Relativistic many-body calculations of $[2p^5 3d]_{J=1}$ excited-state energy levels for neonlike ions

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(Received 20 December 1995)

Energies of the $[2p^5 3d]_{J=1}$ excited states of neonlike ions with nuclear charges in the range $Z=10-92$ are evaluated using an all-orders method based on relativistic many-body perturbation theory. The calculation starts from a multiconfiguration Hartee-Fock (HF) wave function, and includes correlation corrections from both the Coulomb and Breit interactions. The dominant correlation corrections, which are those associated with the $2p$ hole state, are treated to all orders. Reduced-mass and mass-polarization corrections are computed up to first order. The electron self-energy, the vacuum polarization, and the frequency-dependent Breit interaction are also included in first order, using a local potential that approximates the $V^{(N-1)}$ (HF) potential. Comparisons are made with existing measurements and with other calculations.
[S1050-2947(96)07308-8]

PACS number(s): 31.25.Jf, 31.15.Ar, 31.15.Md, 31.30.Jv

I. INTRODUCTION

This is the third in a series of relativistic many-body perturbation theory (RMBPT) studies of the energy levels of particle-hole systems (i.e., closed-shell systems in which a core electron is excited into a valence state). In the first of these studies [1], we derived many-body perturbation formulas up to third order using a V^N Hartree-Fock (HF) potential, and presented an application to the $[2p_{3/2}^{-1}3s_{1/2}]_{J=2}$ state of neonlike Xe. In the second paper of this series [2] we calculated the energies of the $[2p^5 3s]$ particle-hole states of neonlike ions. The present work extends these calculations to include the $[2p^5 3d]_{J=1}$ states, completing a study of accurately measured low-lying transition energies.

In the present study, core and valence states are generated in a V^{N-1} Hartree-Fock (HF) potential, where the excited states are evaluated in the field of a hole in the $2p_{3/2}$ subshell. These single-particle orbitals are used to obtain wave functions for the lowest-order particle-hole states. Our starting assumption is to consider as almost degenerate all the lowest-order particle-hole states coupled to $J=1$, in which the hole orbital belongs to the $n=2$ shell and the valence orbital belongs to the $n=3$ shell. First-order perturbation theory leads to a matrix equation that involves the lowest-order effective Hamiltonian (H^{eff}) [2]. The eigenvalues and eigenvectors of this Hamiltonian provide a first-order approximation of the energies and wave functions of the particle-hole states under consideration. Aside from the expected degeneracy of all three $[2p^5 3d]_{J=1}$ states for low Z, strong mixing is also found between state $[2p_{1/2}^{-1}3d_{3/2}]_1$ and doublet $[2s^{-1}3p]_1$, near $Z=68$. Higher-order Coulomb correlation corrections are evaluated by solving the Schrödinger equation for the correlation operator [3], and by diagonalizing the resulting H^{eff}. These correlation corrections are classified into four sectors: core-core, core-hole, valence-core, and valence-hole. The dominant corrections stem from the core-hole sector alone. Therefore, we iterate the equations corresponding to this sector to all orders, while contributions from the remaining sectors are evaluated to second order only. In this approximation we basically neglect terms of leading-order Z^{-2} a.u. The Breit-Coulomb correlation corrections up to order $Z^4\alpha^4$ a.u. are also calculated using second-order perturbation theory. They are dominated by a single term which is iterated to all orders giving higher-order Breit correlation contributions. Next, we consider the lowest-order corrections to the frequency-dependent Breit interaction and the Lamb shift of orders $Z^5\alpha^4$ and $Z^4\alpha^3$, respectively. These are evaluated in a local potential that approximates the V^{N-1} potential. Because of the mixing with states that involve a $2s$ orbital, the Lamb shift corrections for the $[2p_{1/2}^{-1}3d_{3/2}]_1$ state are enhanced by one order of magnitude for $Z=68$. Finally, the contribution from the mass-polarization corrections is computed in first order, neglecting higher-order relativistic nuclear recoil corrections of leading order $Z^3\alpha^4$ [4].

We find excellent agreement between the theoretically determined energies and the corresponding experimentally measured values for $Z<60$. The discrepancy between theory and experiment starts from ≈ 0.005 a.u. for low Z, and grows to ≈ 0.03 a.u. near $Z=40$, and ≈ 0.1 a.u. at $Z=80$.

II. FORMALISM

In this section we outline the basic steps of our calculation, the details of which have been presented in Ref. [2]. Our first step is to define the ''no-pair'' Hamiltonian [5] using the eigenvalues and eigenfunctions of the single-particle Dirac equation. This many-body Hamiltonian is the sum of an unperturbed part and an interaction potential that accounts for the electron-correlation corrections. This potential is expressed as the difference between the Coulomb interaction among electrons and the $V^{(N-1)}$ (HF) model potential used to approximate this interaction in the single-particle approximation.

