Many-body perturbation-theory calculations of energy levels along the copper isoelectronic sequence

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Energies of the $4s_{1/2}$, $4p_{1/2}$ and $4p_{3/2}$ states of Cu-like ions with nuclear charges in the range $Z = 29 - 92$ are calculated using relativistic many-body perturbation theory. These calculations include the lowest-order Dirac-Fock energies, second- and third-order Coulomb correlation corrections, the lowest-order retarded Breit interaction, second- and third-order correlation corrections to the Breit interaction, finite nuclear size corrections, and corrections for reduced mass and mass polarization. The order of magnitude of the omitted fourth- and higher-order correlation corrections is estimated by chaining second-order Brueckner orbitals. Using this estimate, we find that omitted correlation corrections to the ionization energies are less than the numerical error in the terms included in the calculation for $Z \geq 50$, and that omitted correlation contributions to the $4p_{3/2}$-$4s_{1/2}$ energy intervals are less than the numerical errors for $Z \geq 35$. The theoretical $4p_{3/2}$-$4s_{1/2}$ energy intervals, and the $4p_{3/2}$-$4p_{1/2}$ fine-structure intervals are compared with experiment to determine the QED contributions to the energies. The QED corrections inferred in this way are accounted for approximately by semiempirical values of the $n = 4$ Lamb shift.

I. INTRODUCTION

This is the third in a series of relativistic many-body perturbation theory (MBPT) studies of energy levels of ions having one valence electron outside closed shells. In the first of these studies,[1] we calculated energies of the $2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$ states along the lithium isoelectronic sequence. We found that the perturbation expansion for the correlation corrections to the Coulomb and Breit interactions converged so rapidly that radiative corrections were larger than the omitted higher-order correlation corrections for $Z > 10$. It was, therefore, possible to infer the radiative corrections by comparing theoretical energies with experiment.[2] Indeed, an experiment to measure the Lamb shift in Li-like uranium is in progress.[3] In the second paper of the series,[4] we calculated energies of the $3s_{1/2}$, $3p_{1/2}$, and $3p_{3/2}$ states in Na-like ions. The perturbational treatment of the correlation corrections to energies of Na-like ions was similar to that used to study Li-like ions, except that the dominant terms in the second-order corrections to the Breit interaction and mass-polarization were summed to all orders using random-phase-approximation (RPA) techniques. Here we report calculations of energies of $4s_{1/2}$, $4p_{1/2}$ and $4p_{3/2}$ states of Cu-like ions with nuclear charges in the range $Z = 29 - 92$. These calculations follow the pattern used to study Na-like ions. The calculations are based on Dirac-Fock (DF) wave functions and include second- and third-order Coulomb correlation corrections, the retarded Breit interaction, second- and third-order correlation corrections to the Breit interaction, finite nuclear size corrections, and reduced mass and mass-polarization corrections. Fourth- and higher-order correlation corrections are omitted, as are QED corrections such as the electron self-energy and vacuum polarization.

To estimate the size of the omitted fourth- and higher-order correlation corrections, we iterate the second-order terms to obtain chained Brueckner-orbital (CBO) corrections. For individual term energies, we find that the contributions of the omitted terms are smaller than the numerical errors in the lower-order terms for $Z \geq 50$. For the $n = 4$ energy intervals, the situation is even better; the higher-order terms are found to be smaller than the numerical error in the lower-order terms for $Z \geq 35$. Near the neutral end of the isoelectronic sequence, the principal source of error in the the present calculations of energy intervals is the incomplete treatment of correlation corrections, while for $Z \geq 35$ the error is dominated by the omitted QED corrections.

Measurements of the $4p_{1/2}$-$4s_{1/2}$ and $4p_{3/2}$-$4s_{1/2}$ energy intervals extend along the entire isoelectronic sequence, from neutral copper, $Z = 29$, to Cu-like uranium, $Z = 92$. For neutral copper and for ions in the range $Z \leq 35$, the transition energies are listed by Moore;[5] for ions in the intermediate range of nuclear charge, $Z = 36 - 42$, the energy intervals are found in various research papers;[6-12] and for ions with $Z \geq 44$, the measured intervals are tabulated and smoothed by Seely, Brown, and Feldman.[13] From the point of view of measurement, the copper sequence has been studied more completely than any other isoelectronic sequence.

Theoretical calculations of energies of the ground state and of several excited states of Cu-like ions were carried out previously at the DF level by Cheng and Kim.[14] These calculations, which included the Breit interaction, are in good agreement with our lowest-order results.

Nonrelativistic MBPT calculations of the second- and third-order correlation corrections to the Coulomb interaction for Kr^{7+} and Mo^{13+} were worked out previously by Younger.[15] The values of the correlation energy obtained from these nonrelativistic calculations are not directly comparable to those from the present calculations because a different definition of the lowest-order Hartree-Fock Hamiltonian is used in the two calculations; nevertheless, the values of the Coulomb correlation energy from the two treatments agree to better than 10%.

Semiempirical calculations, based on a relativistic model potential determined from the observed spectrum, were carried out by Ivanov *et al.*[16] These calculations agree very precisely with the observed spectrum; however, because of the semiempirical nature of the model potential, one cannot use these calculations as a guide to understanding the copper sequence at a fundamental level.

Discussions have appeared in the literature over the past few years concerning the role of QED corrections,[17] of nuclear finite size corrections,[18] and correlation corrections[19] in highly-charged ions of the copper sequence. It is partially to address such questions that the present work was carried out.

The theoretical energy intervals determined in the present study differ from the measured intervals in a systematic way along the sequence. We find that the differences between theoretical and experimental intervals are given approximately by scaling the known values of the hydrogenic $n = 2$ self-energy and vacuum-polarization corrections[20,21] to $n = 4$, and then by reducing the nuclear charge from Z to $Z - 15.6$. The resulting semiempirical Lamb-shift corrections can be used to predict energies for ions where precise experimental values are not yet available. The QED corrections taken from Grant's MCDF computer code[22,23] are also found to account well for the energy differences. Determining these atomic QED corrections from *ab initio* calculations remains as an important challenge for atomic theory.

II. DISCUSSION OF RESULTS

In Table I, we list the contributions to the energies of the $4s$ and $4p$ states of Cu-like ions along the sequence. In the third column of the table, we give the lowest-order DF energies, $E^{(0)}$. These energies are calculated in the $V(n-1)$ frozen-core approximation. Finite nuclear size corrections are included in the DF wave functions and in the basis sets used in the perturbation expansion by replacing the Coulomb field of the nucleus by the field of a finite (Fermi) distribution of nuclear charge with parameters determined from experiment.[21] This facilitates the treatment of the large number of ions considered in this paper. If high-accuracy work is done for a particular ion with a nuclear charge distribution known to higher precision, the nuclear finite-size correction should be recalculated along the lines of Ref. 2.

