19	−0.200 794	−0.170 464	−0.142 882	−0.056 903	0.056 760	−0.066 721	−0.008 523	0.021 577
20	−0.250 672	−0.214 393	−0.182 220	−0.078 374	0.070 594	−0.086 954	−0.012 589	0.024 477

The CAS energies, $E_{\rm CAS}$ were obtained from the same program using the same configuration list just by setting the speed of light to a large value and omitting the Lamb shift. There is a positive increment in the relativistic corrections as some of the p electrons are added because of increased shielding of the 2s electrons. Table III gives the numerical Hartree-Fock energies for all the ions, and Table IV gives the CAS energies where they are different. For $N=4,5,6$, the configuration p^{n+2} mixes with s^2p^n to cause the CAS energy to be lower. For $N=8$, there is no possible LS configuration except $p^4\,{}^3P_2$, but in j-j coupling, the $p_{3/2}$ and $p_{1/2}$ orbitals are not constrained to have the same radial parts. This allows some radial correlation to be included, at the expense of mixing in a little ${}^1D_2$ character, even in the nonrelativistic limit.

Finally, we may obtain the "adjusted" nonrelativistic, stationary nucleus $I(N,Z)$ employing the relation

$$I(N,Z)=I_{\rm expt}(N,Z)/2R_Z+\Delta E_{\rm rel}(N,Z)\ . \qquad (11)$$

These are listed in Table V. We can also determine the "experimental" correlation contribution to the ionization energy $\Delta E_c'(N,Z)$ by using Eq. (9). Table VI gives the resulting experimental estimate of $\Delta E_c'(N,Z)$. For Z greater than 18, the data in Table VI shows erratic behavior. But for Z in the range 11–18, the data shows systematic deviation from the expected Laurent series behavior. Figures 1–8 show plots of this data against $1/Z$ to make the anomalous behavior more obvious. These plots show no sign of approaching a constant value of $\Delta E_c'$ for large Z.

It is traditionally assumed that relativistic corrections

TABLE III. Hartree-Fock energies for atomic ions. All values are in hartrees.

	$-E_{\rm HF}(3,Z)$	$-E_{\rm HF}(4,Z)$	$-E_{\rm HF}(5,Z)$	$-E_{\rm HF}(6,Z)$	$-E_{\rm HF}(7,Z)$	$-E_{\rm HF}(8,Z)$	$-E_{\rm HF}(9,Z)$	$-E_{\rm HF}(10,Z)$
3	7.432 727							
4	14.277 395	14.573 023						
5	23.375 991	24.237 575	24.529 061					
6	34.726 061	36.404 495	37.292 224	37.688 619				
7	48.326 851	51.082 317	52.815 792	53.888 005	54.400 934			
8	64.178 046	68.257 711	71.094 705	73.100 193	74.372 606	74.809 398		
9	82.279 494	87.934 053	92.126 768	95.319 608	97.608 978	198.831 720	99.409 349	
10	102.631 109	110.111 013	115.910 851	120.543 566	124.104 215	126.372 113	127.817 814	128.547 098
11	125.232 840	134.788 397	142.446 309	148.770 578	153.855 294	157.423 729	159.997 400	161.676 963
12	150.084 656	161.966 085	171.732 744	179.999 746	186.860 443	191.982 930	195.940 465	198.830 810
13	177.186 536	191.643 998	203.769 901	214.230 491	223.118 550	230.047 540	235.642 844	240.000 348
14	206.538 464	223.822 084	238.557 603	251.462 429	262.628 875	271.616 155	279.101 985	285.180 931
15	238.140 431	258.500 303	276.095 730	291.695 287	305.390 907	316.687 824	326.316 215	334.369 660
16	271.992 428	295.678 629	316.384 193	334.928 873	351.404 281	365.261 878	377.284 380	387.564 603
17	308.094 449	335.357 042	359.422 927	381.163 043	400.668 729	417.337 831	432.005 655	444.764 406
18	346.446 491	377.535 524	405.211 882	430.397 689	453.184 052	472.915 321	490.479 434	505.968 090
19	387.048 551	422.214 066	453.751 020	482.632 729	508.950 094	531.994 074	552.705 257	571.174 928
20	429.900 624	469.392 656	505.040 311	537.868 097	567.966 737	594.573 875	618.682 774	640.384 362

TABLE IV. CASSCF energies for atomic ions. All values are in hartrees.

Z	$-E_{\mathrm{CAS}}(4,Z)$	$-E_{\mathrm{CAS}}(5,Z)$	$-E_{\mathrm{CAS}}(6,Z)$	$-E_{\mathrm{CAS}}(8,Z)$
4	14.616 845			
5	24.296 378	24.563 760		
6	36.480 956	37.335 038	37.706 287	
7	51.167 806	52.866 452	53.909 762	
8	68.355 869	71.152 975	73.125 570	74.809 550
9	88.044 654	92.192 488	95.348 405	98.831 840
10	110.233 903	115.983 910	120.575 677	126.372 219
11	134.923 468	142.526 627	148.805 942	157.423 827
12	162.113 257	171.820 262	180.038 323	191.983 023
13	191.803 212	203.864 573	214.272 256	230.047 629
14	223.993 291	238.659 396	251.507 362	271.616 241
15	258.683 467	276.204 615	291.743 375	316.687 908
16	295.873 720	316.500 148	334.980 106	365.261 961
17	335.564 035	359.545 933	381.217 412	417.337 912
18	377.754 399	405.341 925	430.455 189	472.915 401
19	422.444 806	453.888 087	482.693 355	531.994 153
20	469.635 247	505.184 392	537.931 845	594.573 954

are additive with the correlation energy. However, it may be noted that this assumption must break down with increasing Z. Generally it is believed that it would be reasonable to use this approximation for Z values up to 18. The figures make clear a point noted by Anno and Teruya [5] for the total correlation energy. For Z between 10 and 15, it is clear that there is a systematic deviation from the expected behavior of the $\Delta E_c'$ curve. Nevertheless, because this data deals with correlation-energy increments, it should be relatively less sensitive to the filtering out of large relativistic and Lamb shifts of the 1*s* core electrons. Anno and Teruya [5] had assumed that the strange behavior for Z between 8 and 15 of the total correlation energy was due to an inadequate estimate of the relativistic operator, but the presence of this same behavior in $\Delta E_c'$ makes that explanation unlikely. A second possibility is that the experimental extrapolations of the Rydberg series has some systematic error. Another possibility would be that the implied assumption of additivity of relativistic and correlation effects has broken down. The correct explanation, however, is that in Moore's data [2(b)], the ionization energies beyond a Z of 10 are not experimental but Edlen's theoretical estimates [20] based on his extrapolation formulas for the relativistic correction and Lamb shift. The Lamb shift he has added in is different from the one we have subtracted out. This explains satisfactorily the anomalous behavior beyond $Z=10$, but leaves us without real experimental data for larger Z.