A. Coulomb interaction

The Coulomb correlation corrections are obtained by solving the time-independent Schrödinger equation

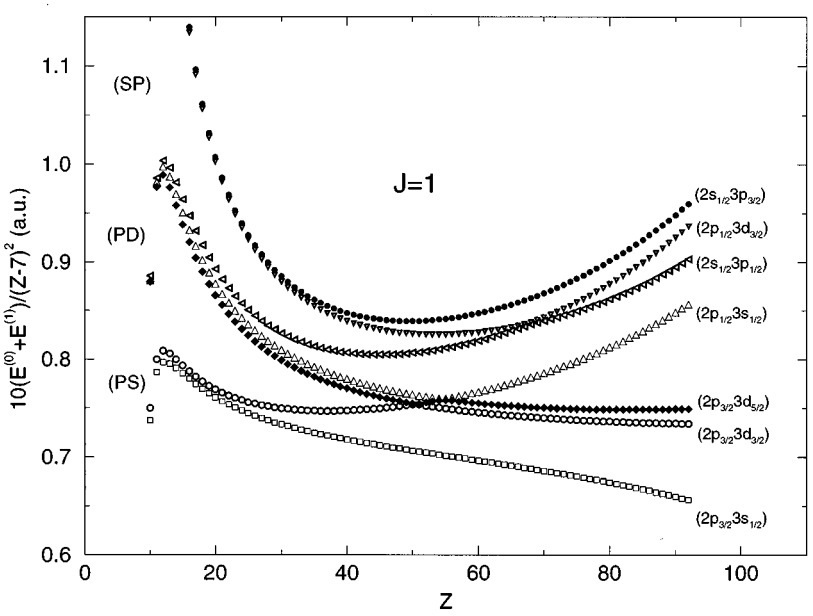

FIG. 1. Sum of the lowest- and first-order energies $E^{(0)}+E^{(1)}$ for the $J=1$ states of neonlike ions from a $V^{(N-1)}$ HF calculation. We show all the states obtained by coupling a $2p$ hole with a $3s$ or $3d$ excited electron and a $2s$ hole with a $3p$ excited electron.

$$H\Psi(JM)=E\Psi(JM). \tag{2.1}$$

The state vector $\Psi(JM)$ is defined with the help of the correlation operator χ_{av} acting on a linear combination of almost degenerate particle-hole wave functions $\Phi_{av}(JM)$ that span a model space,

$$\Psi(JM)=\sum_{\rm av} C_{\rm av}(1+\chi_{\rm av})\Phi_{\rm av}(JM), \tag{2.2}$$

where the indices a and v represent the hole and valence states, respectively. From the above relations we form an eigenvalue equation for the effective Hamiltonian $H^{\rm eff}$,

$$\sum_{\rm av} H^{\rm eff}_{a'v',{\rm av}}C_{\rm av}=EC_{a'v'}, \tag{2.3}$$

where $H^{\rm eff}$ is given by

$$H^{\rm eff}_{a'v',av}=\langle\Phi_{a'v'}(JM)|H(1+\chi_{av})|\Phi_{av}(JM)\rangle. \tag{2.4}$$

Approximating the correlation operator as a sum of single and double excitations, and applying it to the lowest-order state vector, we obtain

$$\begin{aligned}\chi_{av}a_v^\dagger a_a|0_c\rangle=\Bigg\{&\frac{1}{2}\sum_{rsbc}\chi^{rs}_{bc}a_r^\dagger a_s^\dagger a_c a_b a_v^\dagger a_a+\sum_{sbc}\chi^{as}_{bc}a_s^\dagger a_c a_b a_v^\dagger\\&+\sum_{rb}\chi^{r}_{b}a_r^\dagger a_b a_v^\dagger a_a+\sum_{b\neq a}\chi^{a}_{b}a_b a_v^\dagger\\&+\sum_{rsb}\chi^{rs}_{vb}a_r^\dagger a_s^\dagger a_b a_a+\sum_{sb\neq va}\tilde{\chi}^{as}_{vb}a_s^\dagger a_b\\&+\sum_{r\neq v}\chi^{r}_{v}a_r^\dagger a_a+\chi^{a}_{v}\Bigg\}|0_c\rangle,\end{aligned} \tag{2.5}$$

where the indices r, and s represent virtual states, b and c represent core states, α represents either hole or virtual states; and $|0_c\rangle$ denotes the closed-shell state vector.

In lowest order, we set $\chi_{av}=0$. The eigenvalues of $H^{\rm eff}$ give the energies up to first-order $E^{(0)}+E^{(1)}$, and the corresponding eigenvectors define the mixing coefficients among the members of the model space. By inserting the first-order χ_{av} into Eq. (2.4), from the eigenvalues of $H^{\rm eff}$ we obtain the energies up to second-order perturbation theory $E^{(0)}+E^{(1)}+E^{(2)}$. The net second-order contribution $E^{(2)}$ is obtained by subtracting from these eigenvalues the ones up to first order. The correlation coefficients of the first four terms in Eq. (2.5) are responsible for the dominant core-hole corrections to the energy in second-order perturbation theory. Therefore, we calculate them to all orders [2]. The eigenvalues of $H^{\rm eff}$ include the corresponding all-orders corrections $E^{(3+)}$, which are isolated by subtracting the eigenvalues from the previous approximation.

