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Ground-state correlation energies for atomic ions with 3 to 18 electrons

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Recently Davidson *et al.* [Phys. Rev. A **44**, 7071 (1991)] have estimated nonrelativistic correlation energies and relativistic corrections to ionization potentials for atomic ions with up to 10 electrons. In this work, this approach is extended to atomic ions with 11 to 18 electrons. The correlation energies for 3- to 10-electron atomic ions are also recomputed using more recent experimental and theoretical data. Unlike other work the method focuses on the correlation contribution to the individual ionization energies which are obtained by comparing experimental data with relativistic complete-valence-space energies. *Ab initio* estimates of correlation contributions to the ionization energies with extensive configuration-interaction calculations of 3- to 10-electron atomic ions with nuclear charge from 4 through 10 and 18, 36, 50, 72, 100, and 144 have been obtained. The correlation energies obtained from some density-functional models are also compared to these correlation energy data.

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THEORETICAL BACKGROUND

In a recent paper, Davidson *et al.* [1] estimated the exact ground-state correlation energies $E_c(N,Z)$ of hypothetical nonrelativistic atomic ions with N electrons and nuclear charge Z, for N up to 10 electrons. These energies are of considerable interest to theoreticians. They are useful in calibrating density-functional methods and in estimating the basis-set limit of accurate molecular calculations. As most quantum chemistry for molecules is done with a stationary-point-nucleus, nonrelativistic Hamiltonian, it is important to know the atomic energies in this same approximation. In this study, the method used by Davidson *et al.* has been extended for atomic ions up to 18 electrons and the estimates of 2- to 10-electron-ion energies have been reanalyzed and improved.

Scherr, Silverman, and Matsen [2] used tabulations of atomic ionization potentials to obtain correlation energies for atomic ions. Clementi [3] estimated the correlation energies by actually calculating the relativistic corrections from Breit-Pauli perturbation theory [4]. More recently, Anno and Teruya [5] proposed a semiempirical refinement of the relativistic energies and computed the nonrelativistic energies and correlation energies using Moore's revised tables [6].

With the recent improvements in theory [7,8] and experiment [6,9], reasonably accurate estimates of all important high-order corrections in the relativistic atomic model are possible. Further, it is possible with the available recent experimental data [6,9] on ionization potentials to make a discernable refinement and augmentation of the atomic-correlation-energy tables presented in [1].

CORRELATION CONTRIBUTION TO THE IONIZATION ENERGY

The total nonrelativistic, stationary-point-nucleus energy $E(N,Z)$ is defined as the exact ground-state eigenvalue of the nonrelativistic Hamiltonian defined as (in atomic units),

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

Here N denotes the number of electrons and Z the corresponding nuclear charge. The Hartree-Fock (HF) approximation with spin- and symmetry-restricted orbitals furnishes the energy $E_{\mathrm{HF}}(N,Z)$ and the correlation energy $E_c(N,Z)$ is defined by the relation

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

One may show, by treating the electron-electron interaction as a perturbation term and expanding the resulting total energy, that $E(N,Z)/Z^2$ can be expanded in a formal Laurent series in Z^{-1} [2,10–12], viz.,

$$E(N,Z) = B_0(N)Z^2 + B_1(N)Z + B_2(N) + B_3(N)Z^{-1} + B_4(N)Z^{-2} + \cdots \ . \qquad (3)$$

In cases where a single configuration with hydrogenic orbitals is an adequate zeroth-order approximation, one can evaluate the leading terms B_0 and B_1. The spin- and symmetry-restricted Hartree-Fock energy also gives the correct B_0 and B_1 so E_c will begin with a constant term.

For other systems a single configuration does not serve as a satisfactory theoretical model due to the inherent degeneracy of the ground-state solution to (1) for the limit $Z^{-1}=0$, e.g., the $2s^2$-$2p^2$ near-degeneracy mixing in the beryllium isoelectronic series at large Z. In such cases, the Laurent series of $E_c(N,Z)$, as defined in Eq. (3), begins with a residual linear term in Z due to unequal linear coefficients B_1 for the HF and exact energies. The coefficient of this linear term for $E_c(N,Z)$ is defined by $\Delta B_1(N)$, which is simply the difference of the coefficients for the corresponding exact and HF energy series in Eq. (3). $\Delta B_1(N)$ can be exactly determined by diagonalizing the Hamiltonian matrix in the space of degenerate zero-order configurations built from hydrogenic orbitals as demonstrated by Layzer [11] and by Linderberg and Shull [12] for atoms with up to 10 electrons. We have extended the Layzer tables through 18 electrons for atomic ground states considering the full $3s,3p,3d$ orbital degeneracy. In Table I, the coefficients B_0 and B_1 are given for atomic ions through 18 electrons.

In order to eliminate the linear Z dependence, it is preferable to define a modified correlation energy

$$E_c'(N,Z)=E(N,Z)-E_{\mathrm{CAS}}(N,Z)\ , \tag{4}$$

where $E_{\mathrm{CAS}}(N,Z)$ is the complete-active-valence-space multiconfiguration Hartree-Fock (MCHF) energy, that is, the energy from a MCHF calculation including the complex of all configurations that become degenerate at high Z. This includes all arrangements of the valence electrons among the $2s,2p$ orbitals for $N\le 10$ or among the $3s,3p,3d$ orbitals for $10<N\le 18$. Since we needed nonrelativistic results that were the nonrelativistic limits of the relativistic results, in this paper, the CAS MCHF energy is defined as the optimized energy obtained in a calculation for the J level of the observed ground state for $Z=N$ using all jj-coupled configuration states within the nonrelativistic complex of the same parity. These are built from orbitals with $j=l+\frac{1}{2}$ as well as $j=l-\frac{1}{2}$ representing the coupling of the one-electron orbital and spin momenta. Because, for example, the radial parts of $p_{1/2}$ and $p_{3/2}$ are not constrained by this definition to be the same, this definition of the CAS MCHF can lead to lower nonrelativistic energies in some cases than the LS-constrained definition. This CAS MCHF energy will give the correct B_0 and B_1, so E_c' will begin without a linear term.

Numerical computations were performed to determine the HF and CAS energies. The HF energy was determined with a numerical HF program [13]. The CAS energy was determined with GRASP^2 [8] with point nucleus and the speed of light multiplied by 10^5. In most cases where only one LS configuration can be found of the correct symmetry, the HF results and the CAS results are equal within the numerical accuracy of the program. For $N=8$ there is no possible $^3P_2$ LS configuration except p^4, but in the jj coupling the $p_{1/2}$ and $p_{3/2}$ orbitals are not constrained to have the same radial parts and instead of only one configuration state, there are two. This results in a lower CAS energy than the one obtained from an LS-restricted calculation. A difference in the CAS energies is also obtained for atomic ions with 9 electrons where now both representations have only one configuration state, but the jj scheme has two different radial functions. For most cases with more than one configuration in the LS complex, the LS-constrained MCHF and GRASP^2 J-constrained results showed similar differences of a few tenths of a millihartree. Since the LS-constrained CAS and the J-constrained CAS both

TABLE I. Leading coefficients B_0 and B_1 of the Z expansion of the HF and CAS energies. For $N=1$ to $N=10$ B_1 was evaluated using the analytical formulas of Linderberg and Shull [12]. For $N=11$ to $N=18$ we have used the same method to evaluate the coefficients. All values are in hartrees.

N	B_0	B_1 (HF)	ΔB_1	B_1 (CAS)
1	−0.500 000 000 000 000 0	0	0	0
2	−1.000 000 000 000 000 0	0.625 000 000 000 000 0	0	0.625 000 000 000 000 0
3	−1.125 000 000 000 000 0	1.022 805 212 620 027 5	0	1.022 805 212 620 027 5
4	−1.250 000 000 000 000 0	1.571 001 050 240 054 9	−0.011 726 841 838 798 4	1.559 274 208 401 256 5
5	−1.375 000 000 000 000 0	2.334 449 064 548 087 1	−0.006 922 561 338 077 2	2.327 526 503 210 009 9
6	−1.500 000 000 000 000 0	3.261 959 578 856 119 1	−0.003 094 681 348 426 1	3.258 864 897 507 693 0
7	−1.625 000 000 000 000 0	4.353 532 593 164 151 1	0	4.353 532 593 164 151 1
8	−1.750 000 000 000 000 0	5.661 902 482 472 183 5	0	5.661 902 482 472 183 5
9	−1.875 000 000 000 000 0	7.134 334 871 780 216 0	0	7.134 334 871 780 216 0
10	−2.000 000 000 000 000 0	8.770 829 761 088 247 5	0	8.770 829 761 088 247 5
11	−2.055 555 555 555 555 5	9.635 900 970 59	0	9.635 900 970 59
12	−2.111 111 111 111 111 1	10.567 378 430 10	−0.003 573 680 23	10.563 804 749 86
13	−2.166 666 666 666 666 7	11.630 399 033 00	−0.004 397 122 95	11.626 001 910 04
14	−2.222 222 222 222 222 2	12.758 089 774 78	−0.004 838 178 01	12.753 251 596 76
15	−2.277 777 777 777 777 8	13.950 450 655 45	−0.004 885 925 45	13.945 564 729 99
16	−2.333 333 333 333 333 3	15.229 074 556 95	−0.005 811 776 98	15.223 262 779 97
17	−2.388 888 888 888 888 9	16.572 368 597 35	−0.006 497 791 81	16.565 870 805 53
18	−2.444 444 444 444 444 4	17.980 332 776 63	−0.006 926 608 36	17.973 406 168 26

TABLE II. Coefficients of the $(Z+\rho)$ expansion of the $E_{\mathrm{CAS}}-E_{\mathrm{HF}}-\Delta B_1\,Z$ energy. All values are in mhartrees. See Eq. (5).

N	ρ	ΔB_2	ΔB_3	ΔB_4	ΔB_5	ΔB_6	ΔB_7	ΔB_8
4	1.269 237 478 723	10.343 092 862 68	−45.760 902 697 92	−15.813 030 617 26	−1 365. 136 100 350	9 675.323 509 325	−35 850.284 849 29	30 647.145 947 77
5	−0.115 498 743 786 1	7.283 520 794 834	−31.997 320 416 30	0.418 934 106 801 3	−621.119 366 290 8	6 897.356 195 237	−35 113.688 494 79	70 314.793 858 89
6	−2.361 458 982 033	2.243 207 903 990	−5.906 109 873 085	−14.801 223 684 13	−53.198 362 364 97	364.157 404 140 9	−1 199.836 237 101	1 173.350 980 375
8	4.309 603 495 820	0.118 613 247 828 3	−8.328 577 870 333	576.746 659 581 7	−19 988.325 887 63	375 436.030 634 6	−3 614 237.380 997	14 111 480.731 89
9	15.098 607 463 60	0.095 239 973 730 56	−22.193 460 767 77	2 444.542 287 892	−142 566.242 610 0	4 595 471.091 691	−77 290 435.721 13	530 565 520.233 9
12	−4.395 397 153 422	5.297 107 381 919	−81.466 287 023 57	−1 153. 817 495 823	27 822.332 215 17	−349 325.070 835 4	2 229 108.436 207	−6 133 577.453 750
13	−6.651 000 608 321	16.151 086 830 66	−107.519 252 693 8	−746.588 898 218 3	13 403.516 166 84	−142 122.928 118 6	745 164.398 644 9	−1 731 962.211 108
14	−6.759 323 561 721	25.086 313 533 92	−106.668 881 698 1	−1 925.621 824 780	27 605.219 876 84	−297 183.033 375 5	1 689 398.219 161	−4 412 175.949 037
15	−7.220 217 836 788	33.168 319 454 03	−133.568 625 002 6	−2 592.349 734 538	38 984.087 830 06	−410 281.094 337 0	2 287 528.645 756	−5 883 746.685 954
16	−6.796 064 699 310	38.184 712 197 14	−141.281 940 143 5	−4 864.951 197 152	80 121.181 272 50	−991 552.581 169 4	6 646 530.877 386	−20 759 112.981 57
17	−6.825 582 587 196	50.415 126 936 47	−200.970 632 757 7	−9 961.801 299 793	197 508.765 076 8	−2 521 259.844 353	17 441 910.768 37	−54 921 797.569 92
18	−6.703 928 629 690	71.123 949 764 79	−210.713 783 796 4	−24 680.163 858 27	535 065.473 096 0	−6 717 540.639 260	46 326 445.536 88	−144 836 217.101 3

give the correct values for B_0 and B_1, they can only differ beginning with the constant B_2 term.

The residual energy $E_{\mathrm{CAS}}(N,Z)-E_{\mathrm{HF}}(N,Z)\ -\Delta B_1 Z$ was then least-squares fitted to sixth-degree polynomials in $(Z+\rho)^{-1}$ for $Z=4$ to $Z=144$.

$$E_{\mathrm{CAS}}(N,Z)-E_{\mathrm{HF}}(N,Z)-\Delta B_1(N)Z$$

$$=\Delta B_2(N)+\frac{\Delta B_3(N)}{(Z+\rho)}+\frac{\Delta B_4(N)}{(Z+\rho)^2}+\cdots\ . \qquad (5)$$

The optimum ρ and coefficients of the polynomials for $N=4$ to $N=18$ are given in Table II. These coefficients along with ΔB_1 in Table I and $E_{\mathrm{HF}}(N,Z)$ in Table III determine the CAS energy $E_{\mathrm{CAS}}(N,Z)$. Since the polynomial leads to a maximum error of 2 microhartrees in some cases, we thought it prudent to also present the $E_{\mathrm{CAS}}(N,Z)$ in Table IV. The E_{HF} and E_{CAS} values that have already been tabulated in Ref. [1] are not reported.

The quantity $\Delta E_c'(N,Z)$, the modified-correlation-energy increment, which is directly related to the experimental data and forms the focus of this study, is defined as

$$\Delta E_c'(N,Z)=E_c'(N,Z)-E_c'(N-1,Z)\ . \qquad (6)$$

$\Delta E(N,Z)$, $\Delta E_{\mathrm{CAS}}(N,Z)$, and $\Delta E_{\mathrm{HF}}(N,Z)$, the corresponding energy increments for the exact solution, CAS, and HF models, are defined:

$$\Delta E(N,Z)=-I(N,Z)$$

$$=E(N,Z)-E(N-1,Z)\ , \qquad (7)$$

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

$$=E_{\mathrm{HF}}(N,Z)-E_{\mathrm{HF}}(N-1,Z)\ , \qquad (8)$$

$$\Delta E_{\mathrm{CAS}}(N,Z)=-I_{\mathrm{CAS}}(N,Z)$$

$$=E_{\mathrm{CAS}}(N,Z)-E_{\mathrm{CAS}}(N-1,Z)\ . \qquad (9)$$

$I(N,Z)$ is the ionization potential. Thus the relation between $\Delta E_c'(N,Z)$, $E(N,Z)$, and $E_{\mathrm{CAS}}(N,Z)$ may be stated as

$$E(N,Z)=E_{\mathrm{CAS}}(N,Z)+\sum_{n=2}^{N}\Delta E_c'(n,Z)\ . \qquad (10)$$

It is noted here that the above relation dictates that in order to determine $E_c'(N,Z)$ and $E(N,Z)$ it is essential to have accurate knowledge of $\Delta E_c'(n,Z)$ for $n=2$–N. For two electrons $\Delta E_c'(2,Z)$ can be obtained very accurately [14]. Also, recent work on three electron ions [15] has demonstrated that $\Delta E_c'(3,Z)$ can also be calculated to very high precision. In Table V, the two electron energies computed for $Z\geq 21$ are presented.