BETTER ESTIMATES OF EXPERIMENTAL IONIZATION ENERGIES

The data in Table I for two electrons, extended to $Z=144$, can be fit by the equation

$$\Delta E_c'(2,Z) = -0.046\,670\,914 + 0.009\,880\,741/Z - 0.000\,852\,948/Z^2 - 0.000\,795\,98/Z^3 \ . \tag{12}$$

As proposed, we used the tabulation of $\Delta E_c'(N,Z)$ in Table VI to fit the low-Z data for $N=3$–5 satisfactorily to a three-term series in Z^{-1} of the form $a+b/Z+c/Z^2$. The fits are

$$\Delta E_c'(3,Z) \simeq -0.007\,180\,28 + 0.017\,161\,3/Z - 0.003\,380\,10/Z^2 \ , \tag{13}$$

$$\Delta E_c'(4,Z) \simeq -0.008\,569\,78 + 0.029\,544\,3/Z - 0.031\,447\,4/Z^2 \ , \tag{14}$$

TABLE V. Rydberg constants and nonrelativistic, stationary-nucleus ionization potentials. See Eq. (10) of text. All values are in hartrees.

Z	$2R_Z$	$I(3,Z)$	$I(4,Z)$	$I(5,Z)$	$I(6,Z)$	$I(7,Z)$	$I(8,Z)$	$I(9,Z)$	$I(10,Z)$
3	219 457.467	0.198 146							
4	219 461.269	0.669 197	0.342 597						
5	219 463.692	1.393 646	0.924 315	0.304 996					
6	219 464.595	2.369 279	1.759 410	0.896 064	0.414 027				
7	219 466.031	3.595 476	2.845 937	1.743 430	1.088 226	0.534 787			
8	219 467.102	5.071 993	4.183 199	2.843 887	2.019 401	1.291 900	0.500 377		
9	219 468.292	6.798 687	5.770 956	4.195 940	3.202 918	2.306 881	1.284 797	0.641 036	
10	219 468.607	8.775 520	7.609 061	5.799 122	4.638 756	3.572 822	2.330 926	1.506 518	0.794 491
11	219 469.392	11.002 918	9.695 441	7.653 093	6.326 298	5.091 581	3.632 820	2.634 127	1.740 981
12	219 469.610	13.480 730	12.032 245	9.758 263	8.265 229	6.862 478	5.187 265	4.016 273	2.949 969
13	219 470.167	16.208 579	14.618 094	12.114 153	10.455 266	8.884 247	6.992 616	5.650 615	4.416 099
14	219 470.326	19.186 399	17.453 429	14.721 214	12.896 577	11.157 519	9.048 140	7.537 075	6.137 255
15	219 470.743	22.414 451	20.537 181	17.579 770	15.589 193	13.682 437	11.353 025	9.674 166	8.111 535
16	219 470.864	25.893 014	23.869 693	20.689 259	18.532 679	16.458 316	13.906 028	12.061 816	10.337 559
17	219 471.187	29.621 793	27.450 243	24.050 352	21.727 803	19.486 257	16.707 645	14.699 456	12.815 267
18	219.471.617	33.578 584	31.279 019	27.663 253	25.173 907	22.766 041	19.756 566	17.586 553	15.543 697
19	219 471.540	37.799 578	35.404 080	31.527 739	28.870 766	26.297 520	23.052 906	20.723 550	18.523 292
20	219 471.617	42.269 633	39.731 547	35.612 841	32.817 907	30.081 764	26.595 312	24.110 348	21.753 482

TABLE VI. Experimental estimate of correlation-energy contributions to ionization energies. See Eq. (9) of text for details. All values are in hartrees.

Z	$-\Delta E_c'(3,Z)$	$-\Delta E_c'(4,Z)$	$-\Delta E_c'(5,Z)$	$-\Delta E_c'(6,Z)$	$-\Delta E_c'(7,Z)$	$-\Delta E_c'(8,Z)$	$-\Delta E_c'(9,Z)$	$-\Delta E_c'(10,Z)$
3	0.001 835							
4	0.003 101	0.003 147						
5	0.003 889	0.003 928	0.037 615					
6	0.004 411	0.004 515	0.041 982	0.042 778				
7	0.004 790	0.004 981	0.044 784	0.044 915	0.043 615			
8	0.005 089	0.005 376	0.046 781	0.046 805	0.044 865	0.063 433		
9	0.005 320	0.005 796	0.048 106	0.047 002	0.046 308	0.061 935	0.063 505	
10	0.005 524	0.006 267	0.049 115	0.046 990	0.044 284	0.062 922	0.060 906	0.065 224
11	0.006 181	0.004 813	0.049 934	0.046 983	0.042 229	0.064 287	0.060 539	0.061 433
12	0.007 168	0.003 644	0.051 258	0.047 168	0.040 357	0.064 686	0.058 817	0.059 638
13	0.008 130	0.001 418	0.052 792	0.047 583	0.037 953	0.063 537	0.055 388	0.058 607
14	0.009 016	−0.001 398	0.055 110	0.048 611	0.036 006	0.060 773	0.051 319	0.058 321
15	0.010 095	−0.005 855	0.058 622	0.050 433	0.034 905	0.056 024	0.045 848	0.058 101
16	0.011 657	−0.011 599	0.062 831	0.052 722	0.034 141	0.048 348	0.039 385	0.057 348
17	0.013 410	−0.019 342	0.068 453	0.056 324	0.034 940	0.038 462	0.031 702	0.056 528
18	−0.006 845	−0.028 889	0.075 727	0.060 643	0.037 178	0.025 217	0.022 509	0.055 051
19	−0.012 913	0.007 825	0.084 457	0.065 499	0.040 780	0.008 847	0.012 435	0.053 632
20	−0.019 934	−0.003 076	0.063 696	0.070 454	0.046 871	−0.011 904	0.001 516	0.051 905

$$\Delta E_c'(5,Z) \simeq -0.055\,646\,2 + 0.039\,979\,8/Z + 0.251\,176/Z^2 \,. \qquad (15)$$

The expression in Eq. (13) agrees with the experimental data for $N=3$ and Z from 3 to 9 within 1 μhartree. Similar agreements occur for $N=4$ and Z between 4 and 8 with Eq. (14). For $N=5$, the fit is not quite as good and a maximum error of 6 μhartrees occurs at a Z of 8 for Z in the range of 5 to 11. For N equal to 6 and larger, no satisfactory fit to the data for low Z could be found with any series in Z^{-1}.