B. Breit interaction

We add to the ''no-pair'' Hamiltonian a term that accounts for the frequency-independent part of the Breit inter-

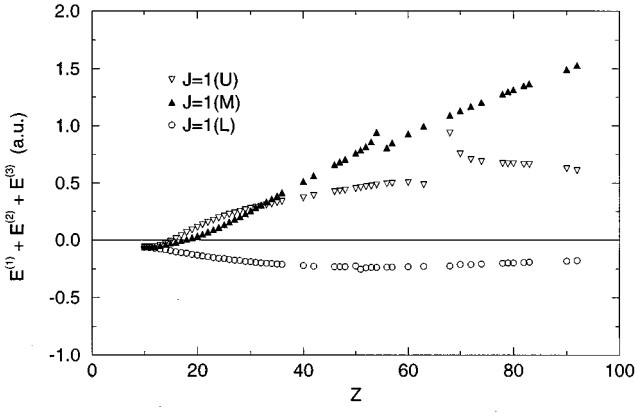

FIG. 2. Electrostatic correlation energy $E^{(1)}+E^{(2)}+E^{(3+)}$ for the $[2p^{-1}3d]_1$ states of neonlike ions obtained from the iteration solution to the all-orders equations.

TABLE I. Contributions to transition energies of the $[2p_{1/2}^{-1}3d_{3/2}]_1$, $(1U)$, $[2p_{3/2}^{-1}3d_{5/2}]_1$, $(1M)$; and $[2p_{3/2}^{-1}3d_{3/2}]_1$, $(1L)$ states of neonlike ions from zeroth- through second-order Coulomb energy, $E^{(0+1)}$ and $E^{(2)}$; all-order hole-core Coulomb correlation energy $E^{(3+)}$; first- and second-order frequency-independent Breit energy $B^{(1)}$ and $B^{(2)}$; RPA correction to the frequency-independent Breit energy, $B^{(3+)}$; first-order frequency-dependent Breit energy, ΔB_ω; the QED correction term QED; and the reduced-mass and mass-polarization correction RM.

Z	State	$E^{(0+1)}$	$E^{(2)}$	$E^{(3+)}$	$B^{(1)}$	$B^{(2)}$	$B^{(3+)}$	ΔB_ω	QED	RM	Total
10	$(1U)$	0.7972	-0.1798	0.1170	-0.0009	0.0013	-0.0007	0.0000	0.0000	0.0000	0.7341
10	$(1M)$	0.7926	-0.1793	0.1171	-0.0006	0.0014	-0.0006	0.0000	0.0000	0.0000	0.7306
10	$(1L)$	0.7919	-0.1790	0.1171	-0.0006	0.0014	-0.0006	0.0000	0.0000	0.0000	0.7303
20	$(1U)$	15.0931	-0.1475	0.0184	-0.0151	0.0054	-0.0008	0.0000	0.0001	0.0002	14.9540
20	$(1M)$	14.8272	-0.0769	0.0161	-0.0127	0.0053	-0.0007	0.0000	0.0000	0.0000	14.7584
20	$(1L)$	14.6366	-0.0734	0.0153	-0.0112	0.0054	-0.0007	0.0001	-0.0001	0.0000	14.5718
30	$(1U)$	43.7387	-0.1317	0.0098	-0.0682	0.0124	-0.0011	0.0001	0.0006	0.0003	43.5609
30	$(1M)$	42.8385	-0.0867	0.0087	-0.0496	0.0126	-0.0011	0.0005	-0.0010	0.0001	42.7222
30	$(1L)$	42.2937	-0.0681	0.0078	-0.0445	0.0127	-0.0010	0.0005	-0.0011	-0.0001	42.1999
40	$(1U)$	87.8683	-0.1256	0.0067	-0.1829	0.0222	-0.0015	0.0004	0.0013	0.0003	87.5894
40	$(1M)$	84.9337	-0.1079	0.0062	-0.1294	0.0227	-0.0014	0.0027	-0.0045	0.0003	84.7224
40	$(1L)$	83.9063	-0.0652	0.0052	-0.1137	0.0230	-0.0014	0.0027	-0.0047	-0.0002	83.7521
50	$(1U)$	149.2046	-0.1300	0.0054	-0.3865	0.0355	-0.0020	0.0012	0.0005	0.0004	148.7291
50	$(1M)$	141.2571	-0.1140	0.0048	-0.2711	0.0360	-0.0018	0.0090	-0.0127	0.0005	140.9078
50	$(1L)$	139.5822	-0.0591	0.0039	-0.2363	0.0362	-0.0018	0.0084	-0.0107	-0.0002	139.3226
60	$(1U)$	230.1182	-0.0540	0.0046	-0.7115	0.0540	-0.0025	0.0025	-0.0111	0.0005	229.4005
60	$(1M)$	212.0444	-0.1156	0.0039	-0.4925	0.0529	-0.0022	0.0239	-0.0323	0.0007	211.4833
60	$(1L)$	209.4293	-0.0597	0.0032	-0.4145	0.0523	-0.0022	0.0228	-0.0330	-0.0003	208.9978
70	$(1U)$	334.6818	-0.1043	0.0045	-1.0294	0.0705	-0.0029	0.0031	-0.0671	0.0002	333.5564
70	$(1M)$	297.7853	-0.1147	0.0033	-0.8028	0.0723	-0.0026	0.0537	-0.0700	0.0008	296.9252
70	$(1L)$	293.6326	-0.0538	0.0027	-0.6752	0.0717	-0.0026	0.0508	-0.0702	-0.0003	292.9556
80	$(1U)$	467.5511	-0.1061	0.0043	-1.9427	0.1162	-0.0040	0.0050	-0.0688	0.0008	465.5557
80	$(1M)$	398.8901	-0.1115	0.0028	-1.2236	0.0968	-0.0031	0.1072	-0.1347	0.0009	397.6249
80	$(1L)$	392.3801	-0.0548	0.0023	-1.0277	0.0935	-0.0031	0.1010	-0.1348	-0.0004	391.3560
90	$(1U)$	637.3728	-0.1336	0.0044	-3.0473	0.1730	-0.0050	0.0019	-0.1680	0.0012	634.1993
90	$(1M)$	515.9347	-0.1078	0.0025	-1.7691	0.1242	-0.0037	0.1958	-0.2397	0.0011	514.1378
90	$(1L)$	505.9021	-0.0538	0.0020	-1.4851	0.1186	-0.0037	0.1838	-0.2398	-0.0004	504.4237