In the fourth column of the table, we list the second-order correlation energies, $E^{(2)}$. These second-order energies are calculated by evaluating the relevant sums over intermediate states[24] using a pseudospectrum constructed from B splines[25] to replace the exact single-particle spectrum. Our pseudospectrum consists of 40 B splines of order 7 for each angular momentum state. The calculations of the double sums over excited states in the expression for $E^{(2)}$ included all orbitals with angular momentum $\ell \leq 8$ explicitly. The contributions to the sums from orbitals with higher angular momentum were estimated by extrapolation. The uncertainty in the extrapolation procedure was the source of the error quoted in column 4 of the table.

The $E^{(2)}$ contributions to the energy are plotted against nuclear charge Z, in Fig. 1. In a nonrelativistic $1/Z$ expansion, the second-order correlation energy would be independent of Z. The variation near $Z = 29$ is due to the fact that we are using perturbation theory based on DF orbitals rather than Coulomb orbitals; the variation seen at high Z is a relativistic effect.

In column 5 of Table I, we list the third-order correlation corrections, $E^{(3)}$. The 84 Brueckner-Goldstone graphs[24] contributing to $E^{(3)}$ are evaluated using the same techniques used to evaluate $E^{(2)}$. This is the most numerically intensive step in the calculation. To make the evaluation of $E^{(3)}$ practical, we included only orbitals with $\ell \leq 5$ and we constructed the basis sets for these orbitals using only 14 B splines of order 4. The error assigned to this term in the table is 2.4%. This error was determined by averaging the error made in a calculation of $E^{(2)}$ using the same limited basis set.

The variation of $E^{(3)}$ as a function of nuclear charge is shown in Fig. 2. A nonrelativistic $1/Z$ expansion would predict that $E^{(3)}$ falls as $1/Z$. The strikingly different behavior seen in Fig. 2 is a result of the factors described above in connection with Fig. 1. It should be noted that $E^{(3)}$ remains about 5% of $E^{(2)}$ even at high Z.

In the sixth column of Table I, we list the values of the first-order Breit interaction, $B^{(1)}$. We follow the scheme used in our previous studies[1,4] and include retardation

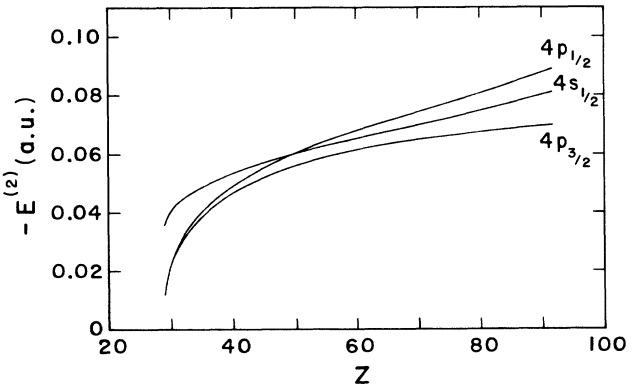

FIG. 1. Second-order correlation energy $E^{(2)}$ for the $4s_{1/2}$, $4p_{1/2}$, and $4p_{3/2}$ states of Cu-like ions as a function of nuclear charge Z.

TABLE I. Contributions to the energies (a.u.) of $4s_{1/2}$, $4p_{1/2}$, and $4p_{3/2}$ states of Cu-like ions. Values in parentheses denote estimated errors in final digits.