To check these estimates of $\Delta E'(3,Z)$ and $\Delta E'(4,Z)$ in Eqs. (13) and (14), we performed some *ab initio* calculations. For the general configuration-interaction (CI) calculations, we have employed the ATOMCI program of Sasaki *et al.* [21]. Recently, Rizzo, Clementi, and Sekiya [22] have calculated the correlation energies of atomic ions with 2, 3, 4, and 10 electrons with large sets of geometrical basis functions. Their emphasis was on the use of Gaussian-type orbitals (GTO's) and the accurate computations of E_c. In this work, we have used Slater-type orbitals (STO's) and have computed $\Delta E_c'(3,Z)$ and $\Delta E_c'(4,Z)$. It is essential for the present analysis to use the same basis set for different N. The basis set used in the computations was an 11s, 10p, 9d, 8f, 6g, 4h, 2i STO set. The exponents for the s functions were opti-

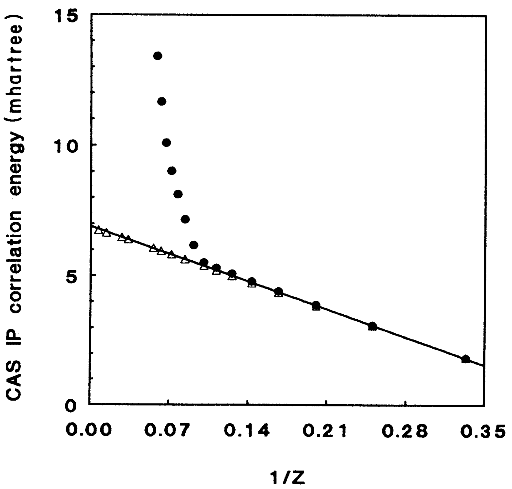

FIG. 1. The CAS correlation contribution to the ionization energy for three electrons, $\Delta E_c'(3,Z)$. Data shown are from Moore [2(b)] (●), our CI (△), and Eq. (16) (——).

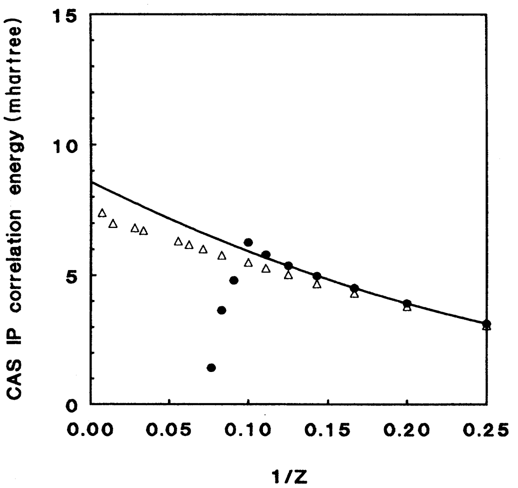

FIG. 2. The CAS correlation contribution to the ionization energy for four electrons, $\Delta E_c'(4,Z)$. Data shown are from Moore [2(b)], our CI, and Eq. (14).

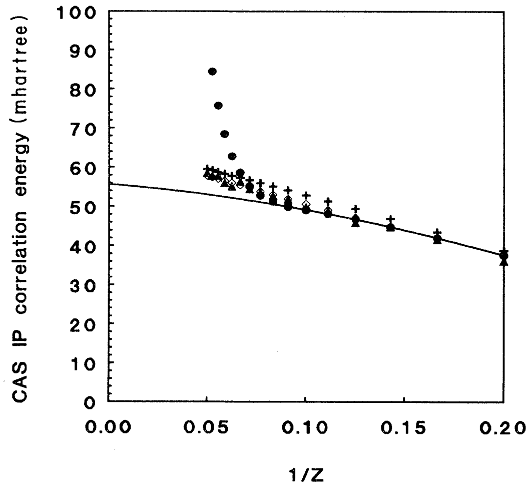

FIG. 3. The CAS correlation contribution to the ionization energy for five electrons, $\Delta E_c'(5,Z)$. Data shown in this and all following figures are from Moore [2(b)] (●); Scherr, Silverman, and Matsen [1] (¤); Clementi [3] (▼); Anno and Teruya [5] (+), and the fit we have used in this paper (——).

mized at the HF level using the brute-force algorithm of Roothaan and Bagus [23,24]. For the orbitals of higher angular momentum, the optimization was done using the same procedure, however, at the single- and double-excitation configuration interaction (SDCI) plus selected triples and quadruples level.

The configurations for the CI calculations for the three- and four-electron ions were determined by making all possible single and double excitations from $(1s2s2p3s3p3d)^3$ and $(1s2s2p3s3p3d)^4$ configurations. For the two-electron ions, we performed a full CI calculation. In order to follow the convergence of the three- and four-electron CI calculations, we list the correlation energies obtained at the SDCI, SDTCI, and SDTQCI levels. In Table VII, S, D, T, and Q denote all single, all double, selected triple, and selected quadrupole excitations from the Hartree-Fock configuration, respectively. From the table, we can see that $E_cS(3,Z)$ slowly increases to about 1 mhartrees for $Z=72$. Single excitations from the HF configuration of the form $1sns2s$ $(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)$ connect with the HF configuration because these "single" excitations are actually double excitations from the 1*s* and 2*s* spin orbitals. Moreover, we note that the SDCI result is almost 100% of the SDTCI correlation energy for the three-electron atomic ions. On the other hand, the convergence of E_c for the four-electron ion sequence is slower. With this basis set, the numerical Hartree-

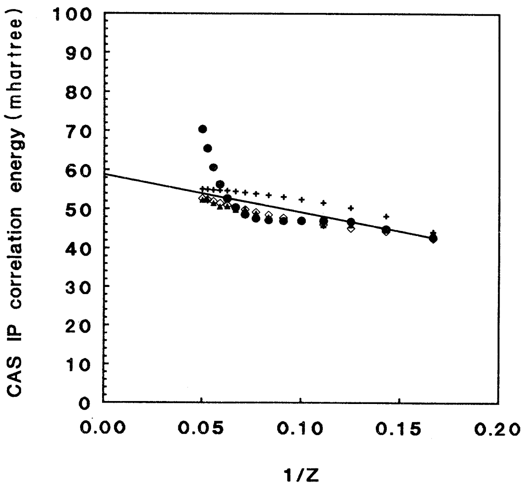

FIG. 4. The CAS correlation contribution to the ionization energy for six electrons, $\Delta E_c'(6,Z)$.