action. Diagonalizing the resulting H^{eff} in lowest order, we obtain eigenvalues that include both first-order Breit and Coulomb corrections. By subtracting the already computed Coulomb corrections up to first order, we obtain the first-order Breit corrections $B^{(1)}$.

The second-order Breit corrections $B^{(2)}$ are obtained by linearizing the second-order perturbation expressions for the Breit plus Coulomb energy in the Breit interaction . The dominant contribution comes from the second-order random-phase approximation (RPA) correction to the core-hole Breit interaction. The higher-order contributions $B^{(3+)}$ are evaluated by computing this leading correction to all orders as in Ref. [2].

C. QED and mass-polarization corrections

The frequency-dependent correction to the Breit interaction, as well as the electron self-energy and vacuum polarization, are evaluated in a local modified core-Hartree potential [6] that approximates the $V^{(N-1)}$ (HF) potential.

Since we use a local potential, the frequency dependence of the Breit interaction can be obtained by calculating one-photon exchange in Feynman gauge and then subtracting the instantaneous Coulomb and Breit interactions. The first-order corrections calculated in this way are designated by ΔB_ω.

The Lamb shift, that consists of the electron self energy and vacuum polarization, was calculated using methods described in Ref. [7]. The only significant differences from the

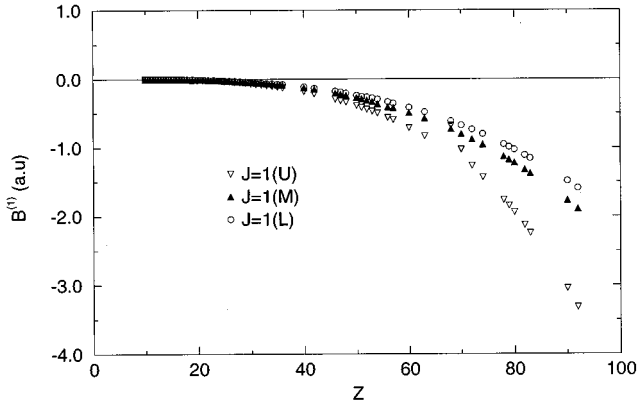

FIG. 3. Lowest-order Breit interaction $B^{(1)}$ for $[2p^{-1}3d]_{J=1}$ particle-hole states of neonlike ions.

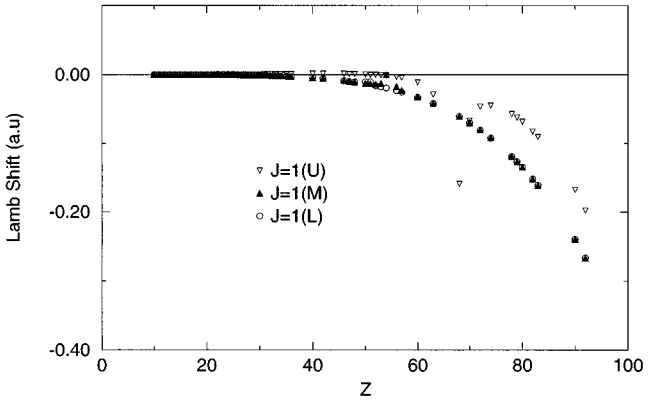

FIG. 5. Correction for the frequency dependence of the Breit interaction ΔB_{ω} for $[2p^{-1}3d]_1$ particle-hole states of neonlike ions.

method described in that paper is that we include 17 partial waves here rather than 13 and carry out a more accurate evaluation of the vertex diagram in momentum space. To check the calculation, we let $U(r)=0$, replaced $V_{\mathrm{nuc}}(r)$ by a Coulomb potential, and obtained good agreement with the values tabulated by Mohr and Kim for the $3s_{1/2}$ states [8] and by Mohr [9] for the $2p_{1/2}$ and $2p_{3/2}$ states. Explicit calculations of the Lamb shift were carried out at $Z=20$–92. Below $Z=20$ the values are <0.0001 a.u. Because two-photon QED effects were not included, this part of the calculation has a theoretical error, which can be taken to be of order $1/Z$ of the Lamb shift. The last contribution to the energies comes from the reduced-mass corrections related to the finite nuclear mass along with the lowest-order mass-polarization corrections, assuming that nuclear motion is nonrelativistic.