ATOMIC ENERGIES, IONIZATION ENERGIES, AND RELATIVISTIC CORRECTIONS

The nonrelativistic ionization energy $I(N,Z)$ can be estimated from the experimental atomic ionization potentials. Each ionization energy is deperturbed individually for nuclear motion, Dirac and Breit relativistic effects,

TABLE III. Hartree Fock energies for atomic ions. All values are in hartrees. For atomic ions with $Z \leq 20$ and $N \leq 10$, refer to [1].

Z		$-E_{\mathrm{HF}}(2)$	$-E_{\mathrm{HF}}(3)$	$-E_{\mathrm{HF}}(4)$	$-E_{\mathrm{HF}}(5)$	$-E_{\mathrm{HF}}(6)$	$-E_{\mathrm{HF}}(7)$	$-E_{\mathrm{HF}}(8)$	$-E_{\mathrm{HF}}(9)$	$-E_{\mathrm{HF}}(10)$
21	Sc	427.986 054	475.002 710	519.071 288	559.079 732	596.103 743	630.233 887	660.654 559	688.411 710	713.595 964
22	Ti	470.361 052	522.354 806	571.249 956	615.869 263	657.339 626	695.751 466	730.235 990	761.891 846	790.809 391
23	V	514.736 050	571.956 911	625.928 654	675.408 890	721.575 711	764.519 415	803.318 061	839.123 006	872.024 374
24	Cr	561.111 048	623.809 024	683.107 379	737.698 599	788.811 972	836.537 682	879.900 685	920.105 048	957.240 691
25	Mn	609.486 046	677.911 143	742.786 127	802.738 380	859.048 387	911.806 227	959.983 788	1004.837 855	1046.458 162
26	Fe	659.861 044	734.263 269	804.964 895	870.528 224	932.284 935	990.325 015	1043.567 311	1093.321 328	1139.676 638
27	Co	712.236 043	792.865 400	869.643 681	941.068 124	1008.521 602	1072.094 016	1130.651 202	1185.555 386	1236.895 994
28	Ni	766.611 041	853.717 536	936.822 483	1014.358 072	1087.758 373	1157.113 207	1221.235 418	1281.539 962	1338.116 127

Z		$-E_{\mathrm{HF}}(11)$	$-E_{\mathrm{HF}}(12)$	$-E_{\mathrm{HF}}(13)$	$-E_{\mathrm{HF}}(14)$	$-E_{\mathrm{HF}}(15)$	$-E_{\mathrm{HF}}(16)$	$-E_{\mathrm{HF}}(17)$	$-E_{\mathrm{HF}}(18)$
11	Na	161.858 912							
12	Mg	199.371 810	199.614 636						
13	Al	241.030 707	241.674 670	241.876 707					
14	Si	286.821 455	287.995 897	288.573 131	288.854 363				
15	P	336.737 321	338.563 395	339.644 995	340.349 776	340.718 781			
16	S	390.774 410	393.369 539	395.077 217	396.332 720	397.173 183	397.504 896		
17	Cl	448.930 230	452.409 820	454.861 642	456.788 894	458.226 463	459.048 591	459.482 072	
18	Ar	511.203 082	515.681 330	518.993 281	521.710 104	523.865 225	525.304 387	526.274 534	526.817 513
19	K	577.591 754	583.182 074	587.468 841	591.091 156	594.081 423	596.258 826	597.891 610	599.017 579
20	Ca	648.095 351	654.910 631	660.286 040	664.928 545	668.869 802	671.903 637	674.320 033	676.154 353
21	Sc	722.713 200	730.865 949	737.443 228	743.219 795	748.226 734	752.233 324	755.551 459	758.214 874
22	Ti	801.444 776	811.047 231	818.939 179	825.963 096	832.149 616	837.244 040	841.580 246	845.190 807
23	V	884.289 671	895.453 861	904.772 958	913.157 085	920.636 516	926.932 993	932.402 392	937.076 428
24	Cr	971.247 556	984.085 355	994.943 837	1004.800 716	1013.685 969	1021.298 092	1028.014 959	1033.867 625
25	Mn	1062.318 165	1076.941 323	1089.451 243	1100.893 170	1111.296 835	1120.337 737	1128.415 728	1135.561 344
26	Fe	1157.501 282	1174.021 450	1188.294 713	1201.433 794	1213.468 218	1224.050 677	1233.602 985	1242.155 259
27	Co	1256.796 728	1275.325 480	1291.473 871	1306.422 061	1320.199 396	1332.435 919	1343.575 383	1353.647 563
28	Ni	1360.204 351	1380.853 198	1398.988 410	1415.857 541	1431.489 785	1445.492 663	1458.331 846	1470.036 822

TABLE IV. CAS MCHF energies of atomic ions. All values are in hartrees. Refer to [1] for CAS energies of atomic ions with 4, 5, and 6 electrons and with $Z \leq 20$.

Z		$-E_{\mathrm{CAS}}(4)$	$-E_{\mathrm{CAS}}(5)$	$-E_{\mathrm{CAS}}(6)$
21	Sc	519.325 717	559.230 818	596.170 609
22	Ti	571.516 213	616.027 346	657.409 608
23	V	626.206 730	675.573 963	721.648 807
24	Cr	683.397 266	737.870 657	788.888 180
25	Mn	743.087 818	802.917 417	859.127 704
26	Fe	805.278 385	870.714 235	932.367 360
27	Co	869.968 963	941.261 106	1008.607 134
28	Ni	937.159 554	1014.558 021	1087.847 012

Z		$-E_{\mathrm{CAS}}(8)$	$-E_{\mathrm{CAS}}(9)$	$-E_{\mathrm{CAS}}(12)$	$-E_{\mathrm{CAS}}(13)$	$-E_{\mathrm{CAS}}(14)$	$-E_{\mathrm{CAS}}(15)$	$-E_{\mathrm{CAS}}(16)$	$-E_{\mathrm{CAS}}(17)$	$-E_{\mathrm{CAS}}(18)$
8	O	74.809 550								
9	F	98.831 840	99.409 371							
10	Ne	126.372 219	127.817 831							
11	Na	157.423 827	159.997 415							
12	Mg	191.983 023	195.940 479	199.646 899						
13	Al	230.047 629	235.642 857	241.713 468	241.925 259					
14	Si	271.616 241	279.101 997	288.040 046	288.631 202	288.914 589				
15	P	316.687 908	326.316 227	338.612 372	339.710 549	340.421 388	340.789 760			
16	S	365.261 961	377.284 392	393.423 049	395.149 319	396.413 335	397.255 240	397.594 359		
17	Cl	417.337 912	432.005 667	452.467 676	454.939 755	456.877 309	458.317 601	459.150 649	459.589 676	
18	Ar	472.915 401	490.479 445	515.743 398	519.077 059	521.805 597	523.964 344	525.417 011	526.395 893	526.942 053
19	K	531.994 153	552.705 268	583.248 259	587.558 047	591.193 252	594.187 829	596.380 841	598.024 799	599.156 794
20	Ca	594.573 954	618.682 785	654.980 857	660.380 500	665.036 911	688.983 021	672.034 280	674.463 880	676.306 518
21	Sc	660.654 636	688.411 721	730.940 156	737.542 810	743.334 185	748.346 426	752.372 064	755.705 174	758.378 880
22	Ti	730.236 067	761.891 857	811.125 373	819.043 780	826.083 324	832.275 525	837.390 488	841.743 261	845.365 872
23	V	803.318 138	839.123 017	895.535 897	904.882 498	913.283 007	920.768 446	927.086 853	932.574 280	937.261 964
24	Cr	879.900 761	920.105 059	984.171 252	995.058 250	1004.932 216	1013.823 764	1021.459 135	1028.195 388	1034.063 168
25	Mn	959.983 864	1004.837 865	1077.031 053	1089.570 474	1101.030 155	1111.440 370	1120.505 780	1128.604 434	1135.766 537
26	Fe	1043.567 386	1093.321 338	1174.114 989	1188.418 717	1201.576 188	1213.617 390	1224.225 571	1233.799 754	1242.369 800
27	Co	1130.651 277	1185.555 397	1275.422 807	1291.602 610	1306.569 799	1320.354 120	1332.617 543	1343.780 038	1353.871 200
28	Ni	1221.235 493	1281.539 972	1380.954 295	1399.121 850	1416.010 570	1431.649 990	1445.680 915	1458.544 239	1470.269 341

TABLE V. Total energy and correlation energy of two-electron atomic ions. All values are in hartrees. Refer to [1] for $Z \leq 20$.

Z		$-E(2)$	$-E_c(2)$
21	Sc	428.032 254	0.046 200
22	Ti	470.407 273	0.046 221
23	V	514.782 290	0.046 240
24	Cr	561.157 306	0.046 258
25	Mn	609.532 320	0.046 274
26	Fe	659.907 333	0.046 289
27	Co	712.282 346	0.046 303
28	Ni	766.657 357	0.046 316

finite nuclear radius, and quantum-electrodynamical corrections, viz., the Lamb shift. The correction for nuclear motion was estimated simply by multiplying each experimental ionization energy by a factor of

$$R_\infty / R_Z = 1 + m_e / M_Z \ , \qquad (11)$$

where R_Z is the Rydberg constant for nuclear charge, Z, m_e is the electron mass, and the nuclear mass M_Z was obtained for the most common isotope of each Z by subtracting Zm_e from the atomic masses A given in Ref. [16]. This approximation neglects the effects of mass polarization and the fact that parts of the relativistic and QED correction [17] scale differently with reduced mass.

The other corrections to the ionization energies, on the other hand, were estimated from a CAS multiconfiguration Dirac Fock (CAS DF) calculation on the complex, including finite nucleus, Breit correction, and Lamb shift, using the GRASP^2 program developed in Grant's laboratory [8]. All the configurations contributing to the ground J level were included from all possible jj-coupled CAS configurations in a multiconfiguration Dirac-Fock calculation that optimized the orbitals as

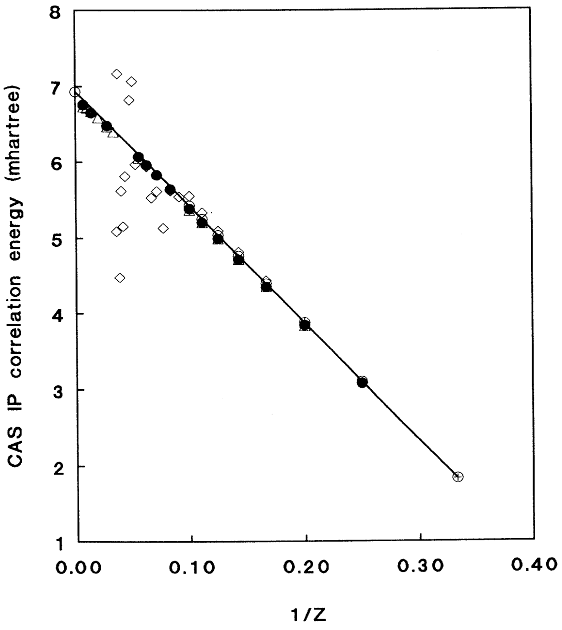

FIG. 1. The CAS correlation contribution to the ionization energy for 3-electron atomic ions, $-\Delta E_c'(3,Z)$ vs $1/Z$. Data (in mhartrees) are the experimental values from Refs. [6,9] (+), theoretical data from Refs. [6,9] (◇), CI data of Ref. [11] (●), and our CI (△). The circled (○) data are used for the fitting, Eq. (16), represented by the solid line.

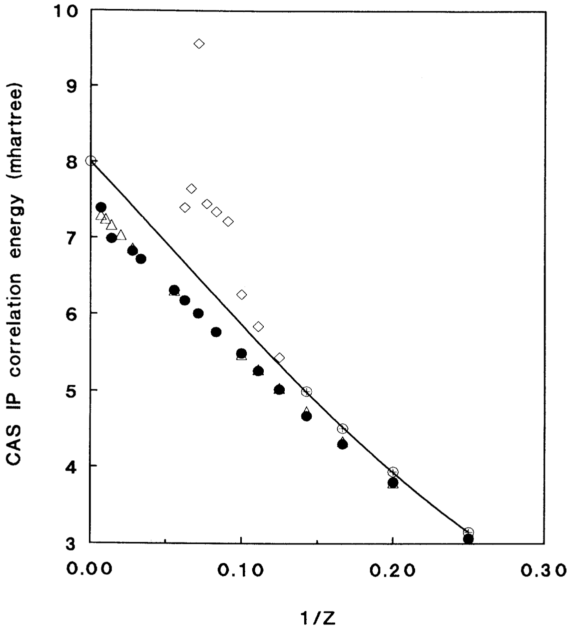

FIG. 2. The CAS correlation contribution to the ionization energy for 4-electron atomic ions, $-\Delta E_c'(4,Z)$ vs $1/Z$.

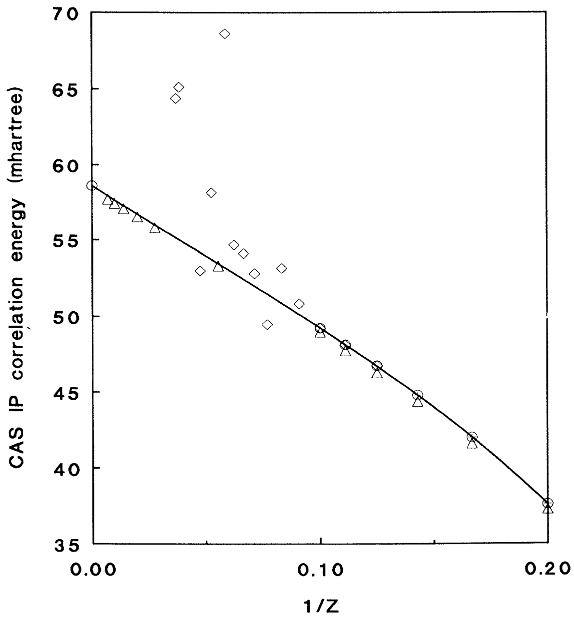

FIG. 3. The CAS correlation contribution to the ionization energy for 5-electron atomic ions, $-\Delta E_c'(5,Z)$ vs $1/Z$.

TABLE VI. Total correction to ionization energies. All values are in hartrees. These values include the Dirac and Breit relativistic corrections and QED corrections and corrections for the finite radius of the nucleus.