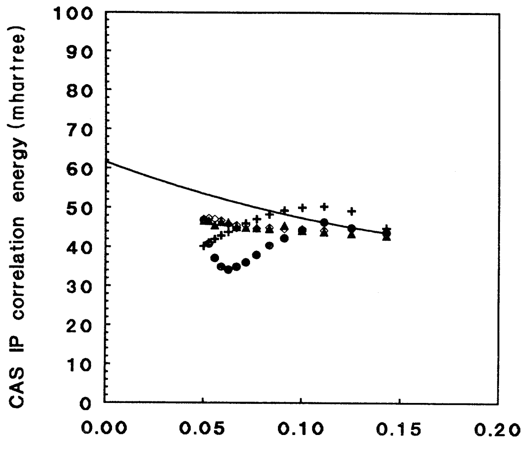

FIG. 5. The CAS correlation contribution to the ionization energy for seven electrons, $\Delta E_c'(7,Z)$.

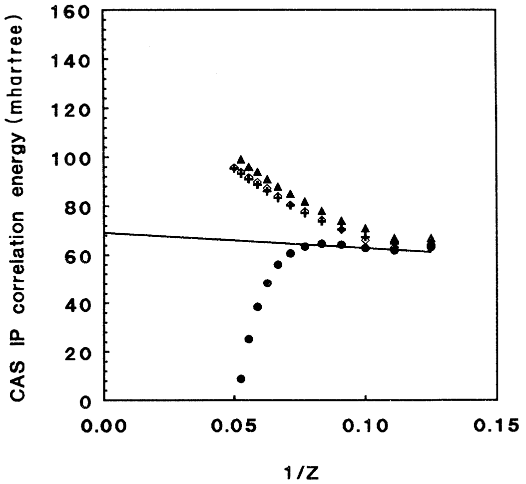

FIG. 6. The CAS correlation contribution to the ionization energy for eight electrons, $\Delta E_c'(8,Z)$.

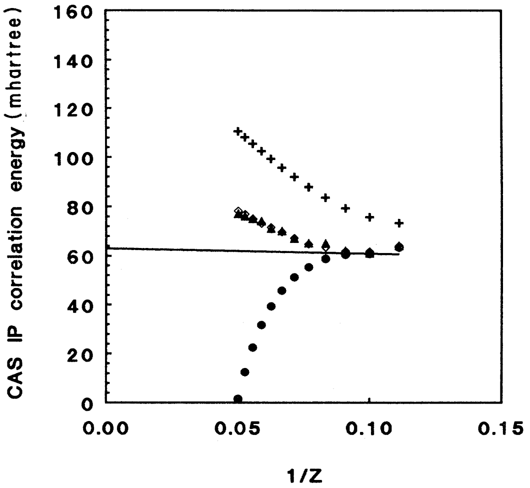

FIG. 7. The CAS correlation contribution to the ionization energy for nine electrons, $\Delta E_c'(9,Z)$.

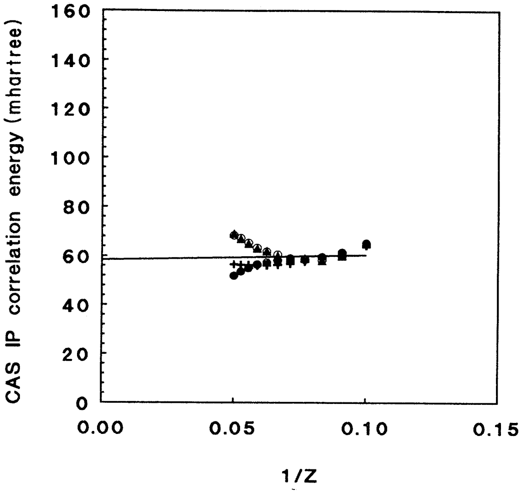

FIG. 8. The CAS correlation contribution to the ionization energy for ten electrons, $\Delta E_c'(10,Z)$.

Fock results agree with our $E_{\mathrm{HF}}(N,Z)$ in Table III to within a few μhartrees. As shown in Table VIII, this basis reproduces the exact two-electron energies within a fraction of a mhartree. Since the core correlation energy almost cancels in computing the CI value of $\Delta E_c'$, this should be adequate.

In Table IX, we list our CI correlation-energy increment $\Delta E_c'(3,Z)$ along with some of the best *ab initio* calculations [25–32] and empirical estimates [1,5] from the literature. Since some of these calculations in Table IX have been done systematically so that the error is nearly independent of Z and others have been pushed to apparent convergence, a subjective estimate of the correlation contribution to the ionization potential can be made. This is listed in Table IX and has been fit by the equation

$$\Delta E_c'(3,Z) = -0.006\,902\,12 + 0.015\,061\,458/Z + 0.000\,595\,561/Z^2 , \tag{16}$$

which differs slightly from the purely empirical fit in Eq. (13). Equation (16) and our CI results are also plotted in Fig. 1. It is believed that this represents the exact solution from the Schrödinger equation to within a few hundreths of a mhartree.

In Table X we list $\Delta E_c'(4,Z)$ from our CI calculations. For comparison, the results of Rizzo, Clementi, and Sekiya [22] are also given. For $Z=4$, these are still 0.1 mhartree from the best results in the literature. Also, the values for $\Delta E_c'(3,Z)$ from Eq. (16) are given to emphasize the strong resemblance to $\Delta E_c'(4,Z)$. Our CI results are

TABLE VII. Correlation-energy results for three- and four-electron systems for various classes of configurations. All values are in hartrees.

Z	$-E_c\mathrm{SDTQ}(4,Z)$	$-E_c\mathrm{SDT}(4,Z)$	$-E_c\mathrm{SD}(4,Z)$	$-E_c\mathrm{SDT}(3,Z)$	$-E_c\mathrm{SD}(3,Z)$	$-E_c\mathrm{S}(3,Z)$
4	0.093 976	0.090 085	0.089 887	0.047 081	0.047 044	0.000 191
5	0.110 827	0.107 255	0.106 973	0.048 221	0.048 194	0.000 297
6	0.125 672	0.122 456	0.121 968	0.048 903	0.048 882	0.000 367
7	0.139 734	0.136 800	0.136 126	0.049 564	0.049 548	0.000 417
8	0.153 277	0.150 498	0.149 738	0.050 091	0.050 078	0.000 473
9	0.166 261	0.163 621	0.162 780	0.050 396	0.050 385	0.000 498
10	0.179 121	0.175 936	0.175 678	0.050 737	0.050 728	0.000 516
12	0.204 099	0.201 274	0.200 719	0.051 153	0.051 147	0.000 552
14	0.228 698	0.226 313	0.225 358	0.051 483	0.051 479	0.000 605
16	0.252 938	0.250 603	0.249 630	0.051 671	0.051 667	0.000 576
18	0.277 058	0.274 757	0.273 770	0.051 870	0.051 867	0.000 598
30	0.419 737	0.416 630	0.416 522	0.052 388	0.052 386	0.000 989
36	0.490 588	0.487 629	0.487 390	0.052 517	0.052 516	0.000 654
72	0.913 503	0.911 410	0.910 360	0.052 476	0.052 476	0.001 101
144	1.758 626	1.756 253	1.755 387	0.052 559	0.052 558	0.001 382

TABLE VIII. Two-electron energies employing CI and error compared with the Kinoshita energies from Table I.

