PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOLUME 38, NUMBER 6 SEPTEMBER 15, 1988

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

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(Received 17 December 1987)

Energies of $3s$ and $3p$ states of sodiumlike ions are calculated from $Z=11$ to $Z=92$ starting from a Dirac-Fock potential and including second- and third-order Coulomb correlation corrections, the lowest-order Breit interaction with retardation treated exactly, second- and third-order correlation corrections to the Breit interaction, and corrections for reduced mass and mass polarization. The calculated energies are compared to measured energies to determine the size of the omitted quantum electrodynamics corrections.

INTRODUCTION

We report calculations of energies of $3s_{1/2}$, $3p_{1/2}$, and $3p_{3/2}$ states of Na-like ions with nuclear charges ranging from $Z=11$ to 92. The calculations employ relativistic many-body perturbation theory, based on Dirac-Fock (DF) wave functions; they include second- and third-order Coulomb correlation corrections, first-order corrections for transverse photon exchange, and correlation corrections of second- and third-order to one transverse photon exchange. Finite nuclear size, reduced mass, and mass-polarization corrections are also included in the calculations, but QED corrections such as the electron self-energy and vacuum polarization are omitted.

Recent measurements of wavelengths for Na-like ions[1] have provided a set of reference values for the $3s$-$3p$ transitions of interest here in the range $Z=18$ to 54. These measurements extend and improve a previous analysis of Edlén,[2] who made a systematic semiempirical study of Na-like ions in the range $Z=16$ to 42. A theoretical analysis of the Na isoelectronic sequence in the range $Z=25$ to 80 based on a model potential with several adjustable parameters has also been made by Ivanov and Ivanova.[3] In previous analyses of the sodium sequence, QED effects have been approximated by scaling the Lamb shift for hydrogenlike ions to an effective charge appropriate to Na-like ions. While this approximation may describe the dominant QED contributions, it can be misleading, since correlation effects omitted in a semiempirical analysis or in model potential studies could be misinterpreted as screening corrections to the Lamb shift. In the present study we compare *ab initio* calculations of the $3s$ and $3p$ energy levels in which QED corrections are omitted with the measurements, with the aim of extracting information on the omitted QED effects. The resulting differences, which are found to be systematically smaller than the one-electron Lamb shift for hydrogenlike ions, provide a basis for future studies of QED corrections in many-electron atoms.

FORMULAS

The present calculation follows the pattern of a previous study of Li-like ions.[4] In lowest order we solve the DF equations,

$$(h+V_{\mathrm{HF}})u_a(\mathbf{r})=\varepsilon_a u_a(\mathbf{r}) , \tag{1}$$

for each orbital $u_a(\mathbf{r})$ of the neonlike core self-consistently. The single-electron Hamiltonian h in Eq. (1) is a one-electron Dirac Hamiltonian which includes the electron-nucleus Coulomb interaction. Finite nuclear size effects are introduced into h by taking the nuclear charge distribution to be a Fermi distribution with parameters determined from electron-nucleus scattering data and from muonic x-ray studies.[5,6] The 10%-90% thickness parameter a of the nuclear charge distribution was taken to be 0.523 fm for all of the ions considered. The 50% falloff radius R_{nuc} was obtained from a least-squares analysis of the data in Refs. 5 and 6. The values of R_{nuc} obtained from this fit, which are accurate to about 0.05 fm, are listed in Table I. The Hartree-Fock potential V_{HF} in Eq. (1) is defined by

$$(V_{\mathrm{HF}})_{ij}=\sum_a (g_{iaja}-g_{iaaj}) , \tag{2}$$

where g_{ijkl} is a two-electron Coulomb matrix element,

$$g_{ijkl}=\int\int d^3x d^3y \frac{1}{|\mathbf{x}-\mathbf{y}|} u_i^\dagger(\mathbf{x})u_k(\mathbf{x})u_j^\dagger(\mathbf{y})u_l(\mathbf{y}) . \tag{3}$$

In Eq. (2) the index a extends over occupied core states.

TABLE I. Parameters used in the calculation of the 3s and 3p levels of sodiumlike ions. R is the radius of the nuclear charge distribution in fm and M is the nuclear mass in amu. The dimensionless Lamb-shift functions $F(nl_j)$ for the 3s and 3p states are taken from Ref. 16.

Z	R	M	$F(3s_{1/2})$	$F(3p_{1/2})$	$F(3p_{3/2})$
11	2.885	22.984	4.4409	−0.1128	0.1311
14	3.127	27.969	3.9431	−0.1068	0.1348
17	3.497	34.960	3.5645	−0.1004	0.1388
20	3.719	39.952	3.2650	−0.0934	0.1431
26	4.118	55.921	2.8183	−0.0781	0.1528
34	4.763	79.898	2.4158	−0.0554	0.1669
42	5.117	97.882	2.1440	−0.0303	0.1823
54	5.702	131.87	1.8821	0.0126	0.2068
74	6.446	183.91	1.6738	0.1041	0.2506
92	6.987	238.00	1.6436	0.2240	0.2916

The orbitals $u_i(\mathbf{r})$ for states outside the core are determined by solving the DF equation in the self-consistent field of the core electrons. The lowest-order ionization energy for the valence state is just the eigenvalue of the valence DF equation $E_v^{(0)}=\varepsilon_v$.