Z	State	$E^{(0)}$	$E^{(2)}$	$E^{(3)}$	$B^{(1)}$	$B^{(2)}$	$B^{(3)}$	RM	E^{tot}
29	$4s_{1/2}$	−0.23830	−0.03540(10)	−0.01000(24)	0.00019	−0.00008	0.00006		−0.28353(26)
	$4p_{1/2}$	−0.12410	−0.01244(3)	−0.00447(11)	0.00007	−0.00002	0.00003		−0.14093(11)
	$4p_{3/2}$	−0.12334	−0.01205	−0.00433(10)	0.00005	−0.00002	0.00002		−0.13966(10)
30	$4s_{1/2}$	−0.61572	−0.04044(13)	−0.00427(10)	0.00038	−0.00019	0.00007	0.00001	−0.66015(16)
	$4p_{1/2}$	−0.41246	−0.02233(4)	−0.00372(9)	0.00027	−0.00009	0.00006		−0.43827(10)
	$4p_{3/2}$	−0.40910	−0.02152(2)	−0.00360(9)	0.00020	−0.00009	0.00004		−0.43407(9)
31	$4s_{1/2}$	−1.08528	−0.04284(14)	−0.00134(3)	0.00061	−0.00031	0.00007	0.00001	−1.12907(14)
	$4p_{1/2}$	−0.80235	−0.02780(6)	−0.00208(5)	0.00054	−0.00019	0.00008	0.00001	−0.83179(8)
	$4p_{3/2}$	-0.79523	−0.02672(6)	−0.00202(5)	0.00040	−0.00019	0.00006	0.00001	−0.82370(8)
32	$4s_{1/2}$	−1.63631	−0.04457(14)	0.00042(1)	0.00088	−0.00044	0.00008	0.00001	−1.67992(14)
	$4p_{1/2}$	−1.27752	−0.03168(7)	−0.00072(2)	0.00089	−0.00031	0.00009	0.00001	−1.30924(7)
	$4p_{3/2}$	−1.26555	−0.03051(7)	−0.00071(2)	0.00064	−0.00031	0.00007	0.00001	−1.29637(7)
33	$4s_{1/2}$	−2.26361	−0.04603(15)	0.00149(4)	0.00119	−0.00058	0.00008	0.00002	−2.30744(15)
	$4p_{1/2}$	−1.83102	−0.03479(8)	0.00030(1)	0.00129	−0.00044	0.00011	0.00001	−1.86454(8)
	$4p_{3/2}$	−1.81305	−0.03346(7)	0.00027(1)	0.00093	−0.00045	0.00008	0.00001	−1.84568(7)
34	$4s_{1/2}$	−2.96421	−0.04734(15)	0.00227(5)	0.00154	−0.00073	0.00009	0.00002	−3.00836(16)
	$4p_{1/2}$	−2.45906	−0.03745(8)	0.00109(3)	0.00176	−0.00058	0.00012	0.00001	−2.49411(9)
	$4p_{3/2}$	−2.43387	−0.03597(8)	0.00103(2)	0.00127	−0.00060	0.00009	0.00001	−2.46804(8)
35	$4s_{1/2}$	−3.73626	−0.04854(16)	0.00276(7)	0.00194	−0.00088	0.00009	0.00003	−3.78086(17)
	$4p_{1/2}$	−3.15935	−0.03980(9)	0.00166(4)	0.00230	−0.00074	0.00013	0.00001	−3.19577(10)
	$4p_{3/2}$	−3.12557	−0.03816(8)	0.00158(4)	0.00166	−0.00076	0.00009	0.00001	−3.16114(9)
36	$4s_{1/2}$	−4.57854	−0.04965(16)	0.00314(8)	0.00238	−0.00105	0.00010	0.00003	−4.62359(17)
	$4p_{1/2}$	−3.93036	−0.04191(9)	0.00212(5)	0.00292	−0.00091	0.00014	0.00002	−3.96798(11)
	$4p_{3/2}$	−3.88652	−0.04012(9)	0.00203(5)	0.00210	−0.00093	0.00010	0.00002	−3.92333(10)
37	$4s_{1/2}$	−5.49024	−0.05069(16)	0.00343(8)	0.00288	−0.00122	0.00010	0.00003	−5.53571(18)
	$4p_{1/2}$	−4.77110	−0.04383(10)	0.00250(6)	0.00360	−0.00109	0.00015	0.00002	−4.80974(11)
	$4p_{3/2}$	−4.71558	−0.04190(9)	0.00239(6)	0.00260	−0.00112	0.00011	0.00002	−4.75348(11)
38	$4s_{1/2}$	−-6.47082	−0.05166(16)	0.00362(9)	0.00342	−0.00140	0.00011	0.00004	−6.51670(18)
	$4p_{1/2}$	−5.68086	−0.04560(10)	0.00278(7)	0.00437	−0.00128	0.00016	0.00002	−5.72041(12)
	$4p_{3/2}$	−5.61190	−0.04351(9)	0.00264(6)	0.00314	−0.00131	0.00012	0.00002	−5.65080(11)
39	$4s_{1/2}$	−7.51991	−0.05257(16)	0.00377(9)	0.00402	−0.00159(1)	0.00011	0.00004	−7.56613(19)
	$4p_{1/2}$	−6.65917	−0.04724(10)	0.00301(7)	0.00522	−0.00148	0.00017	0.00002	−6.69947(13)
	$4p_{3/2}$	−6.57486	−0.04499(10)	0.00286(7)	0.00375	−0.00152	0.00012	0.00002	−6.61461(12)
40	$4s_{1/2}$	−8.63728	−0.05343(17)	0.00389(9)	0.00468	−0.00179(1)	0.00012	0.00005	−8.68377(19)
	$4p_{1/2}$	−7.70573	−0.04876(11)	0.00320(8)	0.00616	−0.00170	0.00018	0.00003	−7.74662(13)
	$4p_{3/2}$	−7.60398	−0.04636(10)	0.00303(7)	0.00441	−0.00174	0.00013	0.00003	−7.64447(12)
41	$4s_{1/2}$	−9.82280	−0.05424(17)	0.00395(9)	0.00539	−0.00200(1)	0.00012	0.00005	−9.86953(19)
	$4p_{1/2}$	−8.82034	−0.05018(11)	0.00333(8)	0.00719	−0.00195	0.00019	0.00003	−8.86174(14)
	$4p_{3/2}$	−8.69890	−0.04762(10)	0.00316(8)	0.00513	−0.00196	0.00014	0.00003	−8.74002(13)
42	$4s_{1/2}$	−11.07644	−0.05500(17)	0.00399(10)	0.00617	−0.00222(1)	0.00013	0.00006	−11.12332(19)
	$4p_{1/2}$	−10.00289	−0.05152(11)	0.00344(8)	0.00831	−0.00216(1)	0.00020	0.00003	−10.04460(14)
	$4p_{3/2}$	−9.85934	−0.04879(11)	0.00326(8)	0.00592	−0.00220	0.00014	0.00003	−9.90097(13)

TABLE I. (*Continued*).