	$-E_{\mathrm{CI}}(2,Z)$	$E_{\mathrm{CI}}(2,Z)-E(2,Z)$
4	13.655 303	+0.000 263
5	22.030 614	+0.000 358
6	32.405 746	+0.000 501
7	44.781 012	+0.000 433
8	59.156 238	+0.000 355
9	75.531 313	+0.000 399
10	93.906 463	+0.000 344
12	136.656 605	+0.000 343
14	187.406 735	+0.000 314
16	246.156 783	+0.000 344
18	312.906 862	+0.000 323
30	881.407 028	+0.000 349
36	1 273.657 072	+0.000 355
72	5 139.156 837	+0.000 704
144	20 646.156 815	+0.000 809

also plotted in Fig. 2 along with the empirical Eq. (13). While our CI results are probably off by 0.5 mhartree for large Z, they do verify that the long extrapolation from low Z given by Eq. (13) is behaving reasonably. Equation (13) is probably in error by no more than 0.5 mhartree at large Z.

In spite of obvious uncertainties in $\Delta E_c'$ for high N, we have made our best estimate of the true correlation energy based on the available experimental and theoretical data. The calculation of Ivanova and Safranova [33] is particularly useful since it gives the leading terms $E_1 Z + E_2$ in the Laurent series for the correlation energy for two–ten electrons. By subtracting a Z^{-1} series for the difference between the CAS and HF energies, we obtained the infinite-Z limit of $\Delta E_c'$. The result agreed well with the results from our empirical procedure for up to six electrons and was used to fix the high-Z limit for more than six electrons. Truncation of the Laurent series for low Z introduces additional errors, so we have chosen to retain the experimental values for small $Z-N$, and use the series only where we felt it was more reliable than the

TABLE IX. Correlation contribution to the ionization energy of three-electron atoms. $-\Delta E_c'(3,Z)$ as defined in text in mhartree units.

Z	a	b	c	d	e	f	g	h	i	j
3	1.65		1.78	1.81	1.70	1.78	1.83	1.84	1.9	1.83
4	3.03	3.08	3.06	3.06	2.91	3.04	3.10	3.16	3.2	3.09
5		3.84	3.83	3.83	3.63	3.79	3.89	4.05	3.9	3.85
6		4.35	4.35		4.10	4.30	4.41	4.67	4.3	4.36
7		4.72			4.44	4.66	4.79	5.11	4.5	4.73
8		4.99			4.69	4.93	5.09	5.44	4.7	5.00
9		5.21					5.32	5.71	4.8	5.22
10	5.34	5.39					5.52	5.90	4.9	5.40
11								6.07	4.9	5.51
12		5.64						6.20	5.0	5.65
13								6.32	5.0	5.75
14		5.83						6.43	5.2	5.84
15								6.50	5.0	5.90
16		5.96						6.58	5.1	5.97
17								6.65	5.2	6.03
18	5.93	6.07						6.71	5.2	6.08
19								6.76	5.2	6.12
20								6.81	5.3	6.16
30	6.17	6.40								6.41
36	6.36	6.48								6.49
54	6.52									
72		6.65								6.66
144		6.75								6.76

[a] Rizzo, Clementi, and Sekiya [22].

[b] Present CI calculations.

[c] Muszynska *et al.* [32].

[d] Pipin and Woznicki [31].

[e] Perkins [29].

[f] Ho [28].

[g] Experimental estimate based on the data of Moore.

[h] Scherr, Silverman, and Matsen [1].

[i] Anno and Teruya [5].

[j] Best estimate from trends in other columns.

TABLE X. Correlation energy increment for three- and four-electron atomic ions.

Z	$-\Delta E_c'(4,Z)$	$-\Delta E_c'(4,Z)$	$-\Delta E_c'(3,Z)$
3			0.001 82[b]
4	0.003 068	0.002 944[a]	0.003 10
5	0.003 801		0.003 87
6	0.004 304		0.004 38
7	0.004 677		0.004 74
8	0.005 026		0.005 01
9	0.005 268		0.005 22
10	0.005 496	0.005 536	0.005 39
12	0.005 771		0.005 64
14	0.006 009		0.005 82
16	0.006 176		0.005 96
18	0.006 312	0.006 508	0.006 06
30	0.006 715	0.007 046	0.006 40
36	0.006 822	0.007 061	0.006 48
72	0.006 986		0.006 69
144	0.007 390		0.006 80

[a] Rizzo, Clementi, and Sekiya [22].

[b] From Eq. (16) of text.

empirical estimates in Table VI. Hence, we have used Eqs. (16), (14), and (15) for $N=3$, 4, and 5, respectively and $Z>N+2$. For $N=6$, we have fit the data for $Z=6$, 7, and 8 to a straight line in Z^{-1} and used the equation

$$\Delta E_c'(6,Z)=-0.058\,777\,311+0.096\,275\,35/Z$$

for $Z>8$. Similarly for $N=7$, we have used the equation

$$\Delta E_c'(7,Z)=-0.061\,601\,749+0.180\,539\,978/Z -0.380\,330\,18/Z^2$$

for $Z>9$. For higher N, no reliable or otherwise trends can be deduced from the data. Consequently, we have replaced all $\Delta E_c'(N,Z)$ by linear fits that agree with Ivanova and Safronova at high Z and the experimental data at low Z. For $N=8$ and 9

$$\Delta E_c'(8,Z)=-0.0691+0.0618/Z\ ,$$

$$\Delta E_c'(9,Z)=-0.0630+0.0209/Z$$

was used for $Z>10$. For $N=10$ it was not possible to fit the experimental data for $Z=10$, 11, and 12 by any reasonable function. Finally we used

$$\Delta E_c'(10,Z)=-0.0584-0.020/Z$$

for $Z>11$. Table XI gives the resulting total correlation energies $E_c(N,Z)$ reported in the conventional way defined in Eq. (2). Finally, these are added to the Hartree-Fock energies to obtain the estimated eigenvalues of Eq. (1) for the atomic ions shown in Table XII.