III. RESULTS

The particle-hole states under consideration, $[2p_{1/2}^{-1}3d_{3/2}]_1$, $[2p_{3/2}^{-1}3d_{5/2}]_1$, and $[2p_{3/2}^{-1}3d_{3/2}]_1$, are designated in our tables and diagrams as the $J=1(U)$ or $(1U)$, $J=1(M)$ or $(1M)$, $J=1(L)$ or $(1L)$, respectively. The energies are calculated in the $V^{(N-1)}$ frozen-core approximation. Finite nuclear size corrections are included by replacing the Coulomb field of a point nucleus by the field of a finite Fermi distribution of the nuclear charge with parameters determined from experiment [10]. The higher-order Coulomb and Breit-Coulomb corrections presented below are calculated by evaluating the relevant sums over intermediate states using a pseudospectrum constructed from B splines to replace the exact single-particle spectrum [11]. Our pseudospectrum consists of 40 B splines of order 7 for each angular momentum state. The calculations of the double sums over excited states included all orbitals with angular momentum $l\leqslant 9$ explicitly. The contributions to the sums from orbitals with higher angular momentum were estimated by extrapolation. The uncertainty in the extrapolation procedure gives an error of order 0.0001 a.u.

In Fig. 1 we present the eigenvalues of the lowest order H^{eff}. They correspond to particle-hole energies up to first order $E^{(0)}+E^{(1)}$. A preliminary seven-channel approach is necessary at this level of approximation, in order to cover all possible mixings of these states with any other particle-hole state, coupled to $J=1$, in which the hole orbital belongs to the second shell and the valence orbital belongs to the third.

For $Z\leqslant 20$ we have three groups of almost degenerate multiplets. The $[2s^5 3p]_1$ (SP) doublet, the $[2p^5 3d]_1$ (PD) triplet, which is the subject of the present study, and the $[2p^5 3s]_1$ (PS) doublet that was part of our previous work

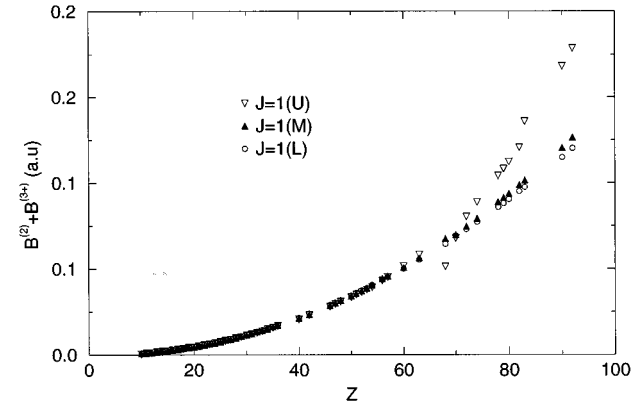

FIG. 4. Breit-Coulomb correlation corrections $B^{(2)}+B^{(3+)}$ for $[2p^{-1}3d]_1$ particle-hole states of neonlike ions.

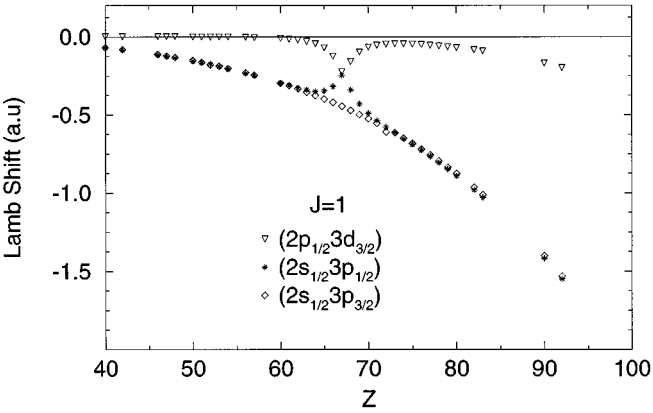

FIG. 6. QED corrections for $[2p^{-1}3d]_1$ states of neonlike ions.

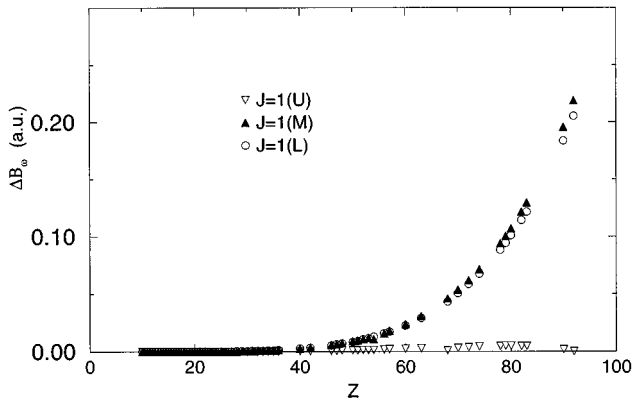

FIG. 7. QED corrections for $[2p_{1/2}^{-1}3d_{3/2}]_1$ and $[2s^{-1}3p]_1$ states of neonlike ions for $40 \leqslant Z \leqslant 92$.