The dominant correction to the valence energy is the second-order Coulomb correlation correction given by[7]

$$E_v^{(2)}=-\sum_{a,n,m}\frac{g_{vanm}(g_{nmva}-g_{nmav})}{\varepsilon_n+\varepsilon_m-\varepsilon_v-\varepsilon_a}+\sum_{a,b,m}\frac{g_{vmab}(g_{abvm}-g_{abmv})}{\varepsilon_v+\varepsilon_m-\varepsilon_a-\varepsilon_b} . \quad (4)$$

In Eq. (4) the indices a and b designate core orbitals, n and m orbitals outside the core, while v designates a valence orbital. Including contributions from negative energy orbitals in the first term of Eq. (4) would give rise to two kinds of additional terms, one in which one orbital has positive energy and the other negative energy, and one in which both orbitals have negative energy. The first kind of term is not allowed by QED: including it would lead to vanishing energy denominators, a feature associated with the continuum dissolution problem.[8–10] The second type of term is allowed by QED but contributes at the level of screening of the Lamb shift, as discussed in Ref. 4. As we are not directly evaluating QED corrections in this paper (although we will later compare the difference between experiment and our theoretical results with the unscreened Lamb shift), we omit such negative-energy contributions throughout the calculation. To carry out sums such as those occurring in Eq. (4) we replace the actual spectrum of DF states by a finite pseudospectrum constructed from B splines:[11] the restriction to positive-energy states is straightforward.

The most time consuming part of the present calculation was the evaluation of the third-order Coulomb correlation energy $E_v^{(3)}$. The expression for $E_v^{(3)}$, which contains 12 multiple sums, is written out in Refs. 4 and 7 and will not be repeated here. One term in the third-order energy contains sums over four virtual orbitals; this term accounted for about 90% of the computer time used in the entire calculation. Fourth- and higher-order Coulomb correlation corrections were not included in the present calculation, but some idea of their size may be gained by iterating the second-order contribution from Eq. (4). For the 3s removal energies in Na and Fe^{15+} we find contributions of 4.5% and 0.17% of $E^{(2)}$, respectively.

The first-order correction due to the exchange of transverse photons between the valence electron and the core electrons is given by

$$B_v^{(1)}=-\sum_a b_{vaav} . \quad (5)$$

The transverse-photon exchange matrix element b_{vaav} in Eq. (5) is[4]

$$b_{vaav}=-\frac{1}{2\pi^2}\int\int d^3x\,d^3y\int d^3k\frac{1}{\mathbf{k}^2-\mathbf{k}_0^2}e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{y})}\times(\delta_{ij}-\hat{\mathbf{k}}_i\hat{\mathbf{k}}_j)\times[u_v^\dagger(\mathbf{x})\alpha_i u_a(\mathbf{x})u_a^\dagger(\mathbf{y})\times\alpha_j u_v(\mathbf{y})] , \quad (6)$$

where $k_0=|\varepsilon_v-\varepsilon_a|/\hbar c$. If we make the approximation that $k_0=0$, Eq. (6) reduces to an exchange matrix element of the Breit interaction[12]

$$B_{12}=-\frac{1}{2r_{12}}[\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2+(\boldsymbol{\alpha}_1\cdot\hat{\mathbf{r}}_{12})(\boldsymbol{\alpha}_2\cdot\hat{\mathbf{r}}_{12})] . \quad (7)$$

We retain k_0 only in our first-order calculations and use the approximate form of the interaction given in Eq. (7) to calculate the second- and third-order correlation corrections to transverse photon exchange.

The second-order correction from one Coulomb interaction and one transverse interaction $B_v^{(2)}$ is[4]

$$B_v^{(2)}=-2\sum_{a,n,m}\frac{b_{vanm}(g_{nmva}-g_{nmav})}{\varepsilon_n+\varepsilon_m-\varepsilon_v-\varepsilon_a}+2\sum_{a,b,m}\frac{b_{vmab}(g_{abvm}-g_{abmv})}{\varepsilon_v+\varepsilon_m-\varepsilon_a-\varepsilon_b}+B_{\mathrm{RPA}}^{(2)} , \quad (8a)$$

where

$$B_{\mathrm{RPA}}^{(2)}=\sum_{a,n}\frac{b_{an}(g_{nvva}-g_{nvav})}{\varepsilon_n-\varepsilon_a}+\text{c.c.} , \quad (8b)$$

with

$$b_{an}=-\sum_b b_{abbn} . \quad (8c)$$

As mentioned above, we approximate the two-electron matrix element of the transverse photon interaction b_{ijkl} in Eqs. (8a)–(8c) by a matrix element of the Breit interaction given in Eq. (7). The first two terms in Eq. (8a) are evaluated in exactly the same way as the two corresponding terms in Eq. (4). The third term in Eq. (8a), the random-phase approximation contribution $B_{\mathrm{RPA}}^{(2)}$, is found to be an order of magnitude larger than the first two terms; indeed, this term is nearly equal, but opposite in sign, to the first-order correction for neutral sodium. Because the third term is so large, it was separated off from the first two and evaluated together with terms having similar denominator structure from third- and higher-order perturbation theory using the techniques described below.