Tables XI and XII can be compared with previous estimates in the literature. They agree to within ±1 mhartree the values given by Silverman [15] for the neutral atoms. Compared with Scherr *et al.*, they differ by 30 mhartree for the ionization energy at $Z=20$ and $N=8$. On the other hand, they differ from the results of Anno and Teruya [5] by 27 mhartree for a neon atom, and up to 70 mhartree for high Z. Compared with Veillard and Clementi [17(b)], they are within 0.1 mhartree for neutral atoms except for F and Ne, where they differ by 2 mhartree. The difference from the older tables of Clementi [3] for the total correlation energy reach a maximum of 57 mhartree at $Z=20$ and $N=10$. Rizzo, Clementi, and

TABLE XI. Estimated values for total correlation energy.

Z	$-E_c(3,Z)$	$-E_c(4,Z)$	$-E_c(5,Z)$	$-E_c(6,Z)$	$-E_c(7,Z)$	$-E_c(8,Z)$	$-E_c(9,Z)$	$-E_c(10,Z)$
3	0.045 33							
4	0.047 37	0.094 34						
5	0.048 63	0.111 36	0.124 87					
6	0.049 43	0.126 40	0.138 74	0.156 37				
7	0.050 02	0.140 50	0.150 45	0.166 47	0.188 32			
8	0.050 46	0.153 99	0.160 82	0.174 74	0.194 22	0.2578		
9	0.050 81	0.167 08	0.170 31	0.181 5	0.198 97	0.2610	0.3244	
10	0.051 08	0.179 90	0.179 21	0.187 4	0.202 7	0.2657	0.3265	0.3917
11	0.051 31	0.192 52	0.187 71	0.192 8	0.205 8	0.2693	0.3303	0.3916
12	0.051 50	0.205 00	0.195 91	0.197 7	0.208 4	0.272	0.334	0.394
13	0.051 66	0.217 35	0.203 90	0.202 4	0.210 6	0.275	0.336	0.396
14	0.051 79	0.229 62	0.211 71	0.206 8	0.212 5	0.277	0.339	0.398
15	0.051 91	0.241 81	0.219 40	0.211 0	0.214 1	0.279	0.341	0.400
16	0.052 01	0.253 95	0.226 98	0.215 0	0.215 6	0.281	0.342	0.402
17	0.052 11	0.266 04	0.234 48	0.219 0	0.216 9	0.282	0.344	0.404
18	0.052 19	0.278 09	0.241 91	0.222 8	0.218 0	0.284	0.346	0.405
19	0.052 26	0.290 10	0.249 28	0.226 5	0.219 1	0.285	0.347	0.406
20	0.052 32	0.302 09	0.256 60	0.230 2	0.220 0	0.286	0.348	0.407
∞	0.053 57	∞	∞	∞	0.238 3	0.307	0.370	0.429

TABLE XII. Estimated atomic energies, $E(N,Z)$.

	$-E(3,Z)$	$-E(4,Z)$	$-E(5,Z)$	$-E(6,Z)$	$-E(7,Z)$	$-E(8,Z)$	$-E(9,Z)$	$-E(10,Z)$
3	7.478 06							
4	14.324 76	14.667 36						
5	23.424 62	24.348 93	24.653 93					
6	34.775 49	36.534 90	37.430 96	37.8450				
7	48.376 87	51.222 82	52.966 25	54.0545	54.5893			
8	64.228 51	68.411 70	71.255 53	73.274 9	74.5668	75.067		
9	82.330 30	88.101 14	92.297 07	95.5011	97.8080	99.093	99.734	
10	102.682 19	110.290 92	116.090 06	120.7310	124.3069	126.638	128.144	128.939
11	125.284 15	134.980 92	142.634 02	148.9634	154.0610	157.693	160.328	162.069
12	150.136 15	162.171 08	171.928 66	180.1975	187.0688	192.255	196.274	199.224
13	177.238 19	191.861 35	203.973 80	214.4329	223.3291	230.323	235.979	240.397
14	206.590 26	224.051 70	238.769 32	251.6692	262.8413	271.893	279.441	285.579
15	238.192 34	258.742 12	276.315 13	291.9062	305.6050	316.967	326.657	334.770
16	272.044 44	295.932 58	316.611 17	335.1439	351.6199	365.543	377.627	387.967
17	308.146 56	335.623 08	359.657 40	381.3820	400.8856	417.620	432.350	445.168
18	346.498 68	377.813 61	405.453 79	430.6205	453.4021	473.199	490.825	506.373
19	387.100 81	422.504 17	454.000 29	482.8593	509.1692	532.279	553.052	571.581
20	429.952 95	469.694 74	505.296 91	538.0983	568.1867	594.860	619.031	640.792

Sekiya [22] recently published an *ab initio* calculation for the $N=10$ case. While they get only -0.380 for the neon correlation energy, they predict that the correlation energy changes by -0.014 for $Z=18$, in good agreement with our estimate. Their value, -0.4125, for $Z=54$ also agrees well with the result obtained by using the extrapolation equations given here, -0.4207. The infinite-Z values in Table XII also agree within 1 mhartree with Ivanova and Safronova.

From the work of Scherr, Silverman, and Matsen [1], Clementi [3], and Anno and Teruya [5] it is possible to extract $\Delta E_c'$. We have included their values and our own along with the values based on Moore's tables [2(b)] in Figs. 3–8. Only for $N=8$ does our estimate at $Z=20$ differ greatly from the other papers. The $N=8$ nonrelativistic ionization energies of Scherr *et al.* after subtracting our ΔE_{CAS} ionization energies give correlation energies that can be fit by the equation

$$\Delta E_c'(8,Z)=-0.15419+1.4363/Z-5.6692/Z^2 .$$

This equation would give -154 mhartree for $\Delta E_c'$ at infinite Z, which is more than twice our estimate. The $\Delta E_c'$ data for $N=5$, 6, 7, where the electron is removed from a singly occupied p orbital, are all similar. Also, the $\Delta E_c'$ data for $N=8$, 9, 10 (and the extrapolated data for $N=9$ and 10) are all similar. Hence, the previous literature extrapolations for $\Delta E_c'$ for $N=8$ do not seem plausible. In any case, Figs. 3–8 make it clear that extrapolation to high Z from the few low-Z points is subject to substantial uncertainty. This uncertainty is greatly reduced by use of the high-Z limit, but then no low-order polynomial in Z^{-1} will fit the data very well.