Z	State	$E^{(0)}$	$E^{(2)}$	$E^{(3)}$	$B^{(1)}$	$B^{(2)}$	$B^{(3)}$	RM	E^{tot}
44	$4s_{1/2}$	−13.78816	−0.05643(17)	0.00405(10)	0.00791	−0.00269(1)	0.00014	0.00007	−13.83511(20)
	$4p_{1/2}$	−12.57180	−0.05396(12)	0.00362(9)	0.01085	−0.00268(1)	0.00022	0.00004	−12.61372(14)
	$4p_{3/2}$	−12.37597	−0.05089(11)	0.00341(8)	0.00770	−0.00271	0.00016	0.00004	−12.41827(14)
45	$4s_{1/2}$	−15.24644	−0.05710(17)	0.00407(10)	0.00889	−0.00294(1)	0 .00014	0.00007	−15.29331(20)
	$4p_{1/2}$	−13.95827	−0.05509(12)	0.00368(9)	0.01228	−0.00295(1)	0.00023	0.00004	−14.00009(15)
	$4p_{3/2}$	−13.73188	−0.05185(11)	0.00346(8)	0.00869	−0.00298	0.00016	0.00004	−13.77436(14)
46	$4s_{1/2}$	−16.77321	−0.05774(17)	0.00408(10)	0.00994	−0.00319(1)	0.00015	0.00008	−16.81989(20)
	$4p_{1/2}$	−15.41290	−0.05616(12)	0.00373(9)	0.01381	−0.00324(1)	0.00023	0.00004	−15.45448(15)
	$4p_{3/2}$	−15.15272	−0.05274(11)	0.00350(8)	0.00975	−0.00326	0.00017	0.00004	−15.19525(14)
47	$4s_{1/2}$	−18.36864	−0.05836(17)	0.00408(10)	0.01107	−0.00346(1)	0.00015	0.00008	−18.41508(20)
	$4p_{1/2}$	−16.93586	−0.05719(12)	0.00377(9)	0.01547	−0.00354(1)	0.00024	0.00005	−16.97706(15)
	$4p_{3/2}$	−16.63843	−0.05359(11)	0.00352(8)	0.01089	−0.00355	0.00017	0.00005	−16.68094(14)
48	$4s_{1/2}$	−20.03295	−0.05896(17)	0.00408(10)	0.01227	−0.00374(1)	0.00016	0.00008	−20.07906(20)
	$4p_{1/2}$	−18.52734	−0.05816(12)	0.00379(9)	0.01724	−0.00385(1)	0.00025	0.00005	−18.56802(15)
	$4p_{3/2}$	−18.18898	−0.05437(12)	0.00354(8)	0.01211	−0.00385	0.00018	0.00005	−18.23133(14)
49	$4s_{1/2}$	−21.76641	−0.05954(18)	0.00407(10)	0.01356	−0.00403(1)	0.00016	0.00009	−21.81210(20)
	$4p_{1/2}$	−20.18758	−0.05911(12)	0.00381(9)	0.01914	−0.00417(1)	0.00026	0.00005	−20.22760(15)
	$4p_{3/2}$	−19.80435	−0.05513(12)	0.00355(9)	0.01340	−0.00416	0.00019	0.00005	−19.84645(15)
50	$4s_{1/2}$	−23.56930	−0.06009(18)	0.00406(10)	0.01493	−0.00433(1)	0.00017	0.00009	−23.61448(20)
	$4p_{1/2}$	−21.91682	−0.06000(12)	0.00383(9)	0.02117	−0.00451(1)	0.00027	0.00005	−21.95601(15)
	$4p_{3/2}$	−21.48453	−0.05583(12)	0.00355(9)	0.01478	−0.00449	0.00019	0.00005	−21.52627(15)
53	$4s_{1/2}$	−29.39764	−0.06170(18)	0.00402(10)	0.01957	−0.00529(2)	0.00018	0.00011	−29.44074(20)
	$4p_{1/2}$	−27.52150	−0.06254(13)	0.00385(9)	0.02807	−0.00560(2)	0.00029	0.00006	−27.55736(16)
	$4p_{3/2}$	−26.91423	−0.05775(12)	0.00354(8)	0.01941	−0.00552(1)	0.00021	0.00006	−26.95428(15)
54	$4s_{1/2}$	−31.48146	−0.06220(18)	0.00400(10)	0.02131	−0.00563(2)	0.00019	0.00011	−31.52369(20)
	$4p_{1/2}$	−29.52981	−0.06332(13)	0.00385(9)	0.03066	−0.00599(2)	0.00030	0.00006	−29.56424(16)
	$4p_{3/2}$	−28.85398	−0.05832(12)	0.00353(8)	0.02114	−0.00589(1)	0.00022	0.00007	−28.89324(15)
56	$4s_{1/2}$	−35.86307	−0.06320(18)	0.00396(10)	0.02509	−0.00636(2)	0.00020	0.00012	−35.90325(21)
	$4p_{1/2}$	−33.75875	−0.06485(13)	0.00385(9)	0.03631	−0.00681(2)	0.00032	0.00007	−33.78987(16)
	$4p_{3/2}$	−32.92860	−0.05940(13)	0.00351(8)	0.02486	−0.00665(1)	0.00023	0.00007	−32.96599(15)
57	$4s_{1/2}$	−38.16168	−0.06368(18)	0.00394(9)	0.02714	−0.00673(2)	0.00020	0.00012(1)	−38.20068(21)
	$4p_{1/2}$	−35.98020	−0.06558(13)	0.00384(9)	0.03938	−0.00725(2)	0.00033	0.00007	−36.00941(16)
	$4p_{3/2}$	−35.06362	−0.05990(13)	0.00349(8)	0.02686	−0.00705(1)	0.00023	0.00008	−35.09992(15)
60	$4s_{1/2}$	−45.49433	−0.06509(18)	0.00388(9)	0.03397	−0.00794(2)	0.00022	0.00014(1)	−45.52914(21)
	$4p_{1/2}$	−43.07775	−0.06768(13)	0.00383(9)	0.04963	−0.00859(2)	0.00036	0.00008	−43.10012(16)
	$4p_{3/2}$	−41.86058	−0.06126(13)	0.00345(8)	0.03347	−0.00831(1)	0.00025	0.00009	−41.89289(16)
62	$4s_{1/2}$	−50.75179	−0.06603(19)	0.00383(9)	0.03913	−0.00881(3)	0.00023	0.00015(1)	−50.78329(21)
	$4p_{1/2}$	−48.17533	−0.06904(14)	0.00381(9)	0.05739	−0.00959(3)	0.00037	0.00009(1)	−48.19231(17)
	$4p_{3/2}$	−46.71947	−0.06211(13)	0.00341(8)	0.03839	−0.00922(1)	0.00026	0.00009(1)	−46.74863(16)
63	$4s_{1/2}$	−53.49293	−0.06649(19)	0.00381(9)	0.04190	−0.00927(3)	0.00024	0.00015(1)	−53.52258(21)
	$4p_{1/2}$	−50.83547	−0.06970(14)	0.00380(9)	0.06157	−0.01011(3)	0.00038	0.00009(1)	−50.84944(17)
	$4p_{3/2}$	−49.24752	−0.06250(13)	0.00338(8)	0.04102	−0.00968(1)	0.00027	0.00010(1)	−49.27494(16)

TABLE I. (*Continued*).