The Breit interaction is nominally a two-body interaction, but when expressed in second quantization and normally ordered with respect to the core, it contains zero-, one-, and two-body parts. The zero-body part never contributes in higher-order perturbation theory. The RPA contribution to $B_v^{(2)}$ arises from the one-body part of the Breit interaction, while the small remaining contribution to $B_v^{(2)}$ is from the two-body part. Thus we evaluate only the contributions to $B_v^{(3)}$ that arise from the one-body part of the Breit interaction, assuming these to be the dominant ones. Furthermore, we restrict the set of one-body contributions in $B_v^{(3)}$ to the "Brueckner-orbital" terms $B_{\rm BO}^{(3)}$ and the "RPA" terms $B_{\rm RPA}^{(3)}$, which are known to give the largest effects for other one-body operators such as the hyperfine interaction or the dipole operator,[13]

$$B_v^{(3)} \approx B_{\rm BO}^{(3)} + B_{\rm RPA}^{(3)} , \tag{9a}$$

$$B_{\rm BO}^{(3)} = 2 \sum_{\substack{i \\ i\neq v}} \frac{b_{vi}}{\varepsilon_i - \varepsilon_v} \sum_{a,n,m} \frac{g_{ianm}(g_{nmva} - g_{nmav})}{\varepsilon_n + \varepsilon_m - \varepsilon_v - \varepsilon_a} - 2 \sum_{\substack{i \\ i\neq v}} \frac{b_{vi}}{\varepsilon_i - \varepsilon_v} \sum_{a,b,m} \frac{g_{imab}(g_{abvm} - g_{abmv})}{\varepsilon_v + \varepsilon_m - \varepsilon_a - \varepsilon_b} , \tag{9b}$$

$$B_{\rm RPA}^{(3)} = \sum_{a,b,n,m} \left[\frac{(g_{vnva} - g_{vnav}) b_{bm} (g_{amnb} - g_{ambn})}{(\varepsilon_n - \varepsilon_a)(\varepsilon_m - \varepsilon_b)} + \text{c.c.} \right] + \sum_{a,b,n,m} \left[\frac{(g_{mnab} - g_{mnba}) b_{bm} (g_{avvn} - g_{avnv})}{(\varepsilon_n - \varepsilon_a)(\varepsilon_m - \varepsilon_b)} + \text{c.c.} \right] , \tag{9c}$$

where b_{ij} is defined in Eq. (8c). The sum over i in Eq. (9b) includes both core and excited states.

To evaluate the term $B_{\rm BO}^{(3)}$, we first construct the nonlocal second-order correlation potential $\Sigma^{(2)}(\varepsilon)$,

$$[\Sigma^{(2)}(\varepsilon)]_{ij} = - \sum_{a,n,m} \frac{g_{ianm}(g_{nmja} - g_{nmaj})}{\varepsilon_n + \varepsilon_m - \varepsilon - \varepsilon_a} + \sum_{a,b,m} \frac{g_{imab}(g_{abjm} - g_{abmj})}{\varepsilon + \varepsilon_m - \varepsilon_a - \varepsilon_b} , \tag{10}$$

and then solve the inhomogeneous one-electron Dirac equation,

$$(h + V_{\rm HF} - \varepsilon_v)\delta u_v(\mathbf{r}) = [\delta\varepsilon_v - \Sigma^{(2)}(\varepsilon_v)] u_v(\mathbf{r}) , \tag{11}$$

to obtain approximate Brueckner-orbital corrections $\delta u_v(\mathbf{r})$ to the valence orbital $u_v(\mathbf{r})$. The energy shift $\delta\varepsilon_v$ due to $\Sigma^{(2)}(\varepsilon_v)$ is precisely $E_v^{(2)}$. From Eqs. (9b) and (8c) it follows that

$$B_{\rm BO}^{(3)} = -2 \sum_b b_{(\delta v) bbv} . \tag{12}$$

The RPA corrections $B_{\rm RPA}^{(2)}$ and $B_{\rm RPA}^{(3)}$ are the first two terms in the iterative solution to the equations

$$B_{\rm RPA} = \sum_{a,n} \frac{t_{an}(g_{nvva} - g_{nvav})}{\varepsilon_n - \varepsilon_a} + \sum_{a,n} \frac{(g_{avvn} - g_{avnv}) t_{na}}{\varepsilon_n - \varepsilon_a} , \tag{13a}$$

$$t_{na} = b_{na} + \sum_{b,m} \frac{t_{bm}(g_{nmba} - g_{nmab})}{\varepsilon_m - \varepsilon_b} + \sum_{b,m} \frac{(g_{nbma} - g_{nbam}) t_{mb}}{\varepsilon_m - \varepsilon_b} , \tag{13b}$$

$$t_{an} = b_{an} + \sum_{b,m} \frac{t_{bm}(g_{ambn} - g_{amnb})}{\varepsilon_m - \varepsilon_b} + \sum_{bm} \frac{(g_{abmn} - g_{abnm}) t_{mb}}{\varepsilon_m - \varepsilon_b} . \tag{13c}$$