For low Z the atomic energies are known to better accuracy than this procedure can give. For the lithium atom, the exact energy is well established [34] to be $-7.478\,062$ in agreement with Table XII. Similarly, Mårtensson-Pendrill *et al.* [35] have extrapolated the energy of Be to be $-14.667\,37$, which differs from Table XII by 0.000 01. This difference comes from the differences between our estimate for the relativistic plus Lamb correction between Be and Be^{2+} of $-0.000\,116$ in Table II, and their estimate of $-0.000\,102$. The Laurent series coefficients for small N has also been extensively studied by theoretical calculations. For $N=3$, the best estimate is given by Yung, Sanders, and Knight [36]. When converted to $\Delta E_c'$, their result is equivalent to

$$\Delta E_c'(3,Z)=-0.006\,976+0.015\,61/Z$$

in good agreement with the first two terms of Eq. (16).

PAIR CORRELATION ENERGIES AND HIGHER-ORDER ENERGIES

In our endeavor to understand the source of the correlation-energy contributions in three- and four-electron systems, we needed an adequate partitioning scheme of the CI calculation into one-body, two-body, three-body, and four-body contributions. We note the earlier works of Nesbet [37], Sinanoğlu [38] and Allen, Clementi, and Gladeney [39]. In their works, they have proposed that one could meaningfully use the pair correlation data to calculate the total correlation energy. Notwithstanding the fact that this approach may lead to incorrect estimation of the total correlation energy [40], the practical utility of this partitioning has been reexamined. The total correlation energy $E_c(4,Z)$ can be written as a sum

$$E_c(4,Z)=\epsilon_{1s,1s}+\epsilon_{2s,2s}+4\bar{\epsilon}_{1s,2s}+2\bar{\epsilon}_{1s,1s,2s}+2\bar{\epsilon}_{2s,2s,1s}+\epsilon_{1s,1s,2s,2s} , \qquad (17)$$

where $\epsilon_{1s,1s}$ is the $1s$ pair energy, $\bar{\epsilon}_{1s,2s}$ is termed the "average" $\epsilon_{1s,2s}$ pair energy, since it is composed of a strong α-β spin interaction and a weak α-α spin interac-

TABLE XIII. Pair correlation energies and higher-order corrections for four-electron atomic ions. Subscripts refer to principal quantum number of s orbital. All values are in hartrees.

	ϵ_{1122}	$\bar{\epsilon}_{122}$	$\bar{\epsilon}_{112}$	$\bar{\epsilon}_{12}$	ϵ_{11}	ϵ_{22}	ϵ'_{22}
4	−0.0004	0.0005	0.0000	−0.0015	−0.0424	−0.0461	−0.0023
5	−0.0004	0.0007	0.0000	−0.0021	−0.0422	−0.0613	−0.0025
6	−0.0002	0.0007	−0.0000	−0.0024	−0.0420	−0.0751	−0.0026
7	−0.0001	0.0007	−0.0000	−0.0027	−0.0420	−0.0882	−0.0027
8	−0.0001	0.0008	0.0000	−0.0029	−0.0420	−0.1010	−0.0028
9	−0.0001	0.0008	−0.0000	−0.0031	−0.0420	−0.1135	−0.0029
10	−0.0007	0.0012	0.0000	−0.0032	−0.0420	−0.1259	−0.0030
12	−0.0004	0.0010	0.0000	−0.0034	−0.0420	−0.1503	−0.0031
14	−0.0001	0.0010	0.0000	−0.0035	−0.0420	−0.1744	−0.0032
16	−0.0001	0.0010	0.0000	−0.0036	−0.0420	−0.1983	−0.0032
18	−0.0001	0.0010	0.0000	−0.0037	−0.0420	−0.2221	−0.0033
30	−0.0008	0.0014	0.0000	−0.0039	−0.0420	−0.3640	−0.0034
36	−0.0007	0.0014	0.0000	−0.0040	−0.0420	−0.4347	−0.0034
72	−0.0001	0.0011	0.0000	−0.0041	−0.0417	−0.8575	−0.0035
144	−0.0003	0.0012	0.0000	−0.0042	−0.0416	−1.7023	−0.0037

tion, and $\epsilon_{1s,2s,2s}$ and $\epsilon_{2s,2s,1s}$ represent the three-body interactions like $1s\alpha$, $1s\beta$, and $2s\alpha$ electrons. There is only one pair-pair interaction term, viz., $\epsilon_{1s,1s,2s,2s}$. Adopting Nesbet's [37] procedure of making only selected excitations from the HF configurations, the six terms of the correlation energy in Eq. (17) can be determined. A suitable notation we employ is an excitation operation, $\hat{e}_{1s}$, which means a single $1s$ electron is excited to any orbital including itself to give an allowed configuration of LS symmetry. We have calculated CI energies for the following sets of configurations:

$$E(\hat{e}_{1s}\hat{e}_{1s}\hat{e}_{2s}\hat{e}_{2s}(1s^2 2s^2))=E_{\rm HF}+\epsilon_{1s,1s}+\epsilon_{2s,2s}+4\bar{\epsilon}_{1s,2s} +\epsilon_{1s,1s,2s}+2\epsilon_{2s,2s,1s} +\epsilon_{1s,1s,2s,2s}\ , \tag{18}$$

$$E(\hat{e}_{1s}\hat{e}_{2s}(1s^2 2s^2))=E_{\rm HF}+4\bar{\epsilon}_{1s,2s}\ , \tag{19}$$

$$E(\hat{e}_{2s}\hat{e}_{2s}(1s^2 2s^2))=E_{\rm HF}+\epsilon_{2s,2s}\ , \tag{20}$$

$$E(\hat{e}_{1s}\hat{e}_{1s}(1s^2 2s^2))=E_{\rm HF}+\epsilon_{1s,1s}\ , \tag{21}$$

$$E(\hat{e}_{1s}\hat{e}_{2s}\hat{e}_{2s}(1s^2 2s^2))=E_{\rm HF}+2\epsilon_{2s,2s,1s}+4\bar{\epsilon}_{1s,2s}+\epsilon_{2s,2s}\ , \tag{22}$$

$$E(\hat{e}_{2s}\hat{e}_{1s}\hat{e}_{1s}(1s^2 2s^2))=E_{\rm HF}+2\epsilon_{1s,1s,2s} +4\bar{\epsilon}_{1s,2s}+\epsilon_{1s,1s}\ . \tag{23}$$

$E_{\rm HF}$ is determined by a routine Hartree-Fock calculation. The CI calculations for the above six sets of configurations were done, and Eqs. (18)–(23) were solved for the interactions. In Table XIII, we show the results. Again, it is essential to note that the pair correlation $\varepsilon_{2s,2s}$ contains a linear term in Z due to the so-called degeneracy effect of the $2s$ and $2p$ orbitals, which when removed by subtracting out the CAS correlation energy, yields $\epsilon'_{2s,2s}$, the multiconfiguration pair correlation energy. From Table XIII, we also note that the valence-core pair correlation $\bar{\epsilon}_{1s,2s}$ is a large contribution to the total correlation energy $E'_c(4,Z)$. The three-body term $\epsilon_{1s,1s,2s}$ is almost 0 in contrast to the $\epsilon_{2s,2s,1s}$ effect which is positive, indicating that the pair energy model overestimates the $2s,2s,1s$ interaction for the four-electron atomic ions.