Z	State	$E^{(0)}$	$E^{(2)}$	$E^{(3)}$	$B^{(1)}$	$B^{(2)}$	$B^{(3)}$	RM	E^{tot}
64	$4s_{1/2}$	−56.30973	−0.06693(19)	0.00378(9)	0.04481	−0.00974(3)	0.00024	0.00016(1)	−56.33740(21)
	$4p_{1/2}$	−53.57058	−0.07034(14)	0.00379(9)	0.06595	−0.01065(3)	0.00039	0.00009(1)	−53.58134(17)
	$4p_{3/2}$	−51.84148	−0.06285(13)	0.00336(8)	0.04375	−0.01016(1)	0.00028	0.00010(1)	−51.86700(16)
66	$4s_{1/2}$	−62.17304	−0.06784(19)	0.00374(9)	0.05105	−0.01072(3)	0.00025	0.00017(1)	−62.19638(21)
	$4p_{1/2}$	−59.26818	−0.07162(14)	0.00377(9)	0.07537	−0.01177(3)	0.00041	0.00010(1)	−59.27193(17)
	$4p_{3/2}$	−57.22761	−0.06355(14)	0.00332(8)	0.04955	−0.01114(1)	0.00029	0.00010(1)	−57.24905(16)
68	$4s_{1/2}$	−68.34684	−0.06875(19)	0.00369(9)	0.05789	−0.01176(4)	0.00026	0.00018(2)	−68.36533(21)
	$4p_{1/2}$	−65.27320	−0.07289(14)	0.00375(9)	0.08570	−0.01297(4)	0.00043	0.00011(1)	−65.26908(17)
	$4p_{3/2}$	−62.87897	−0.06421(14)	0.00328(8)	0.05581	−0.01218(1)	0.00030	0.00011(1)	−62.89586(16)
70	$4s_{1/2}$	−74.83671	−0.06967(19)	0.00365(9)	0.06536	−0.01286(4)	0.00027	0.00024(2)	−74.84971(22)
	$4p_{1/2}$	−71.59113	−0.07415(14)	0.00373(9)	0.09699	−0.01424(4)	0.00045	0.00015(1)	−71.57820(17)
	$4p_{3/2}$	−68.79672	−0.06482(14)	0.00323(8)	0.06254	−0.01326(2)	0.00031	0.00016(1)	−68.80856(16)
73	$4s_{1/2}$	−85.17816	−0.07106(19)	0.00360(9)	0.07786	−0.01464(4)	0.00029	0.00020(2)	−85.18191(22)
	$4p_{1/2}$	−81.66789	−0.07603(15)	0.00371(9)	0.11590	−0.01628(4)	0.00048	0.00012(1)	−81.63998(18)
	$4p_{3/2}$	−78.17555	−0.06567(14)	0.00317(8)	0.07356	−0.01497(2)	0.00033	0.00013(1)	−78.17899(16)
74	$4s_{1/2}$	−88.79024	−0.07153(19)	0.00358(9)	0.08238	−0.01527(5)	0.00030	0.00020(2)	−88.79057(22)
	$4p_{1/2}$	−85.19002	−0.07666(15)	0.00370(9)	0.12276	−0.01700(4)	0.00049	0.00013(1)	−85.15660(18)
	$4p_{3/2}$	−81.43642	−0.06593(14)	0.00315(8)	0.07748	−0.01556(2)	0.00034	0.00014(2)	−81.43681(16)
75	$4s_{1/2}$	−92.48658	−0.07200(19)	0.00356(9)	0.08711	−0.01591(5)	0.00030	0.00021(2)	−92.48331(22)
	$4p_{1/2}$	−88.79522	−0.07729(15)	0.00369(9)	0.12992	−0.01774(5)	0.00050	0.00013(2)	−88.75601(18)
	$4p_{3/2}$	−84.76487	−0.06619(14)	0.00313(8)	0.08153	−0.01617(2)	0.00034	0.00014(2)	−84.76208(16)
79	$4s_{1/2}$	−108.13123	−0.07395(20)	0.00350(8)	0.10807	−0.01869(5)	0.00033	0.00023(3)	−108.11174(22)
	$4p_{1/2}$	−104.06562	−0.07985(15)	0.00367(9)	0.16169	−0.02093(5)	0.00054	0.00015(2)	−104.00036(18)
	$4p_{3/2}$	−98.75820	−0.06715(14)	0.00305(7)	0.09904	−0.01866(2)	0.00037	0.00016(2)	−98.74139(16)
82	$4s_{1/2}$	−120.79721	−0.07546(20)	0.00346(8)	0.12616	−0.02098(6)	0.00034	0.00024(4)	−120.76345(23)
	$4p_{1/2}$	−116.43980	−0.08182(15)	0.00366(9)	0.18914	−0.02357(6)	0.00057	0.00015(2)	−116.35168(19)
	$4p_{3/2}$	−109.97213	−0.06780(14)	0.00298(7)	0.11358	−0.02070(3)	0.00039	0.00017(3)	−109.94352(16)
83	$4s_{1/2}$	−125.20299	−0.07598(20)	0.00345(8)	0.13269	−0.02179(6)	0.00035	0.00024(4)	−125.16404(23)
	$4p_{1/2}$	−120.74613	−0.08250(15)	0.00365(9)	0.19904	−0.02450(6)	0.00058	0.00016(3)	−120.64971(19)
	$4p_{3/2}$	−113.84814	−0.06800(14)	0.00296(7)	0.11869	−0.02145(3)	0.00039	0.00017(3)	−113.81538(17)
90	$4s_{1/2}$	−158.75571	−0.07985(21)	0.00338(8)	0.18630	−0.02820(8)	0.00039	0.00027(6)	−158.67342(24)
	$4p_{1/2}$	−153.57100	−0.08745(15)	0.00363(9)	0.28037	−0.03183(8)	0.00066	0.00018(4)	−153.40544(20)
	$4p_{3/2}$	−142.93517	−0.06932(15)	0.00282(7)	0.15842	−0.02675(4)	0.00044	0.00020(4)	−142.86936(17)
92	$4s_{1/2}$	−169.25774	−0.08104(21)	0.00336(8)	0.20448	−0.03027(8)	0.00041	0.00028(6)	−169.16053(25)
	$4p_{1/2}$	−163.85747	−0.08900(16)	0.00363(9)	0.30797	−0.03425(9)	0.00069	0.00019(4)	−163.66823(20)
	$4p_{3/2}$	−151.88124	−0.06967(15)	0.00278(7)	0.17104	−0.02838(4)	0.00046	0.00021(5)	−151.80480(17)

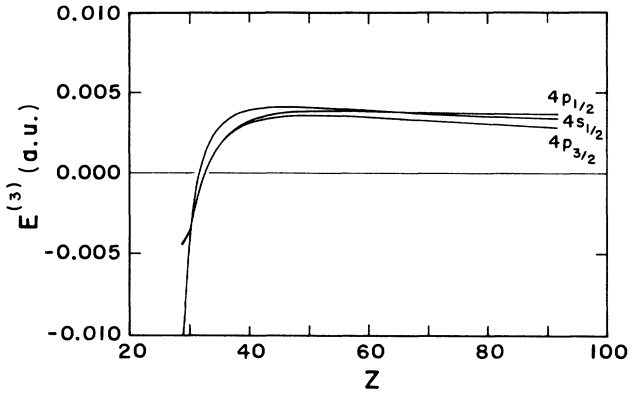

FIG. 2. Third-order correlation energy $E^{(3)}$ for the $4s_{1/2}$, $4p_{1/2}$, and $4p_{3/2}$ states of Cu-like ions as a function of nuclear charge Z.

effects exactly in $B^{(1)}$. Near the neutral end of the sequence $B^{(1)}$ is slightly smaller in magnitude than $E^{(2)}$, while for high Z, $B^{(1)}$ dominates the energy corrections. The variation of $B^{(1)}$ with nuclear charge is shown in Fig. 3.