Z	$E_{\mathrm{rel}}(3)$	$E_{\mathrm{rel}}(4)$	$E_{\mathrm{rel}}(5)$	$E_{\mathrm{rel}}(6)$	$E_{\mathrm{rel}}(7)$	$E_{\mathrm{rel}}(8)$	$E_{\mathrm{rel}}(9)$	$E_{\mathrm{rel}}(10)$	$E_{\mathrm{rel}}(11)$	$E_{\mathrm{rel}}(12)$	$E_{\mathrm{rel}}(13)$	$E_{\mathrm{rel}}(14)$	$E_{\mathrm{rel}}(15)$	$E_{\mathrm{rel}}(16)$	$E_{\mathrm{rel}}(17)$	$E_{\mathrm{rel}}(18)$
3 Li	−0.000 010															
4 Be	−0.000 088	−0.000 020														
5 B	−0.000 342	−0.000 144	0.000 038													
6 C	−0.000 914	−0.000 516	−0.000 040	0.000 202												
7 N	−0.002 036	−0.001 254	−0.000 359	0.000 364	0.000 554											
8 O	−0.003 967	−0.002 585	−0.001 129	0.000 511	0.001 177	0.000 038										
9 F	−0.006 965	−0.004 873	−0.002 490	0.000 502	0.002 160	−0.000 193	0.000 756									
10 Ne	−0.011 411	−0.008 402	−0.004 777	0.000 311	0.003 422	−0.000 767	0.001 143	0.001 960								
11 Na	−0.017 796	−0.013 303	−0.008 596	−0.000 267	0.005 192	−0.001 779	0.001 382	0.003 215	−0.000 212							
12 Mg	−0.026 373	−0.020 394	−0.013 878	−0.001 397	0.007 440	−0.003 717	0.001 584	0.004 711	−0.000 748	−0.000 275						
13 Al	−0.037 898	−0.029 805	−0.021 325	−0.003 473	0.010 479	−0.006 546	0.001 610	0.006 395	−0.001 682	−0.000 927	0.000 114					
14 Si	−0.052 723	−0.041 849	−0.031 622	−0.006 756	0.014 526	−0.010 735	0.001 191	0.008 364	−0.003 124	−0.002 024	−0.000 100	0.000 582				
15 P	−0.071 470	−0.057 985	−0.044 882	−0.011 497	0.019 611	−0.016 657	0.000 504	0.010 635	−0.005 235	−0.003 714	−0.000 821	0.000 717	0.001 928			
16 S	−0.095 196	−0.078 044	−0.061 978	−0.018 252	0.025 929	−0.024 573	−0.000 883	0.013 464	−0.008 184	−0.006 144	−0.002 474	0.000 675	0.003 044	−0.000 304		
17 Cl	−0.123 648	−0.103 301	−0.083 400	−0.027 557	0.033 730	−0.034 929	−0.002 852	0.016 208	−0.012 165	−0.009 473	−0.004 439	0.000 382	0.004 444	−0.000 954	0.000 953	
18 Ar	−0.159 138	−0.133 419	−0.110 034	−0.040 210	0.043 283	−0.048 277	−0.005 407	0.019 082	−0.017 313	−0.013 959	−0.007 136	−0.000 273	0.006 194	−0.002 112	0.001 057	0.003 009
19 K	−0.201 049	−0.170 453	−0.142 764	−0.056 378	0.054 390	−0.064 827	−0.007 937	0.021 631	−0.023 994	−0.019 681	−0.011 114	−0.001 453	0.008 310	−0.003 827	0.000 984	0.004 032
20 Ca	−0.251 010	−0.214 173	−0.182 377	−0.077 728	0.067 763	−0.084 065	−0.013 202	0.025 050	−0.032 241	−0.026 998	−0.016 179	−0.003 229	0.010 760	−0.006 251	0.000 661	0.005 151
21 Sc	−0.309 225	−0.266 052	−0.229 296	−0.105 080	0.084 696	−0.109 618	−0.016 704	0.027 396	−0.042 491	−0.036 178	−0.022 780	−0.005 836	0.013 658	−0.009 575	−0.000 018	0.006 323
22 Ti	−0.379 075	−0.326 619	−0.284 573	−0.139 053	0.103 477	−0.137 759	−0.022 993	0.029 827	−0.054 975	−0.047 377	−0.030 763	−0.009 495	0.017 054	−0.014 083	−0.000 875	0.007 296
23 V	−0.457 153	−0.398 192	−0.349 998	−0.181 103	0.124 838	−0.170 575	−0.029 908	0.032 157	−0.070 054	−0.060 857	−0.040 678	−0.014 462	0.021 016	−0.019 600	−0.002 197	0.008 342
24 Cr	−0.548 580	−0.479 886	−0.425 635	−0.232 182	0.149 194	−0.208 869	−0.036 171	0.034 183	−0.087 914	−0.077 069	−0.053 934	−0.021 063	0.025 652	−0.026 710	−0.003 956	0.009 067
25 Mn	−0.653 128	−0.575 812	−0.511 453	−0.293 571	0.174 936	−0.250 911	−0.046 099	0.036 795	−0.108 973	−0.096 278	−0.069 272	−0.029 640	0.031 036	−0.035 524	−0.006 191	0.009 811
26 Fe	−0.773 565	−0.682 170	−0.612 113	−0.368 532	0.203 875	−0.298 074	−0.053 928	0.035 923	−0.133 440	−0.118 883	−0.086 499	−0.040 170	0.036 773	−0.045 740	−0.008 953	0.010 333
27 Co	−0.908 967	−0.805 428	−0.725 373	−0.452 971	0.230 784	−0.346 719	−0.066 938	0.038 635	−0.161 964	−0.145 167	−0.108 710	−0.053 497	0.043 601	−0.058 252	−0.012 308	0.010 776
28 Ni	−1.058 893	−0.944 178	−0.854 677	−0.556 618	0.262 423	−0.400 840	−0.077 883	0.035 100	−0.194 880	−0.172 805	−0.134 500	−0.069 875	0.051 015	−0.072 684	−0.016 078	0.010 588
29 Cu	−1.230 866	−1.102 297	−1.000 474	−0.669 969	0.290 153	−0.459 087	−0.088 452	0.033 146	−0.232 536	−0.210 661	−0.161 081	−0.089 795	0.058 847	−0.089 048	−0.020 971	0.010 051
30 Zn	−1.419 618	−1.277 819	−1.164 650	−0.803 269	0.314 629	−0.515 916	−0.106 265	0.033 787	−0.275 654	−0.250 282	−0.195 432	−0.113 600	0.067 576	−0.107 989	−0.026 356	0.009 116
31 Ga	−1.632 520	−1.473 024	−1.348 057	−0.955 626	0.333 955	−0.571 516	−0.122 412	0.029 560	−0.324 259	−0.295 583	−0.234 737	−0.141 874	0.076 397	−0.128 557	−0.032 576	0.007 044
32 Ge	−1.869 545	−1.691 266	−1.549 939	−1.131 095	0.354 580	−0.635 385	−0.135 518	0.023 968	−0.378 851	−0.346 805	−0.279 263	−0.175 092	0.084 955	−0.151 432	−0.039 696	0.005 000
33 As	−2.127 230	−1.933 216	−1.780 392	−1.322 437	0.368 331	−0.695 296	−0.154 802	0.012 937	−0.440 315	−0.404 385	−0.326 618	−0.213 815	0.093 486	−0.176 212	−0.047 850	0.001 780
34 Se	−2.418 518	−2.201 012	−2.027 588	−1.545 188	0.376 296	−0.750 333	−0.176 149	0.002 982	−0.508 922	−0.469 015	−0.383 512	−0.258 432	0.101 120	−0.202 678	−0.056 937	−0.001 991
35 Br	−2.729 911	−2.495 268	−2.310 580	−1.784 286	0.380 033	−0.811 178	−0.204 032	−0.005 511	−0.584 954	−0.540 999	−0.447 497	−0.309 695	0.107 706	−0.230 457	−0.067 333	−0.007 114
36 Kr	−3.075 897	−2.819 912	−2.616 390	−2.054 943	0.377 456	−0.873 537	−0.230 425	−0.019 651	−0.669 755	−0.621 131	−0.518 937	−0.368 145	0.113 415	−0.260 399	−0.078 941	−0.013 420

TABLE VII. Slater-type basis functions used for CI calculations. The orbital exponents are obtained using the relation $\zeta_i = AZ + B$.

nl	*A*	*B*	*nl*	*A*	*B*	*nl*	*A*	*B*	*nl*	*A*	*B*	*nl*	*A*	*B*	*nl*	*A*	*B*	*nl*	*A*	*B*
1*s*	4.291	−7.91	2*p*	2.679	−5.79	5*d*	4.425	−1.20	6*f*	4.813	−1.81	7*g*	7.220	−6.03	8*h*	7.437	−3.15	9*i*	7.599	−0.62
1*s*	2.082	0.18	2*p*	1.410	−3.10	3*d*	2.463	−1.13	4*f*	3.314	−1.54	5*g*	3.778	−4.36	6*h*	4.065	−1.42	7*i*	4.547	−2.21
2*s*	2.806	−4.06	4*p*	1.903	−4.03	6*d*	3.890	−0.92	7*f*	4.384	−3.05	6*g*	1.474	0.41	7*h*	1.751	−3.60	8*i*	1.929	−5.49
1*s*	1.000	0.00	5*p*	1.619	−3.19	4*d*	1.146	−0.39	5*f*	1.377	−1.34	7*g*	1.619	−4.39	9*h*	1.942	−4.72	7*i*	1.492	−4.89
2*s*	0.879	−1.59	3*p*	0.987	2.17	7*d*	1.852	−2.70	6*f*	1.397	−3.31	8*g*	0.806	3.52	6*h*	0.640	2.02	9*i*	1.479	−6.62
4*s*	1.194	−1.94	2*p*	0.493	−1.03	5*d*	1.280	−2.30	4*f*	0.430	0.09	5*g*	0.514	0.87	8*h*	0.802	−1.34			
3*s*	0.807	−1.17	2*p*	0.338	−0.68	6*d*	0.396	−0.26	7*f*	0.721	−0.90	6*g*	0.533	−0.21						
2*s*	0.471	−0.81	3*p*	0.310	−0.60	3*d*	0.595	−0.61	5*f*	0.446	−0.85									
3*s*	0.400	−0.60	2*p*	0.212	−0.52	4*d*	0.356	−0.78												
2*s*	0.296	−0.56	4*p*	0.191	−0.51															
4*s*	0.223	−0.13																		

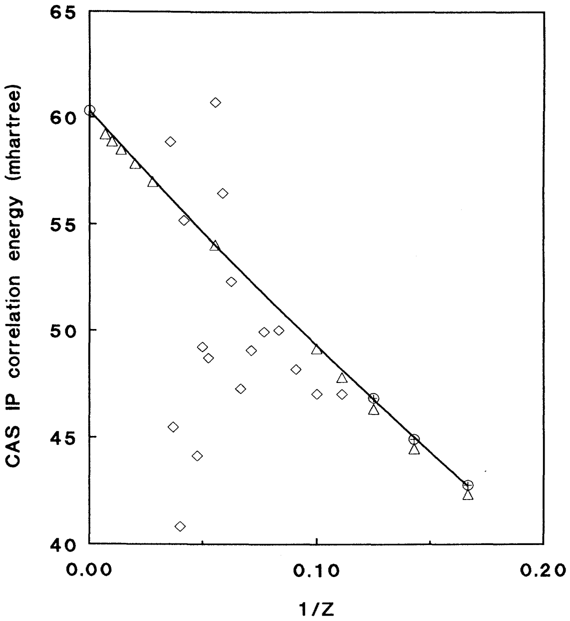

FIG. 4. The CAS correlation contribution to the ionization energy for 6-electron atomic ions, $-\Delta E_c'(6,Z)$ vs $1/Z$.

four-component spinors for this J level. The electron-nuclear potential was modeled using a nucleus with Fermi distribution of positive charge

$$\rho^{\text{nuc}} = \rho_0 / [1 + e^{(r-b)/a}] \; ,$$
$$a = 2.30/4 \ln 3 \; , \qquad (12)$$
$$b = \{[(0.836 A^{1/3} + 0.570)^2 - 1.4\pi^2 a^2]/0.6\}^{1/2} \; ,$$

where a and b are in femtometers. A is in ^{12}C atomic mass units, and ρ_0 is chosen so the total charge is Z [18].

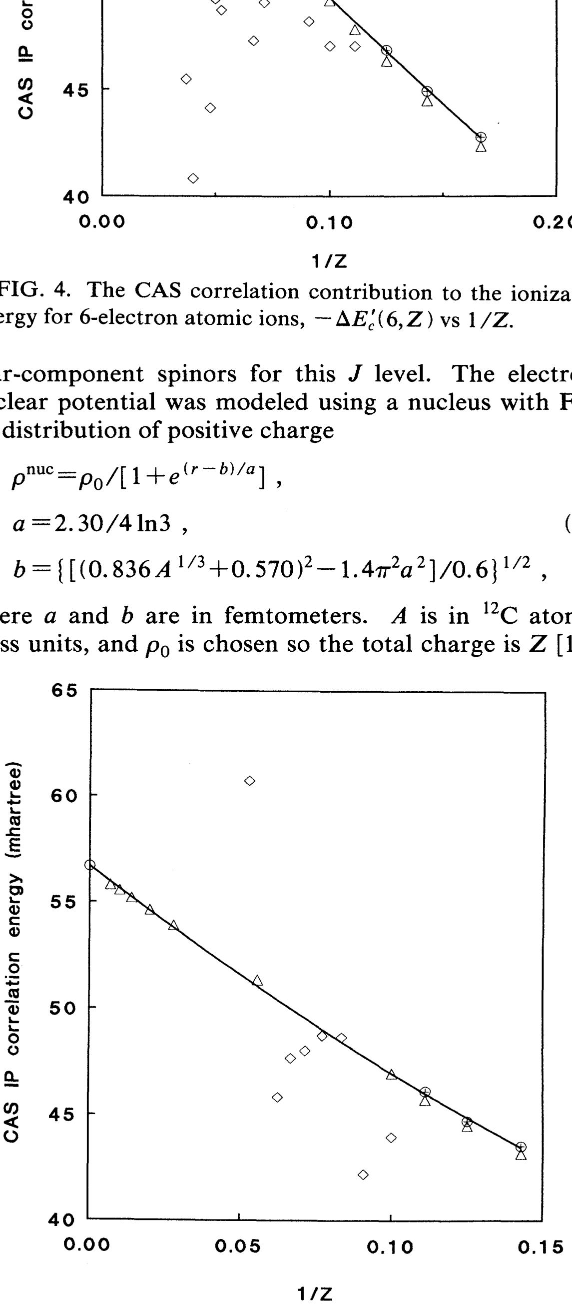

FIG. 5. The CAS correlation contribution to the ionization energy for 7-electron atomic ions, $-\Delta E_c'(7,Z)$ vs $1/Z$.

TABLE VIII. $\Delta E_c'$ determined from CI calculations. All values are in mhartrees. Computed from Eq. (15).

Z	$\Delta E_c'(3)$	$\Delta E_c'(4)$	$\Delta E_c'(5)$	$\Delta E_c'(6)$	$\Delta E_c'(7)$	$\Delta E_c'(8)$	$\Delta E_c'(9)$	$\Delta E_c'(10)$
5	3.831	3.794	37.284					
6	4.350	4.337	41.596	42.350				
7	4.717	4.736	44.353	44.484	43.163			
8	4.993	5.039	46.297	46.315	44.498	60.704		
9	5.208	5.283	47.757	47.800	45.730	59.929	59.868	
10	5.371	5.483	48.971	49.155	47.003	60.445	59.301	64.121
18	6.049	6.307	53.289	54.034	51.348	62.950	58.510	55.812
36	6.467	6.857	55.808	56.979	53.908	65.132	59.809	55.888
50	6.583	7.032	56.525	57.820	54.637	65.843	60.310	56.173
72	6.667	7.164	57.074	58.465	55.194	66.366	60.694	56.406
100	6.712	7.242	57.418	58.852	55.562	66.699	60.959	56.522
144	6.728	7.291	57.693	59.192	55.816	66.966	61.174	56.639

The electron-electron potential was r_{ij}^{-1}.