[2]. As Z becomes higher we see the states splitting from the initial low-Z multiplets. For $Z>40$ the state $[2p_{3/2}^{-1}3d_{5/2}]_1$ clearly separates from the other two members of the triplet, which remain almost degenerate throughout the whole isoelectronic sequence. Strong interactions occur among the states $[2p_{3/2}^{-1}3d_{5/2}]_1$, $[2p_{3/2}^{-1}3d_{3/2}]_1$ and $[2p_{1/2}^{-1}3s_{1/2}]_1$ around $Z=54$, and among the states $[2p_{1/2}^{-1}3d_{3/2}]_1$, $[2s_{1/2}^{-1}3p_{1/2}]_1$, and $[2s_{1/2}^{-1}3p_{3/2}]_1$ around $Z=68$.

The above-mentioned mixing of states determines the composition of the model space over which we carry out the second- and higher-order correlation calculations. Thus for $Z \leqslant 40$ we perform a three-channel calculation over a model space that includes all three states under consideration. For $Z>40$ and for the doublets $[2p_{3/2}^{-1}3d_{5/2}]_1$ and $[2p_{3/2}^{-1}3d_{3/2}]_1$, we perform a four-channel calculation that also includes the states $[2p_{1/2}^{-1}3d_{3/2}]_1$ and $[2p_{1/2}^{-1}3s_{1/2}]_1$. As for the state $[2p_{1/2}^{-1}3d_{3/2}]_1$ and for $Z>40$, we use a three-channel approach that also includes the states $[2s_{1/2}^{-1}3p_{3/2}]_1$ and $[2s_{1/2}^{-1}3p_{1/2}]_1$.

In Fig. 2 we present the total Coulomb correlation corrections $E^{(1)}+E^{(2)}+E^{(3)}$ as a function of Z, where $E^{(2)}$ corresponds to the second-order perturbation theory and $E^{(3)}$ comes from the iteration of the all-orders equations that correspond to the core-hole sector. For $Z \leqslant 20$ this total correction is approximately the same for all three $[2p^5 3d]_1$ states, and of order 0.1 a.u., but as Z increases both the nature and magnitude of the correlations change for every one of these states. For the state $[2p_{1/2}^{-1}3d_{3/2}]_1$, it rises up to $\approx$0.5 a.u., and, after a strong discontinuity of $\approx$0.5 a.u. around $Z=68$, it

TABLE II. Theoretical transition energies for the $[2p_{1/2}^{-1}3d_{3/2}]_1$ $(1U)$, $[2p_{3/2}^{-1}3d_{5/2}]_1$ $(1M)$, and $[2p_{3/2}^{-1}3d_{3/2}]_1$ $(1L)$ states of neonlike ions. Units: a.u.

	Z	E	Z	E	Z	E	Z	E	Z	E	Z	E
$(1U)$	10	0.7341	19	12.8929	28	36.6502	40	87.5894	54	178.4917	74	382.4875
	11	1.5117	20	14.9540	29	40.0293	42	98.3837	56	194.5978	78	436.5143
	12	2.4353	21	17.1576	30	43.5609	46	122.0853	57	202.9693	79	450.8592
	13	3.5011	22	19.5046	31	47.2462	47	128.4642	60	229.4005	80	465.5557
	14	4.7111	23	21.9957	32	51.0869	48	135.0293	63	257.8784	82	496.0428
	15	6.0644	24	24.6319	33	55.0844	50	148.7291	68	311.0330	83	511.8525
	16	7.5596	25	27.4143	34	59.2402	51	155.8692	70	333.5564	90	634.1993
	17	9.1960	26	30.3440	35	63.5558	52	163.2067	72	357.3916	92	673.3128
	18	10.9737	27	33.4222	36	68.0330	53	170.7444				
$(1M)$	10	0.7306	19	12.7325	28	36.0077	40	84.7224	54	167.4993	74	335.3445
	11	1.5045	20	14.7584	29	39.2948	42	94.8167	56	181.4331	78	376.2387
	12	2.4255	21	16.9240	30	42.7222	46	116.7138	57	188.7392	79	386.8530
	13	3.4878	22	19.2296	31	46.2898	47	122.5459	60	211.4833	80	397.6249
	14	4.6858	23	21.6754	32	49.9976	48	128.5219	63	235.5470	82	419.6433
	15	6.0196	33	53.8458	24	24.2614	50	140.9078	68	278.6326	83	430.8911
	16	7.4903	25	26.9876	34	57.8345	51	147.3197	70	296.9252	90	514.1378
	17	9.0989	26	29.8541	35	61.9637	52	153.8804	72	315.8275	92	539.3926
	18	10.8462	27	32.8608	36	66.2337	53	160.5970				
$(1L)$	10	0.7303	19	12.5717	28	35.5628	40	83.7521	54	165.4835	74	330.5693
	11	1.5017	20	14.5718	29	38.8117	42	93.7406	56	179.4200	78	370.5096
	12	2.4120	21	16.7103	30	42.1999	46	115.4021	57	186.6011	79	380.8596
	13	3.4566	22	18.9872	31	45.7272	47	121.1692	60	208.9978	80	391.3560
	14	4.6353	23	21.4027	32	49.3939	48	127.0774	63	232.6782	82	412.7888
	15	5.9490	24	23.9570	33	53.1999	50	139.3226	68	275.0064	83	423.7258
	16	7.3988	25	26.6501	34	57.1454	51	145.6217	70	292.9556	90	504.4237
	17	8.9855	26	29.4820	35	61.2304	52	152.1118	72	311.4720	92	528.8182
	18	10.7097	27	32.4529	36	65.4551	53	158.7274				