If we approximate t_{an} and t_{na} in Eqs. (13b) and (13c) by the inhomogeneous terms b_{an} and b_{na}, respectively, then $B_{\rm RPA}$ in Eq. (13a) reduces to $B_{\rm RPA}^{(2)}$. If we iterate Eqs. (13b) and (13c) once to obtain a second approximation to t_{an} and t_{na}, and use this second approximation in Eq. (13a), we pick up the term $B_{\rm RPA}^{(3)}$ from Eq. (13a). In the present work we continued the iteration solution until convergence at the level of $1/10^7$ was achieved, and thereby included RPA terms to essentially all orders in perturbation theory. This was deemed to be necessary because of the relatively large size of the RPA correction, and because of the relatively slow convergence of the RPA series in perturbation theory. An illustration of the iterative solution of Eqs. (13a)–(13c) is given in Table II, where we show the partial sums of the RPA series, $B_{\rm RPA}^{(2)}$, $B_{\rm RPA}^{(2)} + B_{\rm RPA}^{(3)}, \ldots$, for the $3s_{1/2}$ state in neutral sodium. The iterative solution was cross-checked by reformulating Eqs. (13a)–(13c) as a set of differential equations that

TABLE II. Iteration of RPA equations for the Breit interaction in the 3s state of neutral Na.

n	$S^{(n)} = 10^5 \sum_{2}^{n} B_{\rm RPA}^{(k)}$	$(S^{(n)} - S^{(n-1)})/S^{(n)}$
2	−2.4892	
3	−1.2585	0.980 00
4	−1.7273	0.270 00
5	−1.5416	0.120 00
6	−1.6137	0.045 00
7	−1.5854	0.018 00
8	−1.5964	0.006 90
9	−1.5921	0.002 70
10	−1.5938	0.001 10
11	−1.5932	0.000 41
12	−1.5934	0.000 16
13	−1.5933	0.000 06
14	−1.5934	0.000 03
15	−1.5933	0.000 01

are solved using standard numerical techniques.

It is worth noting that essentially equivalent results could be obtained by incorporating the Breit interaction, Eq. 7, in the self-consistent potential as done by Quiney *et al.*[14] In a perturbation series based on this new potential, all terms involving the one-body part of the Breit interaction vanish identically; our relatively large RPA corrections would appear in the zeroth-order energy, while our corrections $B^{(3)}_{\mathrm{BO}}$ would be part of $E^{(2)}$.

Corrections for the reduced mass were included in the calculation by multiplying the total theoretical energy by the factor $-m/M$, where m is the electron mass and M is the mass of the nucleus. The associated mass-polarization corrections were calculated in perturbation theory, assuming that the mass polarization could be adequately described using the *nonrelativistic* interaction Hamiltonian

$$H_{\mathrm{MP}}=\frac{1}{M}\sum_{\substack{i,j\\ i>j}} \mathbf{p}_i\cdot\mathbf{p}_j \ , \tag{14}$$

where $\mathbf{p}_i$ is the momentum of the ith electron. The values of M used in the present calculation are listed in the third column of Table I.

In lowest order the interaction H_{MP} leads to the energy shift for the valence state,

$$P_v^{(1)}=-\frac{1}{M}\sum_b |\langle v|\mathbf{p}|b\rangle|^2 \ . \tag{15}$$

This mass-polarization correction was found to be just as sensitive to correlation effects as the Breit interaction. The correlation corrections to Eq. (15) were determined following the procedure described previously for the Breit interaction, simply replacing the two-particle matrix elements of the Breit interaction in Eq. (7) by two-particle matrix elements of $(1/M)\mathbf{p}_1\cdot\mathbf{p}_2$. Indeed, we found that the second-order correction with one action of H_{MP} and one Coulomb interaction was larger than the first-order contribution given in Eq. (15) for the $3s_{1/2}$ state in neutral sodium. Again, as in the case of the Breit interaction, the second-order corrections were dominated by the RPA terms, so that these terms were iterated to all orders. Third-order Brueckner-orbital corrections were also included, and were found to be relatively unimportant.