The Breit interaction was then included by first-order perturbation theory using the frequency-dependent transverse-photon-interaction Hamiltonian. The QED effects were estimated as the sum of vacuum polarization and self-energy. The vacuum-polarization contribution is estimated as the expectation value of the lowest-order, bare-nucleus vacuum-polarization potential [19]. A crude estimate of the self-energy is made by expressing the subshell radial functions as linear combinations of hydrogenic orbitals for which self-energies are relatively accurately known [20].

Table VI gives the resulting corrections to the ionization energy from the CAS DF energy $E_{\mathrm{CAS\ DF}}$,

$$\Delta E_{\mathrm{rel}}(N,Z)=[E_{\mathrm{CAS\ DF}}(N,Z)-E_{\mathrm{CAS}}(N,Z)] -[E_{\mathrm{CAS\ DF}}(N-1,Z)-E_{\mathrm{CAS}}(N-1,Z)]\ , \tag{13}$$

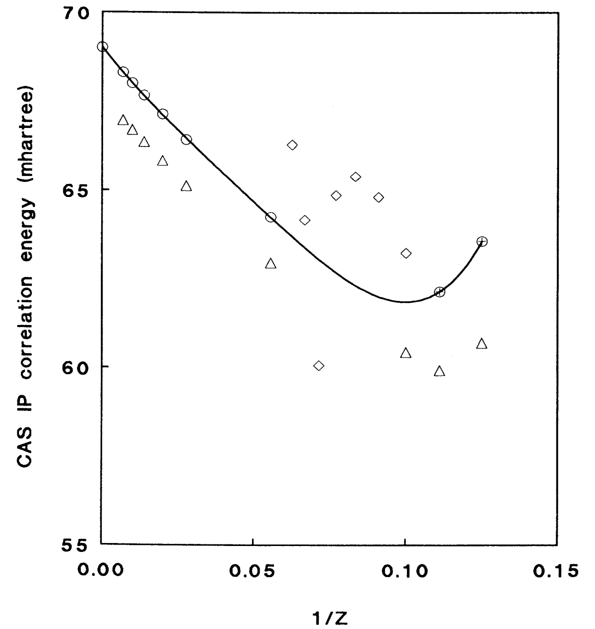

FIG. 6. The CAS correlation contribution to the ionization energy for 8-electron atomic ions, $-\Delta E_c'(8,Z)$ vs $1/Z$.

for atomic ions with 3 to 18 electrons. The numerical values of the total corrections for 3 to 10 electrons are slightly different from those presented in [1] because the recent version of the GRASP^2 program has a revised QED correction. The nuclear-charge distribution is computed from the mass number, which varies somewhat irregularly with Z. It is not possible to fit a smooth polynomial of Z to the total correction. The CAS energies E_{CAS} were obtained from the same program using the same configuration list just by setting the speed of light to a large value, using a point nucleus, and omitting the Breit and QED corrections.

The nonrelativistic stationary-point-nucleus ionization energy $I(N,Z)$ was estimated by employing the relation

$$I(N,Z)=I_{\mathrm{expt}}(N,Z)(R_\infty/R_Z)+\Delta E_{\mathrm{rel}}(N,Z) \tag{14}$$

after converting the literature values, I_{expt} in cm^{-1}, to

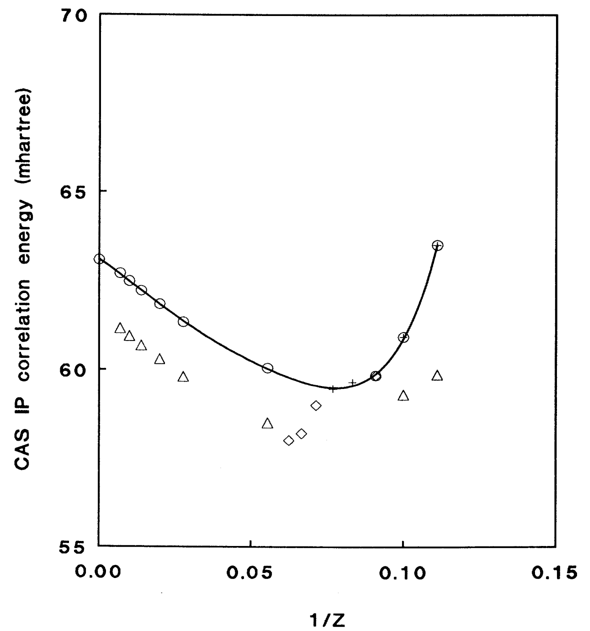

FIG. 7. The CAS correlation contribution to the ionization energy for 9-electron atomic ions, $-\Delta E_c'(9,Z)$ vs $1/Z$.

TABLE IX. Coefficients for the least square $(1/Z)$ polynomial for $-\Delta E_c'(N,Z)$. All values are in mhartrees. See Eq. (16).

N	C_0	C_1	C_2	C_3	C_4	C_5	C_6
2	0.466 632 547 962*D* +02	−0.975 450 114 174*D* +01	0.432 615 999 445*D* +00	0.784 000 989 583*D* +00	0.758 357 254 190*D* +00	−0.318 207 295 427*D* +00	0.944 851 285 465*D* +00
3	0.692 691 300 014*D* +01	−0.145 328 630 038*D* +02	−0.571 012 358 133*D* +01	0.104 334 612 484*D* +02			
4	0.800 016 012 173*D* +01	−0.209 248 582 685*D* +02	−0.104 034 888 501*D* +02	0.661 293 096 769*D* +02			
5	0.585 992 267 316*D* +02	−0.963 082 955 592*D* +02	0.997 564 551 969*D* +02	−0.714 501 616 458*D* +03			
6	0.603 019 138 003*D* +02	−0.116 959 297 933*D* +03	0.697 569 173 623*D* +02				
7	0.567 025 531 264*D* +02	−0.107 406 203 610*D* +03	0.102 924 826 413*D* +03				
8	0.690 101 455 708*D* +02	−0.109 808 487 888*D* +03	0.105 270 787 018*D* +04	−0.168 152 439 123*D* +05	0.101 037 725 502*D* +06		
9	0.631 140 619 777*D* +02	−0.546 157 218 041*D* +02	−0.969 541 665 652*D* +03	0.367 849 637 220*D* +05	−0.495 112 334 333*D* +06	0.256 629 837 126*D* +07	
10	0.583 982 329 429*D* +02	−0.983 869 717 338*D* +01	−0.234 711 990 066*D* +04	0.810 325 148 407*D* +05	−0.106 208 301 032*D* +07	0.564 234 981 510*D* +07	
11	0.310 000 128 788*D* +02	−0.121 068 343 129*D* +03	−0.164 586 682 353*D* +04	−0.243 232 703 651*D* +05	0.834 799 663 115*D* +06	−0.618 950 049 038*D* +07	
12	0.270 001 254 438*D* +02	−0.165 229 682 692*D* +03	−0.270 458 243 430*D* +04	0.544 594 170 127*D* +05	−0.421 889 734 894*D* +06		
13	0.279 998 487 166*D* +02	−0.257 172 254 681*D* +03					
14	0.270 000 000 000*D* +02	−0.378 465 803 275*D* +03	0.329 323 466 958*D* +04				
15	0.280 000 000 000*D* +02	−0.315 693 279 705*D* +03	0.269 718 066 728*D* +04				
16	0.499 985 543 212*D* +02	−0.210 107 084 853*D* +03	0.112 352 071 067*D* +04				
17	0.500 000 000 000*D* +02	−0.702 576 709 699*D* +03	0.861 589 396 190*D* +04				
18	0.500 004 425 155*D* +02	−0.102 780 875 352*D* +04	0.139 450 708 308*D* +05				

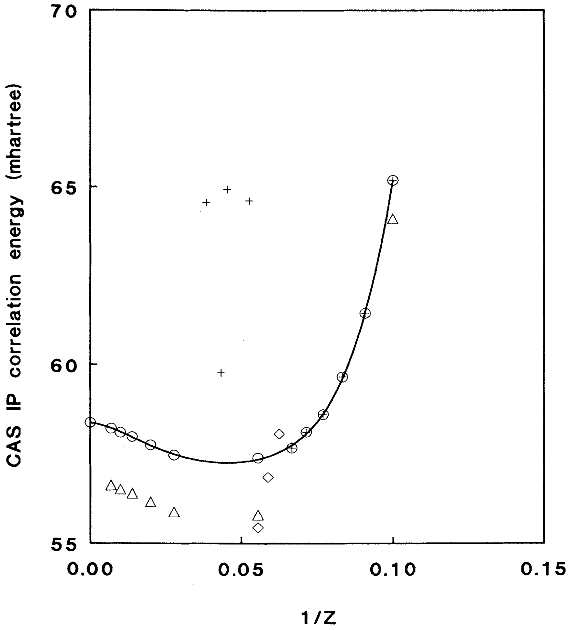

FIG. 8. The CAS correlation contribution to the ionization energy for 10-electron atomic ions, $-\Delta E_c'(10,Z)$ vs $1/Z$.

hartrees using the conversion factor 219 474.630 682 6 cm^{-1}/hartree. The "experimental" CAS correlation contribution to the ionization energy is then simply calculated as

$$-\Delta E_c'(N,Z)=I(N,Z)+\Delta E_{\text{CAS}}(N,Z) \tag{15}$$

and will be discussed later in this study. This assumes ad-

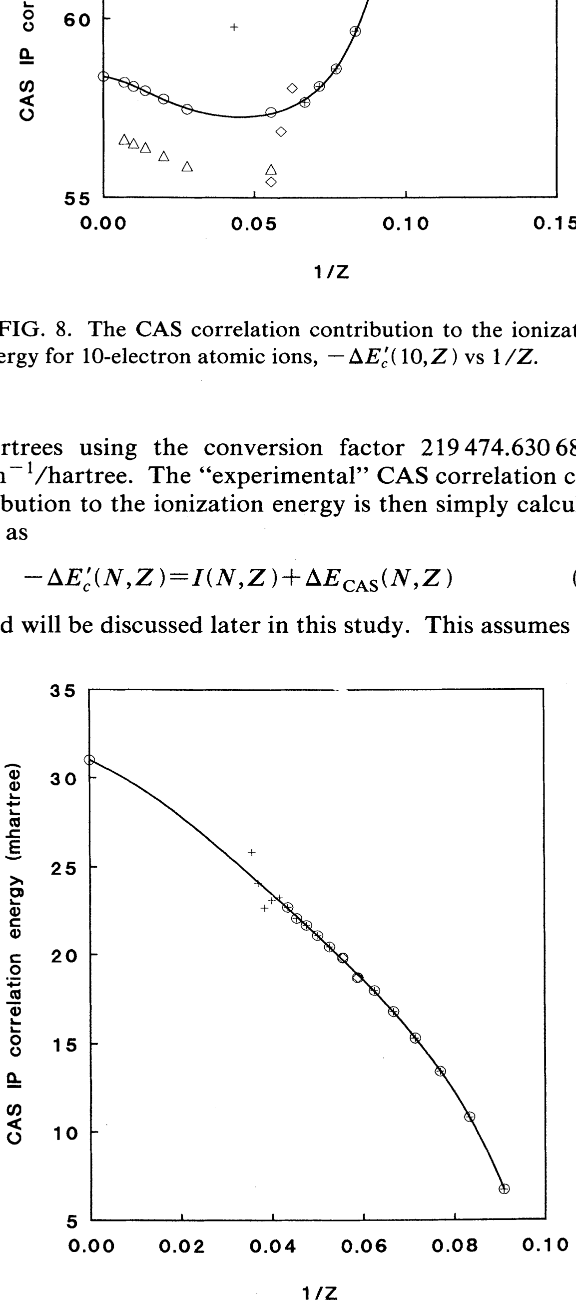

FIG. 9. The CAS correlation contribution to the ionization energy for 11-electron atomic ions, $-\Delta E_c'(11,Z)$ vs $1/Z$.

TABLE X. Estimated total correlation energies. All values are in hartrees. Computed using Eq. (17).

Z		$-E_c(3)$	$-E_c(4)$	$-E_c(5)$	$-E_c(6)$	$-E_c(7)$	$-E_c(8)$	$-E_c(9)$	$-E_c(10)$	$-E_c(11)$	$-E_c(12)$	$-E_c(13)$	$-E_c(14)$	$-E_c(15)$	$-E_c(16)$	$-E_c(17)$	$-E_c(18)$
3	Li	0.045 33															
4	Be	0.047 37	0.094 34														
5	B	0.048 61	0.111 34	0.124 85													
6	C	0.049 45	0.126 44	0.138 80	0.156 40												
7	N	0.050 05	0.140 53	0.150 49	0.166 61	0.188 31											
8	0	0.050 49	0.154 00	0.160 84	0.174 72	0.194 23	0.257 94										
9	F	0.050 84	0.167 08	0.170 35	0.181 59	0.198 84	0.261 09	0.324 53									
10	Ne	0.051 12	0.179 88	0.179 30	0.187 66	0.202 54	0.264 49	0.325 29	0.390 47								
11	Na	0.051 35	0.192 48	0.187 86	0.193 15	0.205 57	0.267 67	0.327 48	0.388 94	0.395 64							
12	Mg	0.051 54	0.204 93	0.196 13	0.198 23	0.208 12	0.270 52	0.330 00	0.389 61	0.400 40	0.438 28						
13	Al	0.051 70	0.217 27	0.204 18	0.202 99	0.210 28	0.273 04	0.332 46	0.391 10	0.404 53	0.451 63	0.469 60					
14	Si	0.051 83	0.229 52	0.212 07	0.207 51	0.212 14	0.275 26	0.334 74	0.392 83	0.408 14	0.462 55	0.486 11	0.505 03				
15	P	0.051 95	0.241 69	0.219 82	0.211 84	0.213 75	0.277 22	0.336 81	0.394 57	0.411 32	0.472 06	0.499 49	0.521 96	0.540 26			
16	S	0.052 05	0.253 81	0.227 47	0.216 01	0.215 17	0.278 95	0.338 67	0.396 23	0.414 13	0.480 61	0.511 13	0.535 85	0.556 10	0.604 76		
17	Cl	0.052 15	0.265 89	0.235 03	0.220 06	0.216 43	0.280 49	0.340 34	0.397 77	0.416 64	0.488 45	0.521 58	0.548 02	0.569 50	0.621 95	0.665 98	
18	Ar	0.052 23	0.277 92	0.242 52	0.224 00	0.217 55	0.281 87	0.341 84	0.399 20	0.418 90	0.495 76	0.531 18	0.559 03	0.581 44	0.636 74	0.683 04	0.722 16
19	K	0.052 30	0.289 92	0.249 95	0.227 85	0.218 56	0.283 10	0.343 19	0.400 50	0.420 93	0.502 63	0.540 12	0.569 21	0.592 37	0.650 04	0.698 10	0.738 66
20	Ca	0.052 36	0.301 89	0.257 33	0.231 62	0.219 46	0.284 22	0.344 42	0.401 70	0.422 78	0.509 15	0.548 52	0.578 74	0.602 55	0.662 28	0.711 89	0.753 68
21	Sc	0.052 42	0.313 84	0.264 66	0.235 33	0.220 28	0.285 23	0.345 54	0.402 80	0.424 46	0.515 37	0.556 50	0.587 76	0.612 14	0.673 73	0.724 79	0.767 76
22	Ti	0.052 48	0.325 77	0.271 95	0.238 98	0.221 03	0.286 16	0.346 56	0.403 82	0.425 99	0.521 35	0.564 12	0.596 35	0.621 25	0.684 56	0.736 99	0.781 14
23	V	0.052 53	0.337 68	0.279 22	0.242 59	0.221 72	0.287 00	0.347 49	0.404 76	0.427 41	0.527 11	0.571 44	0.604 59	0.629 97	0.694 89	0.748 65	0.793 98
24	Cr	0.052 57	0.349 57	0.286 45	0.246 15	0.222 35	0.287 77	0.348 36	0.405 63	0.428 70	0.532 69	0.578 49	0.612 53	0.638 35	0.704 79	0.759 86	0.806 36
25	Mn	0.052 61	0.361 45	0.293 66	0.249 67	0.222 93	0.288 49	0.349 15	0.406 43	0.429 91	0.538 10	0.585 32	0.620 20	0.646 44	0.714 34	0.770 69	0.818 37
26	Fe	0.052 65	0.373 32	0.300 85	0.253 17	0.223 47	0.289 15	0.349 89	0.407 19	0.431 02	0.543 38	0.591 95	0.627 66	0.654 28	0.723 58	0.781 18	0.830 05
27	Co	0.052 68	0.385 18	0.308 01	0.256 63	0.223 96	0.289 76	0.350 57	0.407 89	0.432 05	0.548 52	0.598 41	0.634 91	0.661 90	0.732 56	0.791 39	0.841 43
28	Ni	0.052 72	0.397 03	0.315 16	0.260 07	0.224 43	0.290 33	0.351 21	0.408 54	0.433 01	0.553 55	0.604 71	0.641 98	0.669 33	0.741 30	0.801 34	0.852 55

TABLE XI. Estimated nonrelativistic stationary-point-nucleus atomic energies. All values are in hartrees. Computed using Eq. (10).