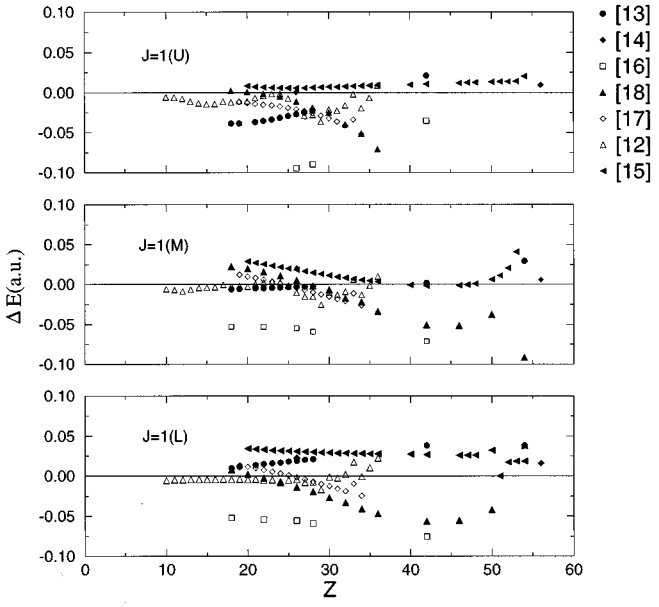

FIG. 8. Comparison of energies of the $[2p^{-1}3d]_1$ states of neonlike ions with other theories.

becomes almost stable, ≈0.7 a.u.. This irregularity arises due to the mixing with the doublet $[2s^5 3p]_1$, as we see in Fig. 1. For the state $[2p_{3/2}^{-1}3d_{3/2}]_1$, this correction becomes almost constant, and ≈−0.2 a.u. throughout the whole isoelectronic sequence, while for the state $[2p_{3/2}^{-1}3d_{5/2}]_1$ it rises almost linearly and becomes ≈1.2 a.u. for Z near 80. Therefore, the Coulomb correlation corrections are practically responsible for the removal of the degeneracy between these two states. Small discontinuities, of orders ≈0.1 and ≈0.02 a.u., can be observed near $Z=54$ for these two states because of mixing with the $[2p_{1/2}^{-1}3s_{1/2}]_1$ state. The above-mentioned irregularities, especially for $Z=68$, can be seen in almost all of the figures where the individual contributions to the energy corrections are presented as functions of Z.

In Table I, we list the contributions to the energies of the particle-hole states under consideration at intervals of $Z=10$. In the third column of this table, we give corrections up to first order $E^{(0)}+E^{(1)}$, while in the fourth and fifth columns we list the second-order correlation energies $E^{(2)}$ and all-orders core-hole corrections designated as $E^{(3+)}$. We see that, for $Z=10$, $E^{(2)}$ and $E^{(3)}$ are of the same order of magnitude. This is due to the fact that perturbation theory does not converge rapidly for neutral and low-Z systems. For $Z\geqslant 20$, $E^{(3)}$ is of the order 5% of $E^{(2)}$. In the sixth column of Table I, as well as in Fig. 3, we present the values of the first-order frequency-independent Breit interaction $B^{(1)}$. Even though near the neutral end of the sequence $B^{(1)}$ is of order 1% of $E^{(2)}$, for $Z>40$ it dominates the energy corrections.

In columns 7 and 8 we list the second-order Breit-Coulomb corrections $B^{(2)}$ and the all-orders random-phase-approximation (RPA) corrections to the dominant core-hole Breit correlation designated as $B^{(3+)}$. The sum $B^{(2)}+B^{(3+)}$ as a function of the nuclear charge is shown in Fig. 4. In both Figs. 3 and 4 we again see the discontinuity around $Z=68$ for the state $[2p_{1/2}^{-1}3d_{3/2}]_1$.