Among the corrections omitted in the present calculations, the most important for highly ionized systems are the electron self-energy and vacuum-polarization corrections. To estimate the size of these omitted Lamb-shift corrections we compare energies calculated from the formulas given above with experiment. For neutral sodium the treatment of correlation given here is not sufficiently complete to make such a comparison meaningful, but for the remaining ions, we expect the higher-order correlation corrections to be smaller than the omitted QED corrections. For hydrogenlike ions the self-energy and vacuum-polarization corrections can be written in the form

$$\Delta E=\frac{\alpha^3 Z^4}{\pi n^3}F(Z\alpha)\ \text{a.u.} \ , \tag{16}$$

where n is the principal quantum number of a level and $F(Z\alpha)$ is a slowly varying function of nuclear charge, which is expected to be insensitive to n.[15] The values of $F(Z\alpha)$ used in the present study are listed in Table I.[16] Hydrogenic values of ΔE are used as a reference with

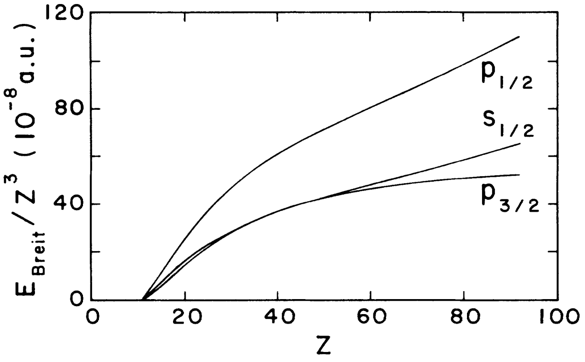

FIG. 2. Breit interaction energy (including correlation) divided by Z^3 for $n=3$ states of sodiumlike ions from $Z=11$ to 92 in units of 10^{-8} a.u.

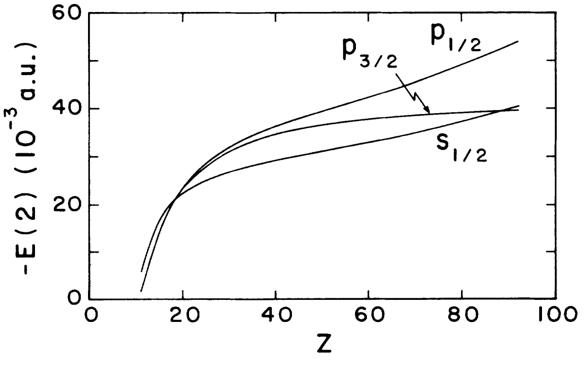

FIG. 1. Second-order correlation energy $E^{(2)}$ for the $n=3$ states of sodiumlike ions from $Z=11$ to 92 in units of 10^{-3} a.u.

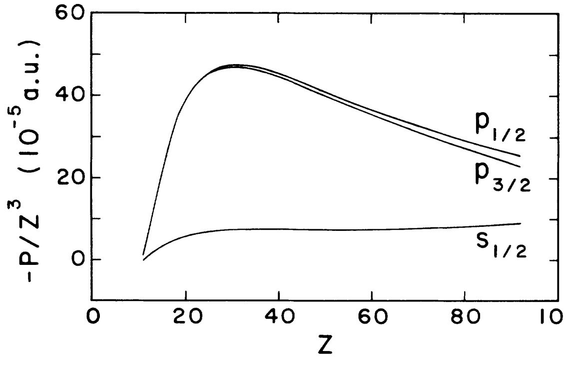

FIG. 3. Mass polarization energy (including correlation) divided by Z^3 for $n=3$ states of sodiumlike ions from $Z=11$ to 92 in units of 10^{-5} a.u.

which the Lamb-shift corrections inferred from experiment are compared. Deviations from the hydrogenic values are referred to as screening corrections to the Lamb shift.

DISCUSSION OF CALCULATIONS

A summary of our calculations is given in Table III, where we list the theoretical energies of the $3s$ and $3p$ states of Na, Si^{3+}, Cl^{6+}, Ca^{9+}, Fe^{15+}, Se^{23+}, Mo^{31+}, Xe^{43+}, W^{63+}, and U^{81+}. The dominant contributions to these energies are the Dirac-Fock eigenvalues listed under the heading $E^{(0)}$ in the table. The column labeled E_{corr} contains the sum of the contributions from the second- and third-order Coulomb correlation corrections $E^{(2)}$ and $E^{(3)}$. In the fourth column we list the total Breit interaction, which includes the lowest-order Breit interaction (with $k_0 \neq 0$), together with the second- and third-order correlation corrections. The fifth column contains the reduced-mass and mass-polarization contributions, and the final column contains the resulting theoretical energies of the $3s$ and $3p$ states. It is clear from the table that the Coulomb correlation corrections

TABLE III. Theoretical energies for $n=3$ states of sodiumlike ions. Units of energy are in a.u. Numbers in parentheses denote errors.