In the seventh column of Table I, we give the results of our calculations of the second-order corrections from one Breit interaction and one Coulomb interaction, $B^{(2)}$. Again, following the previous outline,[1,4] we ignore retardation in calculating corrections to the Breit interaction. Since $B^{(2)}$ is a relatively large correction to the lowest-order Breit interaction, it is neccessary to consider the effects of even higher-order corrections to $B^{(1)}$. Fortunately, it has been possible to isolate the dominant terms in $B^{(2)}$ and to sum these terms to all orders in the Coulomb interaction using RPA techniques.[4] These RPA corrections are included along with $B^{(2)}$ in Table I. In the present calculation, we carry out the RPA calculations using a Dalgarno-Lewis differential equation method.[26,27] This is an efficient way to evaluate sums over excited states; however, in the relativistic case, intermediate states with negative energies, which should be excluded in the no-pair approximation being used here, are automatically included in the solutions of the Dalgarno-Lewis differential equations. The size of the error induced in this way has been estimated by carrying out direct solutions to the RPA equations excluding negative energy intermediate states for selected ions. The error resulting from the RPA terms and the error made in evaluating the remaining sums in the expression for $B^{(2)}$ are both included in the table. In Fig. 4, we plot $B^{(2)}$ against nuclear charge.

In the eighth column of Table I, we list third-order corrections to the Breit interaction from one Breit interaction and two Coulomb interactions, $B^{(3)}$. Following the pattern of our previous work,[4] these third-order corrections are restricted to include only the dominant Brueckner-orbital contributions. These contributions are plotted against nuclear charge in Fig. 5.

The ninth column of Table I contains the reduced mass (RM) and mass-polarization corrections. The mass-polarization corrections include contributions from second- and third-order perturbation theory. These contributions are calculated using precisely the same scheme that was used to calculate correlation corrections to the Breit interaction.[4] The mass-polarization corrections were calculated using the nonrelativistic form of the mass-polarization operator. The errors quoted in column 9 are estimates of the size of the omitted relativistic corrections.

Finally, in the tenth column of Table I, we add the various corrections to give theoretical energies, $E^{\rm tot}$, for the $4s$ and $4p$ states. The errors in the individual terms are combined in quadrature to give the errors shown in the final column. These errors reflect numerical uncertainties only, not the errors from omitted correlation corrections.

In previous studies of neutral cesium,[28] we found that the fourth-order CBO corrections, together with the fourth-order contributions from diagrams with six excited intermediate states, when added to the second- and third-order correlation corrections, led to theoretical ionization energies for the $6s_{1/2}$ and $6p_{1/2}$ states that agreed with experiment to better than 0.2%. For copper, the

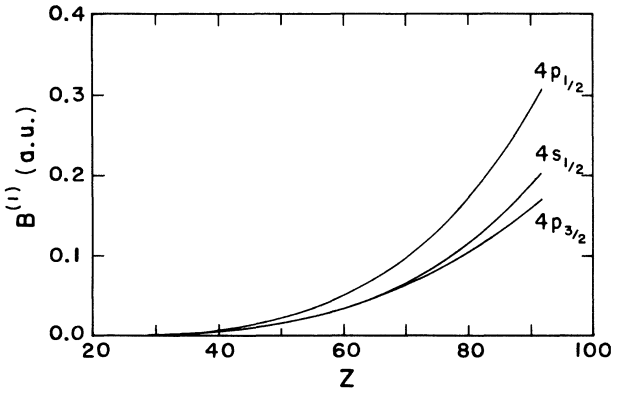

FIG. 3. Lowest-order retarded Breit interaction $B^{(1)}$ for the $4s_{1/2}$, $4p_{1/2}$, and $4p_{3/2}$ states of Cu-like ions as a function of nuclear charge Z.

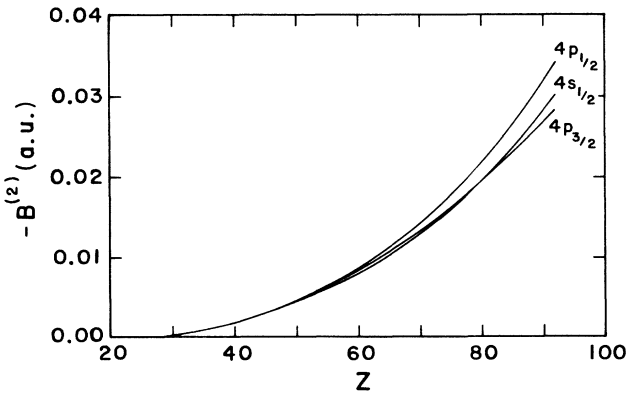

FIG. 4. Second-order correlation correction to the Breit interaction $B^{(2)}$ for the $4s_{1/2}$, $4p_{1/2}$, and $4p_{3/2}$ states of Cu-like ions as a function of nuclear charge Z.

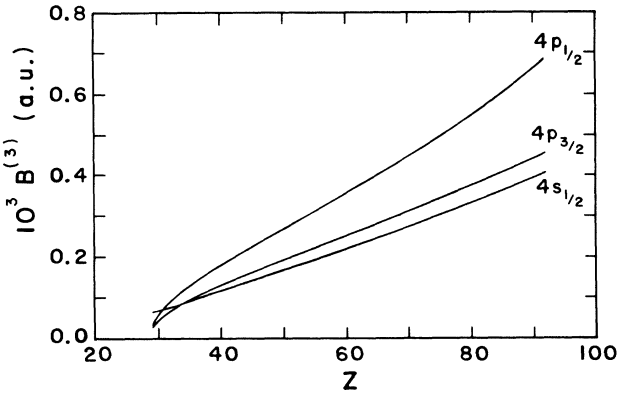

FIG. 5. Third-order correlation correction to the Breit interaction $B^{(3)}$ for the $4s_{1/2}$, $4p_{1/2}$, and $4p_{3/2}$ states of Cu-like ions as a function of nuclear charge Z.