Z	$-E(3)$	$-E(4)$	$-E(5)$	$-E(6)$	$-E(7)$	$-E(8)$	$-E(9)$	$-E(10)$	$-E(11)$	$-E(12)$	$-E(13)$	$-E(14)$	$-E(15)$	$-E(16)$	$-E(17)$	$-E(18)$
3 Li	−7.478 06															
4 Be	−14.324 76	−14.667 36														
5 B	−23.424 60	−24.348 92	−24.653 91													
6 C	−34.775 51	−36.534 93	−37.431 03	−37.8450												
7 N	−48.376 90	−51.222 84	−52.966 28	−54.0546	−54.5892											
8 O	−64.228 54	−68.411 71	−71.255 54	−73.2749	−74.5668	−75.0673										
9 F	−82.330 34	−88.101 13	−92.297 12	−95.5012	−97.8078	−99.0928	−99.7339									
10 Ne	−102.682 23	−110.290 89	−116.090 15	−120.7312	−124.3068	−126.6366	−128.1431	−128.9376								
11 Na	−125.284 19	−134.980 88	−142.634 17	−148.9637	−154.0609	−157.6914	−160.3249	−162.0659	−162.2546							
12 Mg	−150.136 19	−162.171 02	−171.928 87	−180.1980	−187.0686	−192.2535	−196.2705	−199.2204	−199.7722	−200.053						
13 Al	−177.238 23	−191.861 27	−203.974 08	−214.4335	−223.3288	−230.3206	−235.9753	−240.3914	−241.4352	−242.126	−242.346					
14 Si	−206.590 30	−224.051 60	−238.769 67	−251.6699	−262.8410	−271.8914	−279.4367	−285.5738	−287.2296	−288.458	−289.059	−289.359				
15 P	−238.192 38	−258.742 00	−276.315 55	−291.9071	−305.6047	−316.9650	−326.6530	−334.7642	−337.1486	−339.035	−340.144	−340.872	−341.259			
16 S	−272.044 48	−295.932 44	−316.611 67	−335.1449	−351.6195	−365.5408	−377.6230	−387.9608	−391.1885	−393.850	−395.588	−396.869	−397.729	−398.110		
17 Cl	−308.146 60	−335.622 93	−359.657 96	−381.3831	−400.8852	−417.6183	−432.3460	−445.1622	−449.3469	−452.898	−455.383	−457.337	−458.796	−459.671	−460.148	
18 Ar	−346.498 72	−377.813 44	−405.454 40	−430.6217	−453.4016	−473.1972	−490.8213	−506.3673	−511.6220	−516.177	−519.524	−522.269	−524.447	−525.941	−526.958	−527.540
19 K	−387.100 85	−422.503 98	−454.000 97	−482.8606	−509.1686	−532.2772	−553.0484	−571.5754	−578.0127	−583.685	−588.009	−591.660	−594.674	−596.909	−598.590	−599.756
20 Ca	−429.952 99	−469.694 55	−505.297 64	−538.0997	−568.1862	−594.8581	−619.0272	−640.7861	−648.5181	−655.420	−660.835	−665.507	−669.472	−672.566	−675.032	−676.908
21 Sc	−475.055 13	−519.385 13	−559.344 39	−596.3391	−630.4542	−660.9398	−688.7572	−713.9988	−723.1377	−731.381	−738.000	−743.808	−748.839	−752.907	−756.276	−758.983
22 Ti	−522.407 28	−571.575 72	−616.141 22	−657.5786	−695.9725	−730.5221	−762.2384	−791.2132	−801.8708	−811.569	−819.503	−826.559	−832.771	−837.929	−842.317	−845.972
23 V	−572.009 44	−626.266 33	−675.688 11	−721.8183	−764.7411	−803.6051	−839.4705	−872.4291	−884.7171	−895.981	−905.344	−913.762	−921.266	−927.628	−933.151	−937.870
24 Cr	−623.861 59	−683.456 95	−737.985 05	−789.0581	−836.7600	−880.1885	−920.4534	−957.6463	−971.6763	−984.618	−995.522	−1005.413	−1014.324	−1022.003	−1028.775	−1034.674
25 Mn	−677.963 75	−743.147 58	−803.032 04	−859.2981	−912.0292	−960.2723	−1005.1870	−1046.8646	−1062.7481	−1077.479	−1090.037	−1101.513	−1111.943	−1121.052	−1129.186	−1136.380
26 Fe	−734.315 92	−805.338 22	−870.829 07	−932.5381	−990.5485	−1043.8565	−1093.6712	−1140.0838	−1157.9323	−1174.565	−1188.887	−1202.061	−1214.122	−1224.774	−1234.384	−1242.985
27 Co	−792.918 08	−870.028 86	−941.376 14	−1008.7782	−1072.3180	−1130.9410	−1185.9060	−1237.3039	−1257.2288	−1275.874	−1292.072	−1307.057	−1320.861	−1333.168	−1344.367	−1354.489
28 Ni	−853.770 25	−937.219 51	−1014.673 23	−1088.0184	−1157.3376	−1221.5257	−1281.8912	−1338.5247	−1360.6374	−1381.407	−1399.593	−1416.500	−1432.159	−1446.234	−1459.133	−1470.889

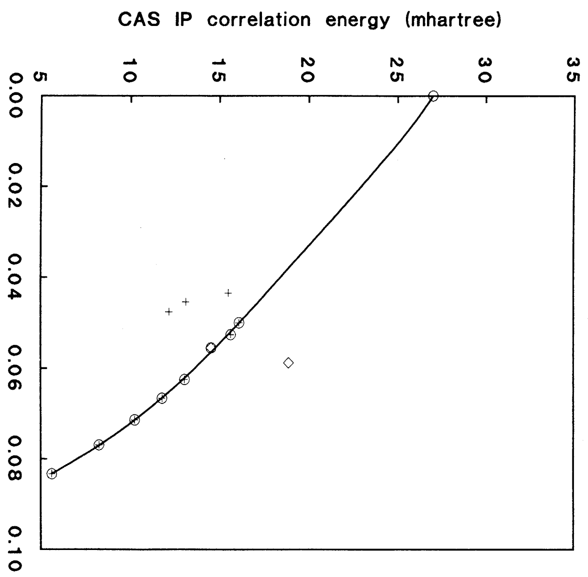

FIG. 10. The CAS correlation contribution to the ionization energy for 12-electron atomic ions, $-\Delta E_c'(12,Z)$ vs $1/Z$.

ditivity of relativistic and correlation effects in the experimental ionization energy for $N \geq 3$. The leading nonadditive term should be of the order of magnitude $\alpha^2 I(N,Z)$ where α is the fine-structure constant. Due to cancellation between I and ΔE_{CAS} in (15), $\Delta E_c'$ is of the magnitude $I(N,Z)/Z_{\text{eff}}^2$. For highly ionized atoms, Z_{eff} is approximately $Z-N$, so the relative error in this deter-

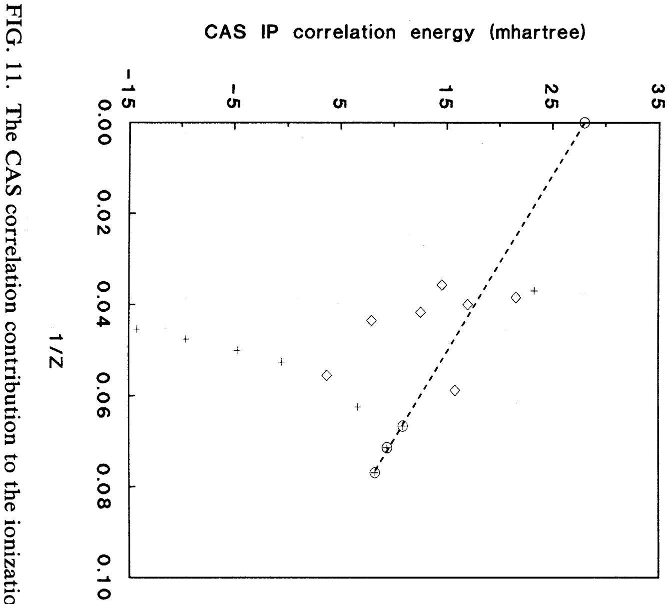

FIG. 11. The CAS correlation contribution to the ionization energy for 13-electron atomic ions, $-\Delta E_c'(13,Z)$ vs $1/Z$.

TABLE XII. Estimated values for the experimental ionization potentials. All values are in eV. Computed using $I^*_{\rm expt} = (-\Delta E_c' - \Delta E_{\rm CAS} - \Delta E_{\rm rel})(R_Z/R_\infty)$.

Z		$I^*_{\rm expt}(3)$	$I^*_{\rm expt}(4)$	$I^*_{\rm expt}(5)$	$I^*_{\rm expt}(6)$	$I^*_{\rm expt}(7)$	$I^*_{\rm expt}(8)$	$I^*_{\rm expt}(9)$	$I^*_{\rm expt}(10)$	$I^*_{\rm expt}(11)$	$I^*_{\rm expt}(12)$	$I^*_{\rm expt}(13)$	$I^*_{\rm expt}(14)$	$I^*_{\rm expt}(15)$	$I^*_{\rm expt}(16)$	$I^*_{\rm expt}(17)$	$I^*_{\rm expt}(18)$
3	Li	5.39															
4	Be	18.21	9.32														
5	B	37.93	25.15	8.30													
6	C	64.49	47.89	24.38	11.26												
7	N	97.89	77.47	47.45	29.60	14.53											
8	O	138.12	113.90	77.41	54.93	35.12	13.62										
9	F	185.19	157.16	114.24	87.17	62.71	34.97	17.42									
10	Ne	239.10	207.27	157.93	126.28	97.20	63.42	40.96	21.56								
11	Na	299.87	264.22	208.49	172.24	138.56	98.84	71.62	47.29	5.14							
12	Mg	367.50	328.03	265.90	225.05	186.75	141.19	109.26	80.14	15.04	7.65						
13	Al	442.02	398.72	330.18	284.71	241.77	190.43	153.83	119.99	28.45	18.83	5.98					
14	Si	523.43	476.28	401.36	351.21	303.58	246.56	205.28	166.77	45.14	33.49	16.35	8.15				
15	P	611.75	560.76	479.42	424.58	372.19	309.58	263.61	220.43	65.02	51.44	30.20	19.77	10.49			
16	S	707.01	652.14	564.39	504.81	447.59	379.49	328.79	280.94	88.05	72.59	47.37	34.82	23.34	10.36		
17	Cl	809.21	750.47	656.29	591.92	529.76	456.28	400.83	348.30	114.20	96.90	67.74	53.15	39.58	23.82	12.97	
18	Ar	918.40	855.74	755.14	685.93	618.69	539.98	479.72	422.51	143.46	124.33	91.28	74.69	59.08	40.72	27.63	15.76
19	K	1034.56	968.00	860.96	786.84	714.39	630.58	565.43	503.55	175.82	154.88	117.97	99.40	81.77	60.92	45.71	31.63
20	Ca	1157.75	1087.24	973.77	894.70	816.85	728.06	658.03	591.40	211.28	188.54	147.78	127.24	107.60	84.35	67.09	50.91
21	Sc	1287.97	1213.52	1093.58	1009.53	926.01	832.54	757.40	686.11	249.84	225.31	180.72	158.20	136.54	110.96	91.68	73.47
22	Ti	1425.30	1346.82	1220.43	1131.35	1041.93	943.89	863.67	787.63	291.50	265.18	216.75	192.27	168.56	140.73	119.44	99.25
23	V	1569.67	1487.24	1354.36	1260.19	1164.59	1062.18	976.76	895.97	336.28	308.16	255.90	229.44	203.64	173.64	150.35	128.19
24	Cr	1721.19	1634.73	1495.36	1396.08	1293.97	1187.43	1096.65	1011.14	384.17	354.26	298.19	269.72	241.78	209.67	184.38	160.28
25	Mn	1879.88	1789.41	1643.45	1539.06	1430.12	1319.59	1223.44	1133.10	435.18	403.48	343.58	313.11	282.97	248.83	221.51	195.47
26	Fe	2045.81	1951.17	1798.75	1689.21	1572.99	1458.69	1356.99	1261.97	489.31	455.83	392.07	359.60	327.20	291.09	261.74	233.77
27	Co	2218.94	2120.21	1961.19	1846.43	1722.72	1604.65	1497.49	1397.56	546.59	511.31	443.74	409.21	374.45	336.48	305.06	275.15
28	Ni	2399.27	2296.46	2130.88	2010.97	1879.13	1757.55	1644.74	1540.12	607.02	569.87	498.54	461.95	424.73	384.97	351.44	319.61

TABLE XIII. Differences from the literature tabulations of ionization potentials. All values are in eV. The first entry of each pair of numbers is the input I_{expt} from the literature minus the output I^{*}_{expt} in Table XII. The second entry (in parentheses) is the estimated uncertainty, where it was given, of the literature value.