State	$E^{(0)}$	E_{corr}	Breit	Reduced mass and mass polarization	Sum
			$Z=11$		
$3s$	−0.182033	−0.006395(50)	0.000012	0.000004	−0.188411(51)
$3p^*$	−0.109490	−0.001972(20)	0.000009	0.000002	−0.111451(19)
$3p$	−0.109417	−0.001964(20)	0.000003	0.000002	−0.111376(19)
			$Z=14$		
$3s$	−1.643077	−0.016021(24)	0.000164	0.000031	−1.658904(24)
$3p^*$	−1.321673	−0.012490(24)	0.000227	0.000018	−1.333919(24)
$3p$	−1.319542	−0.012407(24)	0.000106(1)	0.000018	−1.331825(24)
			$Z=17$		
$3s$	−4.177647	−0.020252(6)	0.000568(1)	0.000062(1)	−4.197269(6)
$3p^*$	−3.617688	−0.019486(7)	0.000854(1)	0.000033(1)	−3.636287(7)
$3p$	−3.608865	−0.019314(7)	0.000456(1)	0.000033(1)	−3.627691(7)
			$Z=20$		
$3s$	−7.743915	−0.022680(12)	0.001328(2)	0.000100(2)	−7.765167(12)
$3p^*$	−6.948437	−0.024035(10)	0.002069(2)	0.000051(1)	−6.970352(10)
$3p$	−6.924760	−0.023756(9)	0.001177(2)	0.000051(1)	−6.947288(9)
			$Z=26$		
$3s$	−17.963529	−0.025681(17)	0.004353(4)	0.000164(6)	−17.984693(19)
$3p^*$	−16.695869	−0.029731(18)	0.007027(4)	0.000082(3)	−16.718492(19)
$3p$	−16.598386	−0.029155(20)	0.004208(4)	0.000081(3)	−16.623252(21)
			$Z=34$		
$3s$	−38.079023	−0.027992(19)	0.012844(2)	0.000241(15)	−38.093930(24)
$3p^*$	−36.166027	−0.034089(21)	0.021120(6)	0.000119(7)	−36.178877(23)
$3p$	−35.798591	−0.032980(21)	0.012926(7)	0.000118(7)	−35.818527(23)
			$Z=42$		
$3s$	−65.834514	−0.029596(18)	0.028525(1)	0.000337(32)	−65.835249(37)
$3p^*$	−63.244907	−0.036983(22)	0.047384(4)	0.000169(16)	−63.234338(27)
$3p$	−62.246321	−0.035151(22)	0.028942(6)	0.000166(16)	−62.252365(28)
			$Z=54$		
$3s$	−122.59725	−0.03177	0.07132	0.00046(7)	−122.55724(7)
$3p^*$	−118.90453	−0.04059	0.11946	0.00024(4)	−118.82543(4)
$3p$	−115.70295	−0.03725	0.07109	0.00023(4)	−115.66889(4)
			$Z=74$		
$3s$	−262.45308	−0.03539	0.22311(1)	0.00069(20)	−262.26467(20)
$3p^*$	−256.55358	−0.04628	0.37602	0.00039(11)	−256.22345(11)
$3p$	−242.67838	−0.03879	0.20421(1)	0.00037(11)	−242.51259(11)
			$Z=92$		
$3s$	−448.01082	−0.04024	0.50795(2)	0.00087(39)	−447.54224(39)
$3p^*$	−439.55520	−0.05375	0.85809(1)	0.00056(25)	−438.75031(25)
$3p$	−399.56203	−0.03942	0.40424(1)	0.00051(23)	−399.19670(23)

TABLE IV. Contributions to the Coulomb correlation energy for Na and Fe^{15+}. Units of energy are in a.u. Numbers in parentheses denote errors.

Z	State	$E^{(2)}_{\text{single}}$	$E^{(2)}_{\text{double}}$	$E^{(2)}$	$E^{(3)}$
11	$3s$	0.001358	−0.007244	−0.005886	−0.000508(50)
11	$3p^*$	0.000753	−0.002539	−0.001786	−0.000186(20)
11	$3p$	0.000754	−0.002531	−0.001777	−0.000187(20)
26	$3s$	0.007955	−0.033807	−0.025852	0.000171(17)
26	$3p^*$	0.008266	−0.038177(1)	−0.029911(1)	0.000180(18)
26	$3p$	0.008164	−0.037499(2)	−0.029335(2)	0.000180(20)

are the dominant corrections for low values of nuclear charge and that the Breit interaction dominates for high Z.

The corrections given in Table III are plotted as functions of the nuclear charge Z in Figs. 1–3. The Coulomb correlation correction E_{corr} is dominated by $E^{(2)}$, shown in Fig. 1 for the three valence states. This correction would be independent of Z in a nonrelativistic $1/Z$ expansion. The energies vary rapidly at low Z because we use a Dirac-Fock basis rather than the Coulomb basis appropriate to the $1/Z$ expansion. The deviations from constancy at high Z are relativistic effects. In Fig. 2 we plot the total Breit correction for the three valence states scaled by Z^3 as functions of Z. The coefficient of $1/M$ in the mass-polarization correction is plotted in Fig. 3. The entries listed under the heading reduced mass and mass polarization in Table III are the sums of the reduced-mass corrections and the mass-polarization corrections.

Contributions to the Coulomb correlation corrections for Na and Fe^{15+} are shown in Table IV. The individual contributions to $E^{(2)}$ in Eq. (4) from single and double excitations are given together with the resulting sum $E^{(2)}$ and the sum of the 12 terms contributing to $E^{(3)}$. The second-order energy was evaluated with high accuracy, the dominant source of error being the truncation of the partial-wave expansion. Nine partial waves were included, and the remainder was estimated by rational extrapolation. The third-order calculation was too computationally intensive to permit similar accuracy, primarily because of the term involving sums over four excited states. In this case, only four partial waves were summed, and the innermost $(1s_{1/2})$ core state was excluded from the core sums. For this reason, a large error estimate of 10% is quoted in Table III. Because of limitations in computer time, $E^{(3)}$ was not evaluated above $Z=42$. Although the third-order energy is relatively small, the associated error is the largest theoretical uncertainty in the calculation for low-Z ions. We are presently investigating methods to allow more accurate evaluation of $E^{(3)}$.