Froese-Fisher and Saxena [14] carried out a similar analysis for Be based on the CAS wave function. They obtained essentially the same results for $\epsilon_{1s,1s}$ and $\epsilon_{2s,2s}$. They considered separately the results of correlating the $1s,2s$ and $1s,2p$ pairs and obtained -0.0045 for the sum of these pairs. The $1s,2p$ pair in the present partitioning is included in $\bar{\epsilon}_{1s,2s,2s}$ along with the effect of scaling down $\epsilon_{1s,2s}$ by the reduced $2s$ population. Hence, the comparable result from Table XIII is $4\bar{\epsilon}_{1s,2s}+2\bar{\epsilon}_{1s,2s,2s}$ or -0.0050. Their [41] total pair energy -0.0928 was somewhat higher than the exact correlation energy -0.0943, while our pair energies sum to -0.0945 (but note our calculated correlation energy including three- and four-body effects is only -0.0939). The earlier work by Nesbet [37], done in the same way as the present analysis, was not as well converged and yielded a pair energy sum of only -0.0926 (after correcting an error in their reported $\epsilon_{2s,2s}$). Byron and Joachim [42], by the same method, obtained a pair sum of -0.0925. In earlier papers Tuan and Sinanoğlu [43] obtained a pair sum of -0.0944, Kelly [44] obtained -0.0909, and Geller, Taylor, and Levine [45] obtained -0.0914. More recently, Bunge [46] obtained a pair sum of -0.0945 and Pettersson and Licht [47] obtained -0.0951.

Only Adams and Jankowski [48] and Pettersson and Licht [47] report pair energies as a function of Z with the earlier Pettersson work being more accurate for Be. Our results for the change of ϵ with Z are in good agreement with these of Pettersson and Licht, except that they find a slightly more rapid decrease in $\epsilon_{2s,2s}$. At $Z=4$ they obtain -0.0463 while at $Z=10$ they obtain -0.1274.

A similar analysis for $E_c(3,Z)$ leads to the following equations and configurations for the three-electron atomic ions:

TABLE XIV. Pair correlation energies and higher-order corrections for three-electron atomic ions. All values are in hartrees.

	ϵ_{112}	ϵ_{11}	$\bar{\epsilon}_{12}$	$\bar{\epsilon}_{1}$
4	−0.0029	−0.0399	−0.0020	−0.0001
5	−0.0028	−0.0401	−0.0025	−0.0001
6	−0.0025	−0.0404	−0.0028	−0.0002
7	−0.0020	−0.0410	−0.0030	−0.0002
8	−0.0030	−0.0402	−0.0032	−0.0002
9	−0.0029	−0.0403	−0.0033	−0.0003
10	−0.0034	−0.0399	−0.0034	−0.0003
12	−0.0031	−0.0403	−0.0036	−0.0003
14	−0.0013	−0.0422	−0.0037	−0.0003
16	−0.0011	−0.0424	−0.0038	−0.0003
18	−0.0012	−0.0424	−0.0038	−0.0003
30	−0.0035	−0.0401	−0.0040	−0.0004
36	−0.0036	−0.0401	−0.0041	−0.0004
72	−0.0034	−0.0400	−0.0042	−0.0004
144	−0.0035	−0.0398	−0.0042	−0.0004

$$E(\hat{e}_{1s}\hat{e}_{1s}\hat{e}_{2s}(1s^2 2s^1)) = E_{\mathrm{HF}} + 2\bar{\epsilon}_{1s} + \epsilon_{1s,1s} + 2\bar{\epsilon}_{1s,2s} + \epsilon_{2s,1s,1s} \ , \tag{24}$$

$$E(\hat{e}_{1s}\hat{e}_{2s}(1s^2 2s^1)) = E_{\mathrm{HF}} + 2\bar{\epsilon}_{1s} + 2\bar{\epsilon}_{1s,2s} \ , \tag{25}$$

$$E(\hat{e}_{1s}\hat{e}_{1s}(1s^2 2s^1)) = E_{\mathrm{HF}} + 2\bar{\epsilon}_{1s} + \epsilon_{1s,1s} + 2\bar{\epsilon}_{1s,2s} \ , \tag{26}$$

$$E(\hat{e}_{1s}(1s^2 2s^1)) = E_{\mathrm{HF}} + 2\bar{\epsilon}_{1s} \ . \tag{27}$$

The results for $\bar{\epsilon}_{1s}$, $\bar{\epsilon}_{1s,2s}$, $\epsilon_{1s,1s}$, and $\epsilon_{2s,1s,1s}$ are listed in Table XIV. If we neglect the one-, three-, and four-body corrections, the increment to the correlation energy $\Delta E_c'(4,Z)$, assuming transferability of pair correlations, would be

$$\Delta E_c'(4,Z) \simeq 2\bar{\epsilon}_{1s,2s} + \epsilon_{2s,2s}' \ ,$$

while

$$\Delta E_c'(3,Z) \simeq 2\bar{\epsilon}_{1s,2s} \ .$$

As noted earlier, $\Delta E_c'(4,Z)$ and $\Delta E_c'(3,Z)$ are nearly equal, which suggested that $\epsilon_{2s,2s}'$ was small. Close inspection of the pair energies, however, show that they vary by amounts as large as $\Delta E_c'$, and $\epsilon_{1s,1s,2s}$ is also large. Thus there is no simple explanation for $\Delta E_c'$ in terms of pair energies. The very small magnitude of $\epsilon_{2s,2s}'$ is notable, as this indicates that almost all of the $2s^2$ pair energy is recovered by the $2p^2$ CAS.

CONCLUSION

The correlation energy of ions with up to ten electrons is estimated from experimental data and *ab initio* calculations. Because of lack of truly experimental data beyond an atomic number of ten and lack of accurate *ab initio* data beyond four electrons, these results still require further careful exploration. Many of the entries in Moore's tables are based on Edlen's extrapolation. These should not be used to obtain experimental atomic energies.

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