Z	*I*(3)	*I*(4)	*I*(5)	*I*(6)	*I*(7)	*I*(8)	*I*(9)	*I*(10)	*I*(11)	*I*(12)	*I*(13)	*I*(14)	*I*(15)	*I*(16)	*I*(17)	*I*(18)
3 Li	0.00(0.00)															
4 Be	0.00	0.00														
5 B	0.00(0.00)	0.00(0.00)	0.00(0.00)													
6 C	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)												
7 N	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00											
8 O	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00	0.00	0.00(0.00)										
9 F	0.00	0.01	0.00	−0.03	0.00(0.00)	0.00(0.00)	0.00(0.00)									
10 Ne	0.00	0.01	0.00(0.05)	−0.06(0.05)	−0.08(0.05)	0.04(0.05)	0.00	0.00								
11 Na	0.00	0.03(0.03)	0.02(0.03)	−0.06(0.05)	−0.15	0.08(0.05)	0.00	0.00(0.00)	0.00(0.00)							
12 Mg	0.00(0.03)	0.03	0.06(0.04)	−0.03(0.06)	0.01(0.06)	0.08	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)						
13 Al	−0.02(0.03)	0.03	−0.05(0.07)	−0.05(0.06)	−0.01(0.09)	0.06(0.05)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)					
14 Si	−0.01	0.08	0.02(0.06)	−0.09(0.12)	−0.04	−0.08	−0.01(0.02)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)				
15 P	−0.01(0.07)	0.03	0.05(0.12)	−0.15(0.25)	−0.06(0.19)	0.02(0.10)	−0.04(0.06)	0.00(0.01)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)			
16 S	0.00(0.08)	0.02	0.05(0.2)	−0.03(0.4)	−0.12(0.3)	0.07(0.19)	−0.05	0.01(0.01)	0.00(0.00)	0.00(0.00)	−0.14(0.01)	−0.03	0.00(0.00)	0.00(0.00)		
17 Cl	0.20	−0.71	0.42	0.08	−0.48	−0.65	−0.77	−0.02	0.00	0.14	0.08	0.31	0.03	−0.01	0.00(0.00)	
18 Ar	−0.36	−0.96	0.61	0.18	−0.43	−1.01	−1.03	−0.05	0.00	−0.01	−0.27	0.33	0.73	0.02	0.00(0.00)	0.00(0.00)
19 K	0.00(0.1)	0.32(2)	0.12(1.7)	−0.15(1.6)	0.26(1.4)	−1.10(1.2)	−0.68(1.0)	0.20(0.6)	0.00(0.00)	0.00(0.05)	−0.41(0.1)	0.04(0.2)	0.89(0.16)	−0.01(0.05)	0.10(0.01)	0.00(0.04)
20 Ca	0.02(0.2)	0.11(2)	0.76(2)	−0.15(1.8)	0.84(1.6)	−1.39(1.4)	−0.78(1.3)	0.50(0.4)	0.00(0.01)	0.00(0.02)	−0.54(0.12)	−0.03(0.2)	1.18(0.20)	0.16(0.17)	0.19(0.13)	0.00(0.00)
21 Sc	0.02(0.37)	−0.94(2)	−0.03(2)	−0.29(2)	1.52(2.0)	−1.71(1.6)	−0.72(1.5)	1.25(0.12)	0.00(0.01)	−0.12(0.05)	−0.69(0.12)	−0.12(0.2)	1.46(0.2)	−0.28(0.05)	0.19(0.2)	0.02(0.00)
22 Ti	0.16(0.4)	−0.35(3)	0.83(2)	−0.60(2)	2.02(2)	−1.97(1.9)	−0.61(1.7)	0.21(0.06)	0.00(0.01)	−0.11(0.06)	−0.83(0.12)	−0.21(0.4)	1.80(0.4)	0.12(0.2)	0.09(0.02)	0.05(0.01)
23 V	−0.01(0.3)	−0.65(3)	0.80(3)	−0.50(2)	3.35(2)	−2.23(2)	−1.00(2)	0.07(0.4)	0.00(0.01)	−0.06(0.4)	−0.24(0.2)	1.05(0.2)	2.17(0.4)	−0.18(0.4)	0.29(0.2)	−0.07(0.02)
24 Cr	−0.03(0.4)	−0.60(3)	1.14(3)	−0.01(3)	5.39(3)	−2.13(2)	0.62(2)	−0.53(0.6)	0.01(0.02)	0.59(0.7)	−0.13(0.6)	1.07(0.5)	2.59(0.5)	−0.38(0.4)	0.36(0.4)	−0.10(0.07)
25 Mn	−0.02(0.4)	−1.54(4)	0.59(3)	−0.41(3)	6.87(3)	−2.86(3)	0.54(2.5)	1.61(0.6)	−0.01(0.03)	−0.53(0.2)	−0.02(0.7)	1.32(0.6)	3.07(0.6)	−0.49(0.5)	0.29(0.5)	−0.94(0.4)
26 Fe	−0.05(0.5)	7.42(3.7)	0.28(4)	−0.54(4)	2.61(0.5)	10.53(4)	4.98(4)	0.20(1.0)	−0.03(0.04)	1.18(2.5)	0.10(0.8)	1.45(0.7)	3.60(0.6)	−0.84(0.6)	0.36(0.1)	−0.18(0.4)
27 Co	0.02(0.6)	−1.30(4)	0.25(4)	−0.29(4)	11.83(3)	−1.52(3)	7.07(1.2)	−0.37(0.5)	0.00(0.04)	0.65(0.06)	0.13(2)	1.80(2)	4.57(1)	−0.48(1)	−0.052(2)	0.22(0.4)
28 Ni	−0.04(0.6)	−1.49(5)	0.43(4)	0.07(4)	15.37(4)	−1.92(4)	3.02(3)	2.13(1)	0.04(0.06)	1.21(0.12)	−0.12(2)	1.76(2)	5.50(2)	−0.62(2)	0.68(2)	1.38(1.0)

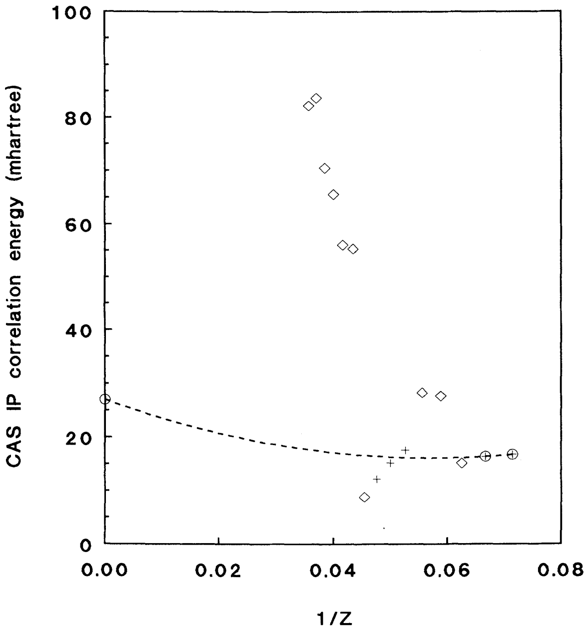

FIG. 12. The CAS correlation contribution to the ionization energy for 14-electron atomic ions, $-\Delta E_c'(14,Z)$ vs $1/Z$.

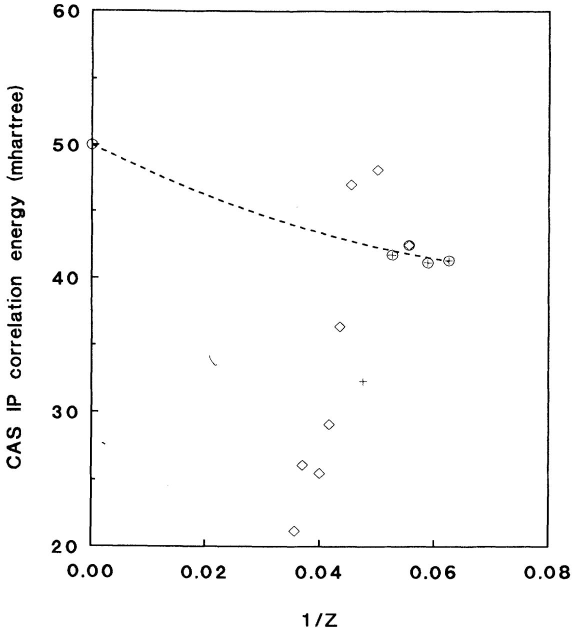

FIG. 14. The CAS correlation contribution to the ionization energy for 16-electron atomic ions, $-\Delta E_c'(16,Z)$ vs $1/Z$.

mination of $\Delta E_c'$ will be of the order of $\alpha^2(Z-N)^2$. This may become significant for $Z-N>13$.

AB INITIO CALCULATIONS

It is also possible to estimate the CAS correlation contribution to the ionization energy by direct *ab initio* configuration-interaction (CI) computations. The package ATOMCI from Sasaki's laboratory [21] has been used for these purposes. The results obtained here were obtained using Slater-type orbitals (STO's). Recently Rizzo, Clementi, and Sekiya [22] have calculated correlation energies of atomic ions with 2, 3, 4, and 10 electrons with large basis sets of Gaussian-type orbitals. The emphasis of our work is on the accurate computation of the extra correlation energy, viz., the CAS ionization-potential (IP) correlation energy $\Delta E_c'(N,Z)$, for 3 to 10 electrons.

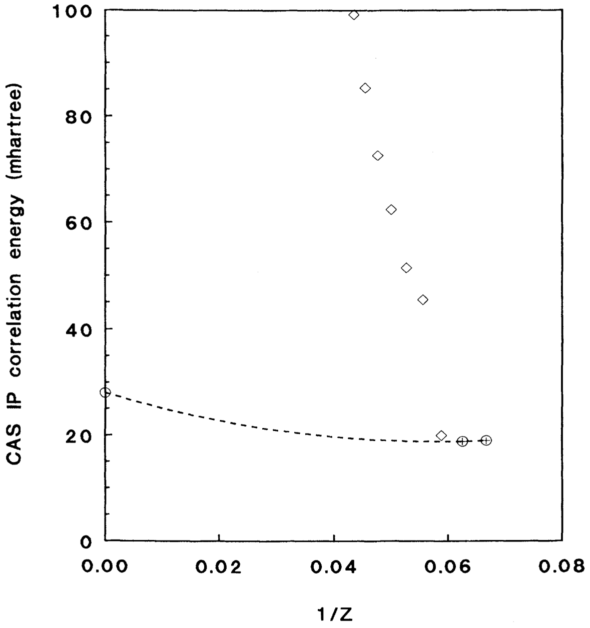

FIG. 13. The CAS correlation contribution to the ionization energy for 15-electron atomic ions, $-\Delta E_c'(15,Z)$ vs $1/Z$.

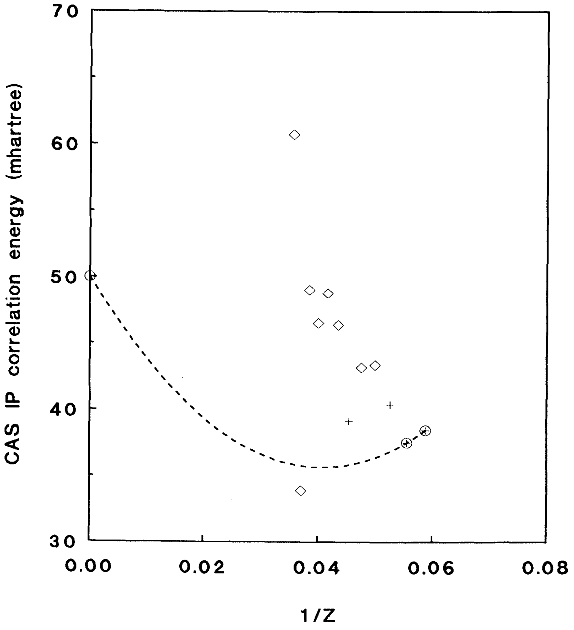

FIG. 15. The CAS correlation contribution to the ionization energy for 17-electron atomic ions, $-\Delta E_c'(17,Z)$ vs $1/Z$.

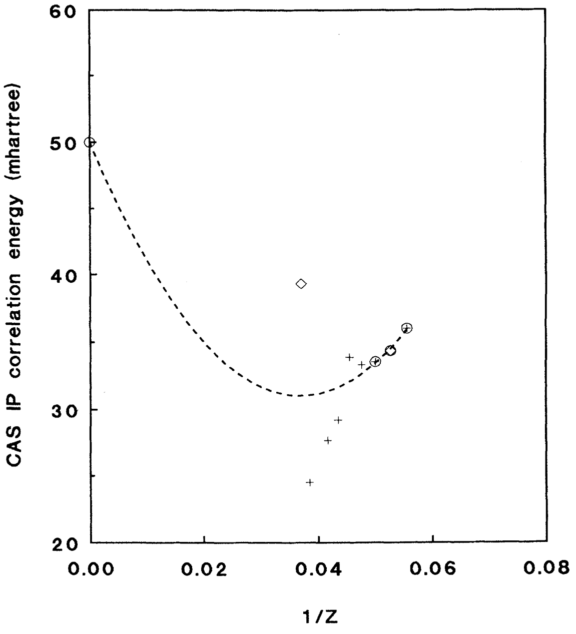

FIG. 16. The CAS correlation contribution to the ionization energy for 18-electron atomic ions, $-\Delta E_c'(18,Z)$ vs $1/Z$.

Therefore STO basis sets were developed for $Z=4$ to $Z=10$, and $Z=18$, 36, 50, 72, 100, and 144 such that the same basis set could be used for calculations of all N. The basis set consisted of 11 s, 10 p, 9 d, 8 f, 7 g, 6 h, and 5 i STO's. The exponents for the s and p functions were chosen at $Z=10$ and $Z=144$ so that the difference between the calculated Hartree-Fock energies and the corresponding numerical Hartree-Fock energies was less than 1 μhartree for all ions with $Z=10$ and 0.1 mhartree for $Z=144$. For the d, f, g, h, and i basis functions single and double configuration interaction (SDCI) was done to optimize manually the orbital exponents. The exponents for all other values of Z were obtained using a

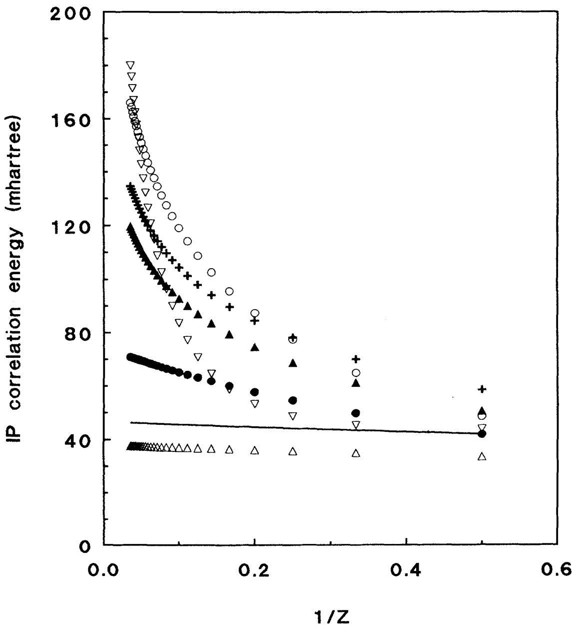

FIG. 17. The correlation contribution to the ionization energy (in mhartrees) for 2-electron atomic ions, $-\Delta E_c(2,Z)$ vs $1/Z$. The solid line represents the best estimate. The density-functional models LYP (△), CS (○), VWN-SPP (+), PZ (▲), B (●), and LC (▽).