In Table V we list the various contributions to the Breit interaction for Na and Fe^{15+}. The dominant contribution $B^{(1)}$ is calculated using the frequency-dependent interaction given in Eq. (6). While a rapid pattern of convergence was found for the Coulomb correlation corrections, the corresponding corrections to the Breit interaction are seen to be much more significant, primarily due to the RPA terms discussed above. Of particular note is the large cancellation of $B^{(1)}$ by this term for neutral Na.

The individual contributions to the mass-polarization energy correction for Na and Fe^{15+} are given in Table VI. The situation is similar to that just discussed for the Breit interaction with large cancellations of the lowest-order correction by the RPA terms. The computational error in the mass-polarization correction is small but there is an error associated with the use of the nonrelativistic mass-polarization Hamiltonian. We used the nonrelativistic Hamiltonian because we do not know of a systematic relativistic treatment of nuclear recoil that would fit into the scheme of our calculations, and yet feel it is important to make some estimate of this effect. We expect the error to be on the order of $(Z\alpha)^2$ times the reduced-mass energy correction. For high Z this uncertainty dominates the theoretical error in the level energies.

In Table VII we compare our values of the $3s_{1/2}$ energy with measured energies. Most of the −0.00045 a.u. difference seen for neutral Na is the result of our incomplete treatment of the Coulomb correlation corrections. If one ignores the Lamb shift entirely, the additional correlation corrections that must arise in fourth and

TABLE V. Contributions to the Breit interaction for Na and Fe^{15+}. Units of energy are in a.u. Numbers in parentheses denote errors.

Z	State	$B^{(1)}$	$B^{(2)}$	B_{RPA}	$B^{(3)}_{\text{BO}}$
11	$3s$	0.000026	−0.000003(1)	−0.000016	0.000004
11	$3p^*$	0.000013	−0.000001	−0.000005	0.000002
11	$3p$	0.000009	−0.000001	−0.000006	0.000001
26	$3s$	0.005480	−0.000195(4)	−0.000967	0.000036
26	$3p^*$	0.008355	−0.000260(4)	−0.001127	0.000058
26	$3p$	0.005648	−0.000271(4)	−0.001208	0.000038

TABLE VI. Contributions to the mass-polarization energy for Na and Fe^{15+}. Terms in table must be multiplied by m/M to obtain energy shift. Units of energy are in a.u. Numbers in parentheses denote errors.

Z	State	$P^{(1)}$	$P^{(2)}$	P_{RPA}	$P_{\mathrm{BO}}^{(3)}$	P_{tot}
11	$3s$	−0.06150	0.02633	0.04653	−0.00701	0.00434
11	$3p^*$	−0.03201	0.00780	0.01340	−0.00477	−0.01558
11	$3p$	−0.03199	0.00779	0.01338	−0.00475	−0.01557
26	$3s$	−2.51638	0.36398	0.90140	−0.01028	−1.26128
26	$3p^*$	−9.82545	0.66803	0.86680	−0.06642	−8.35704
26	$3p$	−9.73257	0.65392	0.84802	−0.06573	−8.29635

TABLE VII. Comparison of theoretical values of the $3s_{1/2}$ energies for sodiumlike ions with experiment. Units of energy are in a.u. Numbers in parentheses denote errors.

Z	Theor.	Expt.	Expt.-Theor.	Unscreened Lamb-shift
11	−0.188411(50)	−0.1888585	−0.000447(50)	0.0002979
14	−1.658904(24)	−1.6589302(10)	−0.000026(24)	0.0006940
17	−4.197269(6)	−4.2004946(90)	−0.003226(11)	0.001364
20	−7.765167(12)	−7.764210(15)	0.000958(19)	0.002393
26	−17.984693(19)	−17.979983(15)	0.004711(24)	0.005900
34	−38.093930(24)			0.01501
42	−65.835249(37)			0.03056
54	−122.55724(7)			0.07332
74	−262.26467(20)			0.2299
92	−447.54224(39)			0.5394

TABLE VIII. Comparison of theoretical values for the $3p_{1/2}$-$3s_{1/2}$ interval in sodiumlike ions with experiment. Units of energy are in a.u. Numbers in parentheses denote errors.