perturbation series converges more slowly than for cesium and has a different structure, so this subset of fourth-order corrections is no longer sufficient to account for the residual correlation energy completely; nevertheless, the size of the fourth-order CBO corrections serves as a guide to the size of the omitted higher-order correlation corrections. In Fig. 6, we plot the CBO contributions to the energies of the $4s$ and $4p$ states of Cu-like ions against nuclear charge. For neutral copper, this correction is found to be about $\frac{1}{3}$ of the third-order correlation energy. As Z increases to 50, the CBO correction decreases to 0.0002 a.u., which is at the level of the numerical errors from the lower-order corrections. Fourth-order terms with six excited intermediate states are found to be approximately the same size as the chained Brueckner-orbital contributions for $Z = 50$. Thus, for $Z \geq 50$, one expects contributions to the term energies from the omitted correlation corrections to be less than or equal to the numerical errors from the lower-order corrections. As illustrated in Fig. 6, the CBO corrections to the $4s_{1/2}$-$4p_{3/2}$ energy intervals are much smaller than the contributions to the individual terms. We find that the contributions of the CBO corrections to these intervals are smaller than

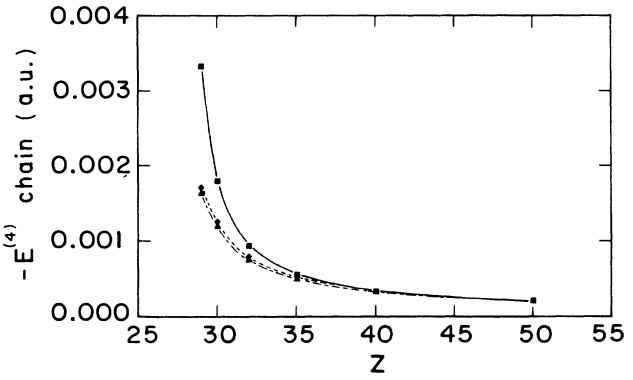

FIG. 6. Fourth-order chained Brueckner-orbital corrections for Cu-like ions. □, $4s_{1/2}$ states; ◇, $4p_{1/2}$ states; △, $4p_{3/2}$ states.

the numerical uncertainties in the lower-order calculations for $Z \geq 35$. The contributions to the energy intervals from fourth-order terms with six excited states were found to be even smaller than the CBO corrections for $Z = 35$. On the basis of these limited fourth-order calculations, we conclude that the correlation corrections to the energies are controlled well enough that differences between the calculated intervals and measured intervals are due only to the omitted QED corrections for $Z \geq 35$.

In Table II, we compare theoretical values for the $4p_{3/2}$-$4s_{1/2}$ energy intervals with measurements. The differences between theoretical and experimental values for the first few members of the sequence are due to the omitted correlation corrections. As Z increases along the sequence, correlation corrections become relatively less important until the differences are completely dominated by the omitted QED corrections for $Z \geq 35$. We compare the differences between theory and experiment for the $4p_{3/2}$-$4s_{1/2}$ interval with semiempirical values of the Lamb shift in Fig. 7. The values of the Lamb shift shown by the solid curve are obtained by scaling hydrogenic values of the $n = 2$ self-energy and vacuum polarization to $n = 4$, and then by replacing Z by an effective charge, $Z_{\text{eff}} = Z - 15.6$. The value 15.6 for the screening charge was determined by a least-squares fit to the data in Table II. The dashed curve in Fig. 7 gives the QED corrections obtained from Grant's multiconfiguration Dirac-Fock program[22,23] using the optimal level (OL) option. The semiempirical QED corrections contained in this code were found to account well for the difference between MBPT calculations and measurement for the $2p$-$2s$ transitions in the lithium isoelectronic sequence by Seely.[29]

Theoretical values for the $4p_{3/2}$-$4p_{1/2}$ fine-structure interval are compared with measurement in Table III.

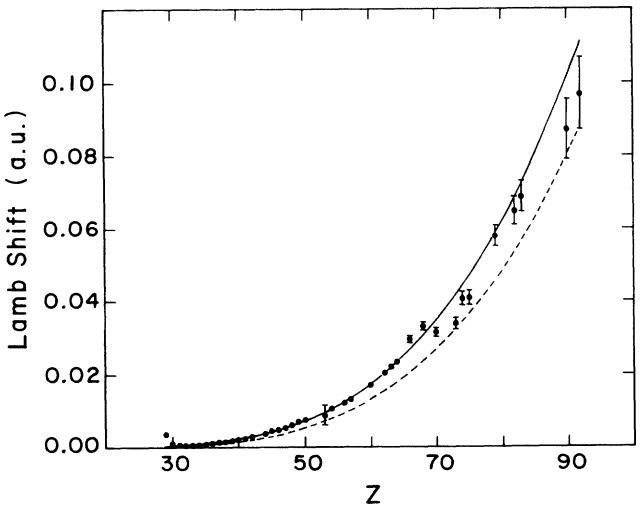

FIG. 7. Theory-experiment for the $4p_{3/2}$-$4s_{1/2}$ energy interval compared with semiempirical values for the $n = 4$ Lamb shift. Solid line: scaled hydrogenic values; dashed line: MCDF values.

TABLE II. Comparison of theoretical values for the $4p_{3/2}$-$4p_{1/2}$ fine-structure interval with measurement. Errors quoted for theoretical values are numerical errors arising in the calculation of the subset of terms in Table I.

Z	Theory	Experiment	Theor.−Expt.	Z	Theory	Experiment	Theor.−Expt.
29	0.1439(3)	0.1403	0.0036(3)	50	2.0882(3)	2.0807(1)	0.0075(3)
30	0.2261(2)	0.2249	0.0012(2)	53	2.4865(3)	2.4776(27)	0.0088(27)
31	0.3054(2)	0.3048	0.0006(2)	54	2.6305(3)	2.6195(1)	0.0109(3)
32	0.3836(2)	0.3832	0.0004(2)	56	2.9373(3)	2.9250(3)	0.0122(4)
33	0.4618(2)	0.4613	0.0005(2)	57	3.1008(3)	3.0877(3)	0.0131(4)
34	0.5403(2)	0.5398	0.0006(2)	60	3.6363(3)	3.6191(4)	0.0171(5)
35	0.6197(2)	0.6190	0.0007(2)	62	4.0347(3)	4.0143(5)	0.0204(6)
36	0.7003(2)	0.6993	0.0010(2)	63	4.2476(3)	4.2255(6)	0.0221(7)
37	0.7822(2)	0.7810	0.0012(2)	64	4.4704(3)	4.4470(7)	0.0234(7)
38	0.8659(2)	0.8644	0.0015(2)	66	4.9473(3)	4.9177(8)	0.0296(8)
39	0.9515(2)	0.9497	0.0018(2)	68	5.4695(3)	5.4363(10)	0.0332(10)
40	1.0393(2)	1.0371	0.0022(2)	70	6.0412(3)	6.0097(12)	0.0314(12)
41	1.1295(2)	1.1270	0.0025(2)	73	7.0029(3)	6.9690(16)	0.0339(16)
42	1.2224(2)	1.2194	0.0029(2)	74	7.3538(3)	7.3131(18)	0.0407(18)
44	1.4168(2)	1.4131	0.0038(2)	75	7.7212(3)	7.6803(19)	0.0409(20)
45	1.5190(2)	1.5144(1)	0.0046(3)	79	9.3704(3)	9.3123(29)	0.0580(29)
46	1.6246(2)	1.6198(1)	0.0049(3)	82	10.8199(3)	10.7550(38)	0.0650(38)
47	1.7341(3)	1.7287(1)	0.0055(3)	83	11.3487(3)	11.2797(42)	0.0689(42)
48	1.8477(3)	1.8416(1)	0.0061(3)	90	15.8041(3)	15.7169(81)	0.0871(81)
49	1.9657(3)	1.9586(1)	0.0071(3)	92	17.3557(3)	17.2589(98)	0.0969(98)