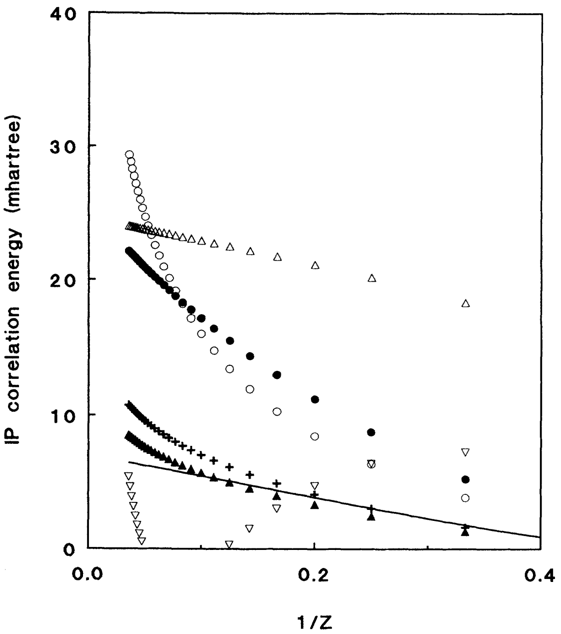

FIG. 18. The correlation contribution to the ionization energy for 3-electron atomic ions, $-\Delta E_c(3,Z)$ vs $1/Z$.

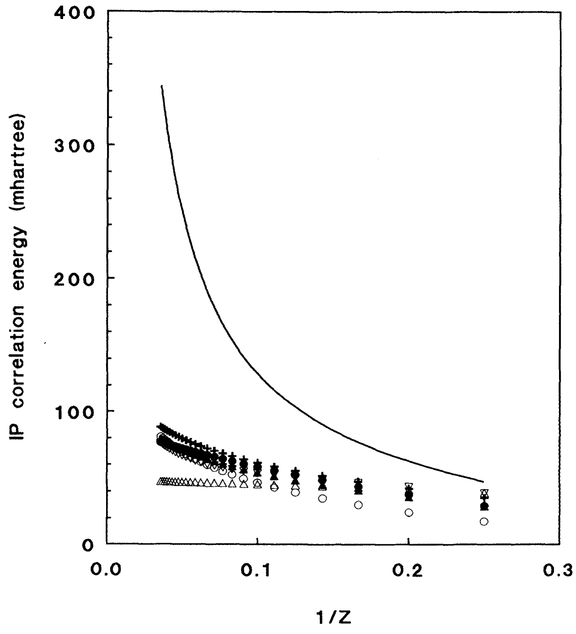

FIG. 19. The correlation contribution to the ionization energy for 4-electron atomic ions, $-\Delta E_c(4,Z)$ vs $1/Z$.

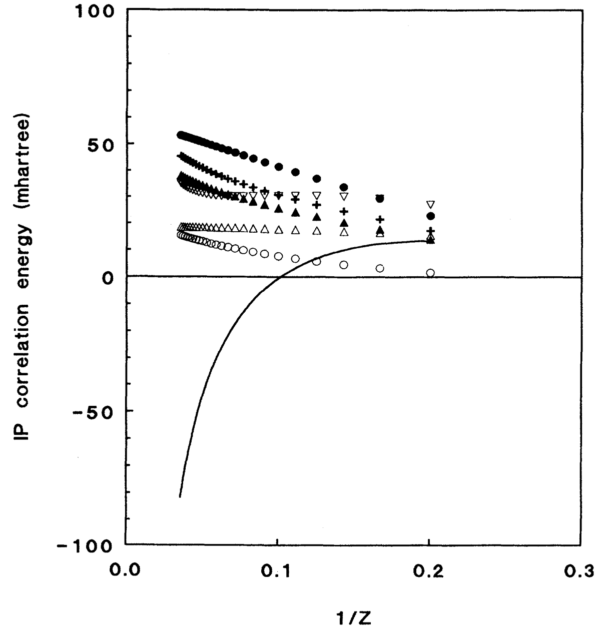

FIG. 20. The correlation contribution to the ionization energy for 5-electron atomic ions, $-\Delta E_c(5,Z)$ vs $1/Z$.

linear fit, viz., $(AZ+B)$ to connect the corresponding exponents of $Z=10$ and $Z=144$ basis sets. The basis sets developed and used for the CI calculations in this work are presented in Table VII.

The CI calculations proceeded in two steps. First, a SDCI calculation was performed to obtain frozen natural orbitals. Then a suitable reference space consisting of single, double, and a few other excitations from the $(2s,2p)$ shell to the $(3s,3p,3d)$ shell was constructed. Perturbation-theory selection of configurations was performed for a subsequent multireference (MR) SDCI calculation of the total correlation energy. The CAS IP correlation contributions have been calculated employing

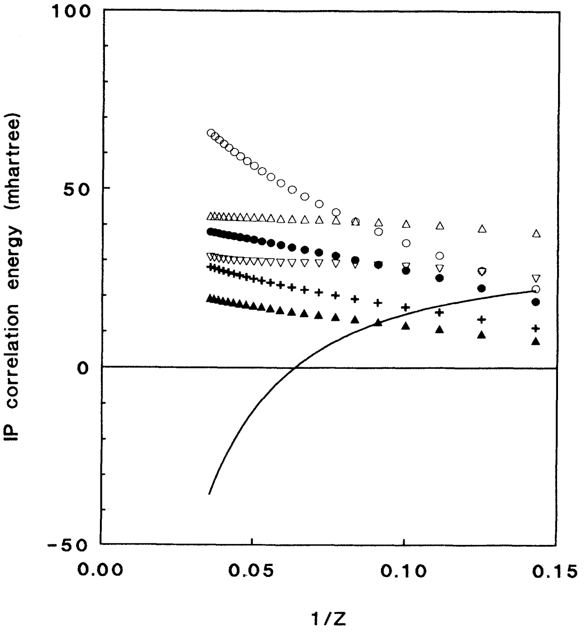

FIG. 22. The correlation contribution to the ionization energy for 7-electron atomic ions, $-\Delta E_c(7,Z)$ vs $1/Z$.

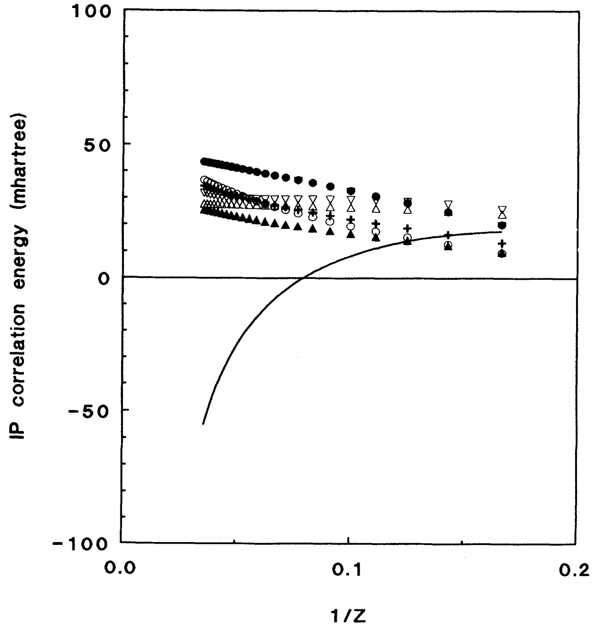

FIG. 21. The correlation contribution to the ionization energy for 6-electron atomic ions, $-\Delta E_c(6,Z)$ vs $1/Z$.

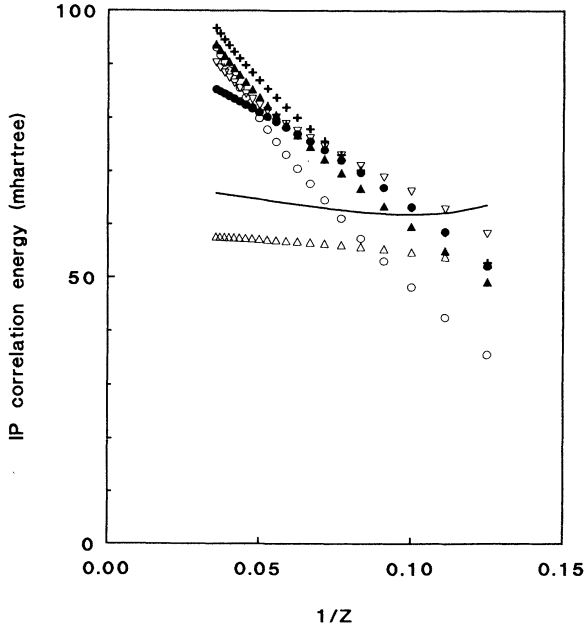

FIG. 23. The correlation contribution to the ionization energy for 8-electron atomic ions, $-\Delta E_c(8,Z)$ vs $1/Z$.

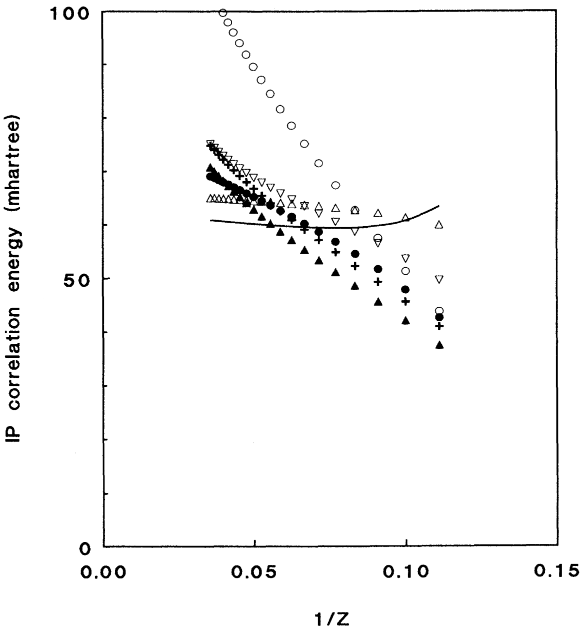

FIG. 24. The correlation contribution to the ionization energy for 9-electron atomic ions, $-\Delta E_c(9,Z)$ vs $1/Z$.

$$\Delta E_c'(N,Z)=[E_{\mathrm{CI}}(N,Z)-E_{\mathrm{CAS}}(N,Z)] -[E_{\mathrm{CI}}(N-1,Z)-E_{\mathrm{CAS}}(N-1,Z)] \qquad (16)$$

and are listed in Table VIII.

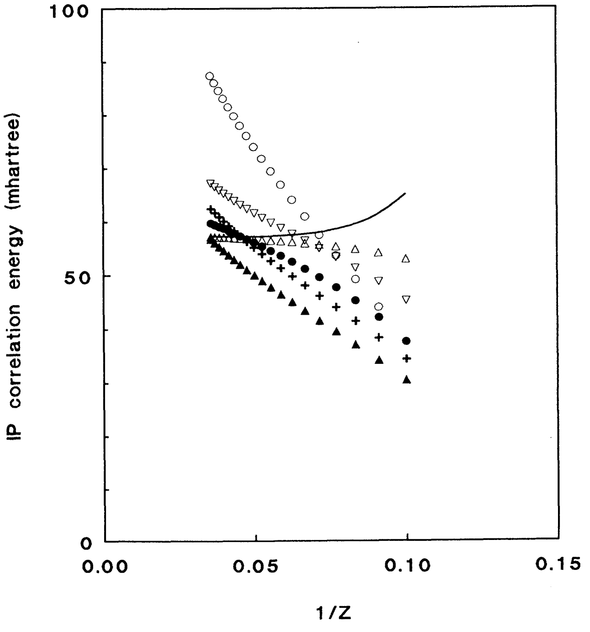

FIG. 25. The correlation contribution to the ionization energy for 10-electron atomic ions, $-\Delta E_c(10,Z)$ vs $1/Z$.

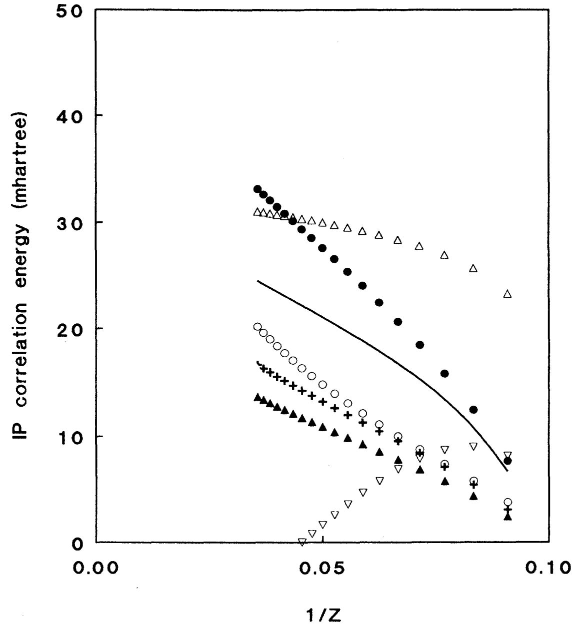

FIG. 26. The correlation contribution to the ionization energy for 11-electron atomic ions, $-\Delta E_c(11,Z)$ vs $1/Z$.

BETTER ESTIMATES OF EMPIRICAL CORRELATION ENERGIES

For the 2-electron ions, the CAS IP correlation energy is determined theoretically [1]. The experimental CAS IP correlation-energy data obtained from Eq. (12) have been plotted in Figs. 1–16 for 3- to 18-electron ions. For N up

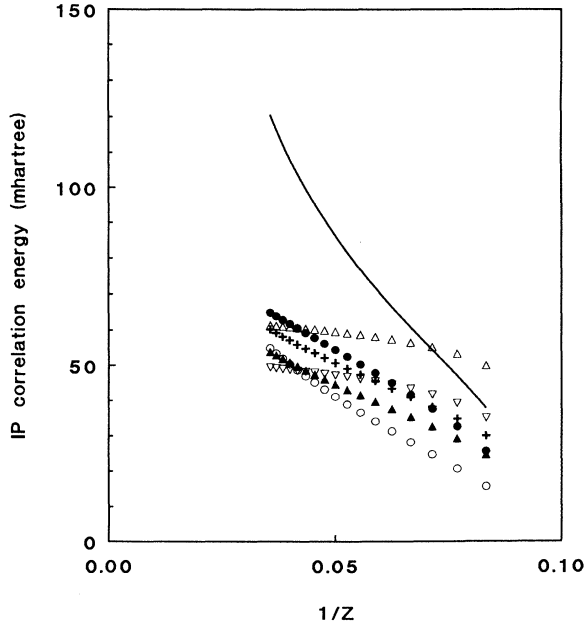

FIG. 27. The correlation contribution to the ionization energy for 12-electron atomic ions, $-\Delta E_c(12,Z)$ vs $1/Z$.