Z	Theor.	Expt.	Expt.-Theor.	Unscreened Lamb-shift
11	0.076960(54)	0.0772581	0.000298(54)	−0.0003054
14	0.324985(34)	0.3248193(5)	−0.000166(34)	−0.0007128
17	0.560982(9)	0.560434(9)	−0.000548(13)	−0.001402
20	0.794815(16)	0.793773(14)	−0.001042(21)	−0.002462
26	1.266201(26)	1.262979(14)	−0.003222(30)	−0.006064
34	1.915053(33)	1.90544(8)	−0.00961(9)	−0.01535
42	2.600911(38)	2.57907(15)	−0.02184(15)	−0.03100
54	3.731805(8)	3.67752(21)	−0.05429(22)	−0.07283
74	6.041224(23)			−0.2156
92	8.791938(47)			−0.4659

TABLE IX. Comparison of theoretical values for the $3p_{3/2}$-$3p_{1/2}$ fine-structure interval in sodiumlike ions with experiment. Units of energy are in a.u. Numbers in parentheses denote errors.

Z	Theor.	Expt.	Expt.-Theor.	Unscreened Lamb-shift
11	0.000076(28)	0.000078	0.000003(28)	0.000016
14	0.002094(34)	0.002097(1)	0.000004(34)	0.000043
17	0.008596(10)	0.008612(9)	0.000016(14)	0.000092
20	0.023065(14)	0.023122(19)	0.000057(24)	0.000173
26	0.095240(28)	0.095459(19)	0.000219(34)	0.000483
34	0.36035(3)	0.36129(14)	0.00094(14)	0.00136
42	0.98197(4)	0.98411(32)	0.00213(32)	0.00303
54	3.15655(1)	3.16146(39)	0.00491(39)	0.00757
74	13.71086(2)			0.0201
92	39.55360(3)			0.0222

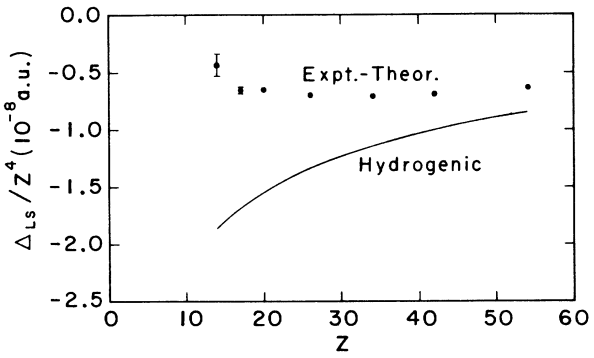

FIG. 4. Inferred QED correction for $3p_{1/2}$-$3s_{1/2}$ splitting divided by Z^4 for sodiumlike ions from $Z=14$ to 54 compared with unscreened hydrogenic values in units of 10^{-8} a.u.

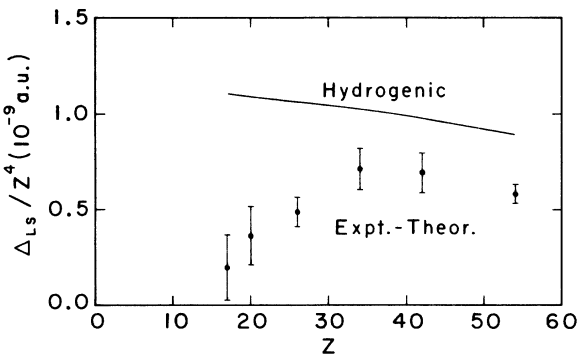

FIG. 5. Inferred QED correction for $3p_{3/2}$-$3p_{1/2}$ splitting divided by Z^4 for sodiumlike ions from $Z=17$ to 54 compared with unscreened hydrogenic values in units of 10^{-9} a.u.

higher order are seen to be of the same order as $E^{(3)}$. There is a complicated interplay between these uncalculated correlation corrections, which should become less important for higher Z, and the uncalculated QED corrections, which although presumably highly screened, should also grow rapidly in importance further along the isoelectronic sequence. For Z larger than 17 it appears that a screened Lamb shift accounts for the difference between theory and experiment. In Table VIII the $3s_{1/2}$-$3p_{1/2}$ energy interval is compared with experiment and the differences between theory and experiment are seen to be systematically smaller than the hydrogenic $3s_{1/2}$-$3p_{1/2}$ Lamb shift, reaching 80% of the hydrogenic value for Xe^{43+}. In Table IX we compare values of the $3p_{1/2}$-$3p_{3/2}$ fine-structure interval with experiment and again find that the differences are significantly smaller than the hydrogenic Lamb-shift (LS) values. A comparison with these values is presented in Figs. 4 and 5 for the case of the $3p_{1/2}$-$3s_{1/2}$ and $3p_{3/2}$-$3p_{1/2}$ intervals, respectively.

In summary, the present calculations of the Coulomb, Breit, and reduced-mass corrections to the energies of the $3s$ and $3p$ states of Na-like ions when compared to experiment lead to differences that are systematically smaller than the differences expected from hydrogenic values of the Lamb shift. Accounting for these residual screening corrections to the Lamb shift for Na-like ions remains as a significant unsolved problem in atomic physics. As discussed in Ref. 4, it is possible to identify Feynman graphs that are associated with these screening corrections, and work is presently in progress to evaluate these graphs.

ACKNOWLEDGMENT

We would like to thank J. Reader for a discussion. This work was supported in part by National Science Foundation Grant Nos. PHY-85-03415 and PHY-86-08101. The calculations were carried out on the National Center for Supercomputing Applications CRAY XMP/48.

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