Again, the discrepancy between theory and measurement is due primarily to the omitted QED corrections for higher values of Z. The small difference between experiment and theory is plotted against Z in Fig. 8, along with the semiempirical values from the $n = 2$ Lamb shift scaled as described above, and the values for the QED corrections obtained from Grant's MCDF code.

In summary, we have applied relativistic MBPT through third order to calculate the $4s_{1/2}$, $4p_{1/2}$, and $4p_{3/2}$ levels along the copper isoelectronic sequence, from neutral copper to copper-like uranium. We have estimated the size of the omitted correlation corrections by

TABLE III. Comparison of theoretical values for the $4p_{3/2}$-$4p_{1/2}$ fine-structure interval with measurement. Errors quoted for theoretical values are numerical errors arising in the calculation of the subset of terms in Table I.

Z	Theory	Experiment	Expt.−Theor.	Z	Theor.	Experiment	Expt.−Theor.
29	0.0013(2)	0.0011	−0.0002(2)	46	0.2592(2)	0.2595(1)	0.0003(2)
30	0.0042(1)	0.0040	−0.0002(1)	47	0.2961(2)	0.2965(1)	0.0004(2)
31	0.0081(1)	0.0078	−0.0003(1)	48	0.3367(2)	0.3372(1)	0.0005(2)
32	0.0129(1)	0.0127	−0.0002(1)	49	0.3812(2)	0.3817(1)	0.0006(2)
33	0.0189(1)	0.0187	−0.0001(1)	50	0.4297(2)	0.4303(2)	0.0005(3)
34	0.0261(1)	0.0260	−0.0001(1)	53	0.6031(2)	0.6049(31)	0.0018(31)
35	0.0346(1)	0.0345	−0.0001(1)	54	0.6710(2)	0.6720(1)	0.0010(2)
36	0.0447(2)	0.0446	−0.0001(2)	57	0.9095(2)	0.9118(4)	0.0023(5)
37	0.0563(2)	0.0562	−0.0001(2)	60	1.2072(2)	1.2082(6)	0.0010(6)
38	0.0696(2)	0.0696	−0.0000(2)	62	1.4437(2)	1.4466(6)	0.0029(6)
39	0.0849(2)	0.0849	−0.0000(2)	63	1.5745(2)	1.5762(8)	0.0017(8)
40	0.1022(2)	0.1022	0.0000(2)	64	1.7143(2)	1.7167(8)	0.0023(8)
41	0.1217(2)	0.1218	0.0000(2)	74	3.7198(2)	3.7251(18)	0.0053(18)
42	0.1436(2)	0.1437	0.0001(2)	79	5.2590(2)	5.2617(29)	0.0028(29)
44	0.1954(2)	0.1957(1)	0.0003(2)	82	6.4082(3)	6.4131(39)	0.0050(39)
45	0.2257(2)	0.2257(1)	0.0000(2)	83	6.8343(3)	6.8367(42)	0.0024(43)

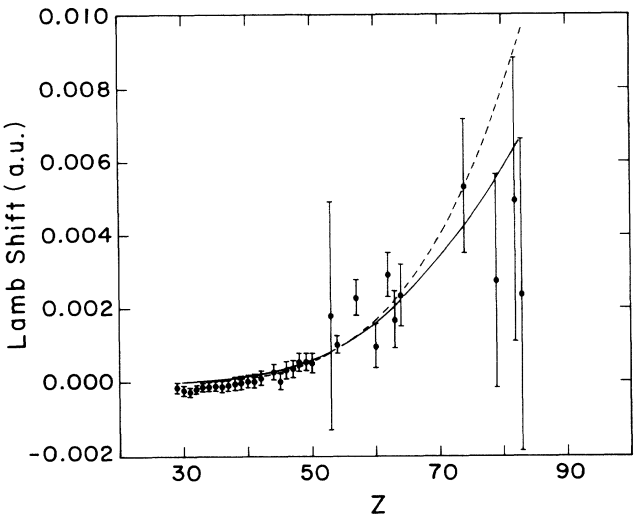

FIG. 8. Experiment-theory for the $4p_{3/2}$-$4p_{1/2}$ fine-structure interval compared with semiempirical values for the $n = 4$ Lamb shift. Solid line: scaled hydrogenic values; dashed line: MCDF values.

evaluating an important subset of fourth-order terms, the chained Brueckner-orbital corrections. Based on this estimate, we expect that the higher-order corrections for the $4s_{1/2}$-$4p_{3/2}$ energy interval will be below the level of numerical uncertainty for $Z \geq 35$. The energy intervals determined in the present study are found to differ from the measured intervals in a systematic way along the sequence. These differences for $Z \geq 35$ can be fit to a semiempirical correction found by scaling the known values of the hydrogenic $n = 2$ Lamb shift[20,21] to $n = 4$, and then by evaluating these corrections using an effective charge, $Z_{\text{eff}} = Z - 15.6$. The differences are also well accounted for by the semi-empirical QED corrections determined from Grant's MCDF code.[22,23] The Feynman diagrams describing the most important omitted QED corrections can be written down easily; their evaluation is a complex numerical task that remains to be done. Until these diagrams are evaluated, the theoretical understanding of copper-like ions remains incomplete.

ACKNOWLEDGMENTS

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