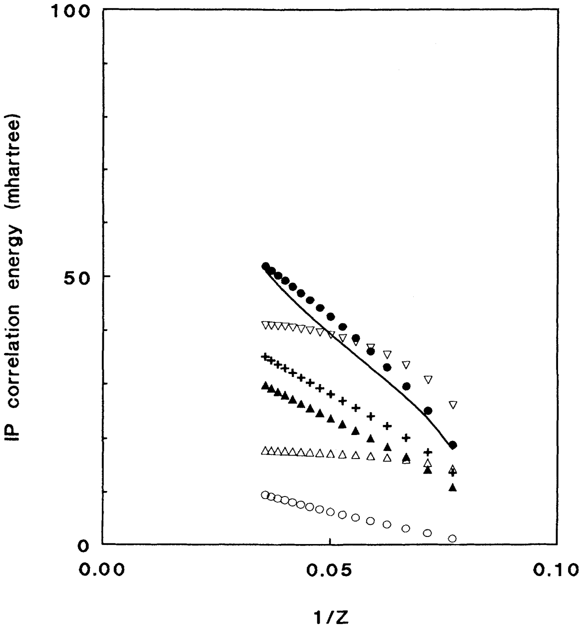

FIG. 28. The correlation contribution to the ionization energy for 13-electron atomic ions, $-\Delta E_c(13,Z)$ vs $1/Z$.

to 10, we have relied heavily on the results of Ivanova and Safronova [23] for the $Z=\infty$ limit. For the 3- to 10-electron ions, the ionization-potential data from [6b] was used in [1]. In the revised figures in this paper, we have included newer tabulations [9] for $Z=11-16$ and 19–28 with the result that the agreement between the literature tabulations and the present approach is improved. However, the ionization potentials for ($N=7$, $Z=27$ and 28), ($N=8$, $Z=26$), and ($N=9$, $Z=27$) still show erratic behavior so that our value lies outside the error bounds estimated in the literature tabulation. The apparent uncertainty in our present approach is less than ±1 mhartree (±0.03 eV) in Figs. 1–8 and these exceptional points are so far off scale that they do not appear at all in these figures.

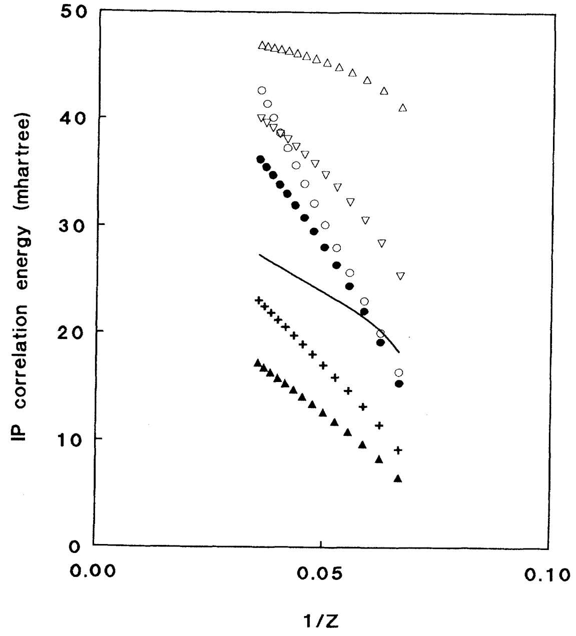

FIG. 30. The correlation contribution to the ionization energy for 15-electron atomic ions, $-\Delta E_c(15,Z)$ vs $1/Z$.

For the ions with $N=11$ through $N=18$ no estimate of the $Z=\infty$ limit is available. For $N=11-18$, the tabu-

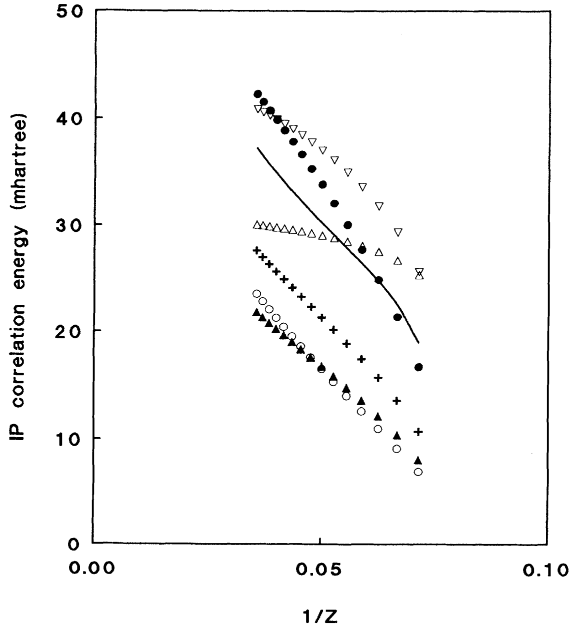

FIG. 29. The correlation contribution to the ionization energy for 14-electron atomic ions, $-\Delta E_c(14,Z)$ vs $1/Z$.

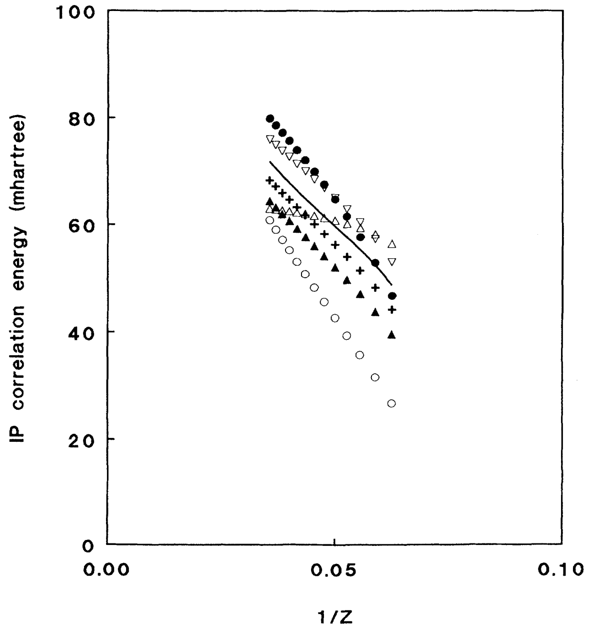

FIG. 31. The correlation contribution to the ionization energy for 16-electron atomic ions, $-\Delta E_c(16,Z)$ vs $1/Z$.

lations listed in [9] were used for all Z except $Z=18$, which came from [6b]. In [1], it was noted that some of the IP data in Moore's tables [6b] are based on Edlen's extrapolations [24]. In the newer tabulations [9] many entries are also based on theoretical calculations and extrapolations. Actually, only the first few ionization potentials for each atom are available to define an "experimental" CAS IP correlation curve independent of previous data smoothing and extrapolations already in the literature. For $N \le 10$, the CI data have provided a stencil for the shape of the CAS IP correlation curve. However, for $N=13-18$ the extrapolations to higher-Z atomic ions are based on similarity to the isovalent $N=5-10$ data and need to be carefully explored before any emphasis is placed on their validity. The value for $Z=\infty$ was simply chosen so that the polynomial fit for low Z would show as little structure as possible and would correspond to roughly the same percentage increase from low Z as found for the isovalent ion with $N \le 11$. This high-Z estimate should not be regarded as accurate. Even so, only the $N=14$ and 15 results lie systematically outside the error bounds on the previous literature values.

In Table IX, the coefficients for the equation that fit the CAS IP correlation energy in the form

$$\Delta E_c'(N,Z)=\sum_{i=0}^{5} C_i(N)/Z^i \tag{17}$$

are given. It may be noted again that for two electrons, rather than using the experimental values of the CAS IP correlation-energy increments, the theoretically calculated energies [1,14] have been used. Also for three electrons, the theoretical data from King [15] have been used. The CAS IP correlation-energy fits in Eq. (13) provide a convenient way to calculate the total correlation energy for the atomic ion from the relation

$$E_c(N,Z)=E_{\mathrm{CAS}}(N,Z)-E_{\mathrm{HF}}(N,Z)+\sum_{n=2}^{N}\Delta E_c'(n,Z) . \tag{18}$$

The results for the total correlation energy for atomic ions is presented in Table X. These may be combined with the $E_{\mathrm{HF}}(N,Z)$ values to yield the nonrelativistic estimates for the total energy $E(N,Z)$ and are given in Table XI.

PREDICTED IONIZATION ENERGY

Another interesting set of results that can be calculated is the estimated experimental ionization potentials I_{expt}^{*} for the respective atomic ions. These estimates are obtained using the relations in Eqs. (14) and (15). These values were converted to eV using (11) with the conversion factor 27.211 608 eV/hartree to yield the IP data presented in Table XII.

Table XIII shows the difference between the literature values used for I_{expt} and our estimation of the ionization potentials given in Table XII. This table also gives the estimated uncertainty of the literature values. As noted earlier, few of the entries in the literature tabulations are based purely on analysis of experimental data. Most have been derived by semiempirical fitting and/or extrapolation procedures similar in spirit to the one used here. If enough of the coefficients in a series of decreasing powers of Z, beginning with Z^4, are to be determined from experiment, then at least six accurate experimental ionization potentials are required for each N. These are gen-

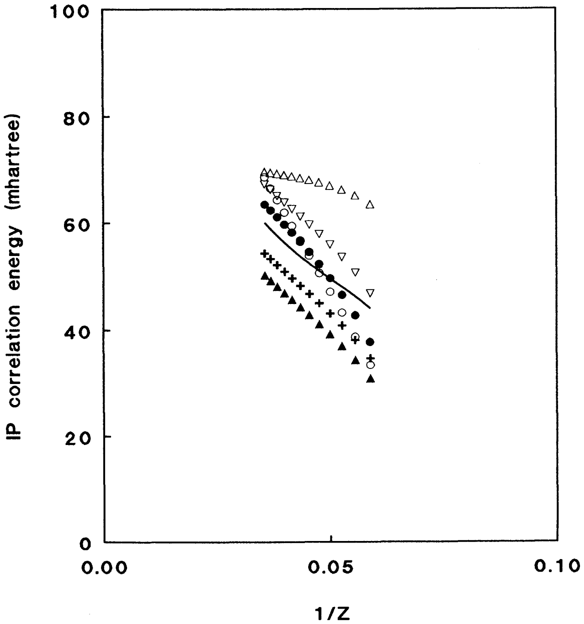

FIG. 32. The correlation contribution to the ionization energy for 17-electron atomic ions, $-\Delta E_c(17,Z)$ vs $1/Z$.

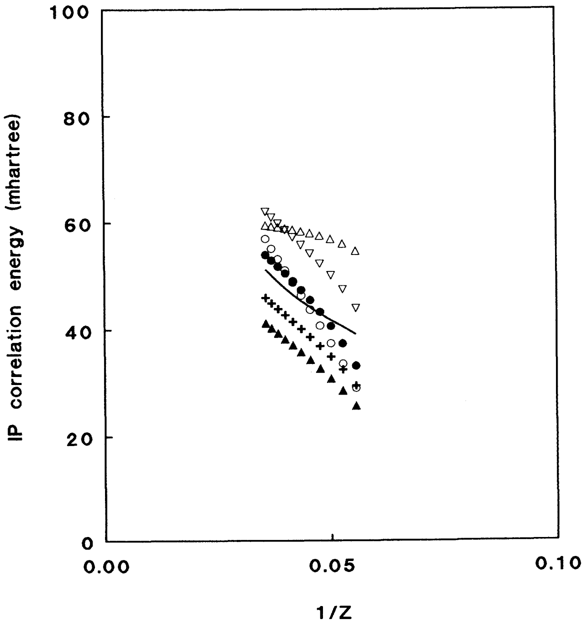

FIG. 33. The correlation contribution to the ionization energy for 18-electron atomic ions, $-\Delta E_c(18,Z)$ vs $1/Z$.

erally not available and some other way of estimating the coefficients must be used. We have relied more heavily than the previous literature on theoretical calculations to remove the dependence of the results on positive powers of Z by subtracting a computed energy with the same coefficients for positive powers. Consequently, only a relatively constant function need be extrapolated and fewer data points are needed. There does not seem to be a discernable dependence on a positive power of Z in our figures. For $N \leq 12$, with the four exceptions mentioned earlier, our results lie within the previous error limits. For this range of N, the present results should be an improvement over the literature values up to $Z=28$. For higher Z, there still could be a problem with the relativity-correlation coupling that is not included in our extrapolating polynomials.

For higher N, there is obvious arbitrariness in our graphs. Even so, our results lie within the error limits of the previous literature for $Z \leq 28$ except for $N=14$ and 15. For $N=15$ we differ from the published literature by a positive power of Z. The sources used in compilations [9g] for $N=15$ for higher Z were extrapolations by Ekberg and Svensson [25a] and Lotz [25b]. Lotz solved the problem of determining an extrapolating polynomial from only two or three pieces of data by assuming that $I(N,Z)$ differs from $I(11,Z+11-N)$ by a linear polynomial $A+CZ$ for $N=12-18$. It is true that $B_0(N)-B_0(N-1)=B_0(11)-B_0(10)$, so the quadratic term is the same for all of these ionization energies. Unfortunately the relativistic corrections for ionization from $3p$ or $3s$ differ significantly in their Z^4 dependence so it is not valid to use the $N=11$ ionization energies as estimators for $N=13-18$. This is clearly shown in our Table VI and is the cause of much of the disagreement in Figs. 11–18 between our curve and the tabulated literature extrapolations.

Kelly [26] has produced another tabulation of ionization energies that we have not used in constructing our extrapolations. Many of the entries in Kelly's tables are taken from the sources we have used, so these entries provide no new information. For one of the exceptional values noted above, ($N=8$, $Z=26$), Kelly gives $I=1456$ eV in much better agreement with our estimate of $I=1458.7$ eV.

DENSITY-FUNCTIONAL MODELS

The correlation-energy data presented in this study is useful in measuring the performance of various density-functional models for correlation energy [27–35]. In particular, the models due to Colle and Salvetti (CS) [27,28], the models of Perdew and Zunger (PZ) [29] with gradient corrections [30], the model of Lee, Yang, and Parr (LYP) [31], the model of Becke (B) [32], the model of Lie and Clementi (LC) [33], and that of Vosko, Wilk, and Nusair [34] with self-interaction correction (VWN-SPP) [35] have been used to compute the density-functional correlation energies. The density-functional correlation-energy estimates were calculated within the restricted Hartree Fock (RHF) model with the GTO basis of Ref. [36]. The self-consistent-field (SCF) energies are in agreement with the numerical HF results to within 1 mhartree. The spin densities and total density was calculated from the resulting RHF wave function of desired LS symmetry. As before, it is convenient to compare the correlation contribution to each individual ionization energy. In Figs. 17–33, the results for the density-functional models are plotted along with the "experimental" estimate. From a gross point of view it may be seen that the performance of the density-functional models improves with increasing number of electrons. However, the density-functional models seem to perform poorly for $N \leq 10$ whenever there is degeneracy effect or inherent CAS nature of the zero-order approximation of the respective state. For the ions computed in the study, only the 2-, 3-, 7-, 8-, 9-, and 10-electron ions have no degeneracy effect. This failure has been well documented in the literature [33,37] and some suitable solutions to overcome the problem of degeneracy have been recommended.

CONCLUSION

The correlation energy of ions with up to 18 electrons is estimated from experimental data and *ab initio* calculations. The correlation data for 3–11 electrons is reliable enough to facilitate high-Z extrapolations. However, for 12–18 electrons, due to the lack of theoretical estimates for the high-Z limit and the lack of reliable compilations of ionization potentials, the present predictions of total energies require further careful explorations.

ACKNOWLEDGMENTS

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