The strong mixing among the state $[2p_{1/2}^{-1}3d_{3/2}]_1$ and the doublet $[2s^{-1}3p]_1$ (mainly with the state $[2s_{1/2}^{-1}3p_{1/2}]_1$), as well as the difference in the relative magnitude of the corresponding Lamb shift corrections between them, causes a particularly strong discontinuity for $Z=68$. In Fig. 5 we present Lamb shift corrections for the $[2p^5 3d]_1$ triplet as a function of Z, and in Fig. 6 we show in detail, for $Z\geqslant 40$, the same correction for the state $[2p_{1/2}^{-1}3d_{3/2}]_1$ along with the

TABLE III. Comparison of the present MBPT calculations of $[2p_{3/2}^{-1}3d_{5/2}]_1$ energies (a.u.) for Ag^{37+}, Xe^{44+}, La^{47+}, and Nd^{50+} with the MCDF calculations and experiments of Ref. [19].

	E_{Coulomb}	E_{Breit}	E_{QED}	E_{Tot}	E_{Exp}	Δ(Theon−Expt)
$Z=47$ Ag^{37+}						
MBPT	122.740	-0.185	-0.010	122.546	-0.005(3)	
MCDF	122.736	-0.192	-0.003	122.542	122.551(3)	-0.009(3)
Diff.	0.004	0.007	-0.007	0.004		
$Z=54$ Xe^{44+}						
MBPT	167.814	-0.315	-0.002	167.499		0.005(6)
MCDF	167.811	-0.323	0.006	167.494	167.494(6)	0.000(6)
Diff.	0.003	0.008	-0.008	0.003		
$Z=57$ La^{47+}						
MBPT	189.121	-0.359	-0.023	188.739		-0.015(8)
MCDF	189.115	-0.370	-0.011	188.735	188.754(8)	-0.019(8)
Diff.	0.006	0.011	-0.012	0.004		
$Z=60$ Nd^{50+}						
MBPT	211.933	-0.418	-0.032	211.483		-0.017(15)
MCDF	211.929	-0.429	-0.018	211.483	211.500(15)	-0.017(15)
Diff.	0.004	0.011	-0.014	0.000		

TABLE IV. Comparison of theoretical and experimental energies for the $[2p_{1/2}^{-1}3d_{3/2}]_1$ state of neonlike ions. Units: a.u.

Z	Theory	Expt.	Theor.−Expt.	Ref.	Z	Theory	Expt.	Theor.−Expt.	Ref.
10	0.7341	0.7401(1)	-0.0060	[20]	26	30.3440	30.353(4)	-0.009	[29,31,32]
11	1.5117	1.5178(1)	-0.0061	[21]	27	33.4222	33.424(6)	-0.002	[31,32]
12	2.4353	2.4429(1)	-0.0076	[22]	28	36.6502	36.652(8)	-0.002	[29,31,32]
13	3.5011	3.5122(1)	-0.0111	[22]	29	40.0293	40.020(9)	0.010	[31,32]
14	4.7111	4.7245(1)	-0.0134	[23]	30	43.5609	43.556(11)	0.005	[31,32]
15	6.0644	6.0789(5)	-0.0145	[24]	31	47.2462	47.250(25)	-0.004	[31]
16	7.5596	7.5735(1)	-0.0139	[25]	32	51.0869	51.091(11)	-0.004	[31,32]
17	9.1960	9.2071(2)	-0.0111	[26]	34	59.2402	59.289(14)	-0.049	[31,32]
18	10.9737	10.984(8)	-0.011	[27]	35	63.5558	63.556(44)	-0.000	[31]
19	12.8929	12.9049(5)	-0.0120	[28]	36	68.0330	68.066(51)	-0.033	[33,34]
20	14.9540	14.9644(5)	-0.0104	[28]	40	87.5894	87.574(17)	0.016	[34,35]
21	17.1576	17.1652(6)	-0.0076	[28]	42	98.3837	98.390(19)	-0.006	[32,34,35]
22	19.5046	19.5082(8)	-0.0036	[28]	47	128.4642	128.467(4)	-0.003	[36]
23	21.9957	21.994(2)	0.001	[28]	54	178.4917	178.505(7)	-0.013	[19]
24	24.6319	24.633(2)	-0.001	[28,29]	70	333.5564	333.526(92)	0.031	[37]
25	27.4143	27.421(2)	-0.007	[30]	79	450.8592	450.577(261)	0.282	[38]

$[2s_{1/2}^{-1}3p_{3/2}]_1$ and $[2s_{1/2}^{-1}3p_{1/2}]_1$ states. We see that, because of the mixing with a state involving a 2s orbital, the Lamb shift corrections for the state $[2s_{1/2}^{-1}3p_{3/2}]_1$ near $Z=68$, where the strongest mixing occurs, are ≈ 0.2 a.u, which is an order of magnitude larger than the corresponding correction for other high-Z cases where no significant mixing occurs (i.e., $Z=80$).

In Fig. 7, we present the correction due to the frequency-dependent Breit interaction. Both the frequency-dependent Breit and Lamb shift corrections were evaluated in a local potential that approximates the $V^{(N-1)}$ (HF) potential. These corrections are also listed in Table I, in columns 9 and 10 respectively, while in column 11 we present the sum of the reduced-mass and mass-polarization corrections. In Table II we show the theoretically estimated energies for the three $[2p^5 3d]_1$ states for the 52 ions considered here.

Comparing with other theories, we start from the semi-empirical calculation of Hibbert, Le Dourneuf, and Mohan based on the configuration-interaction method (CI) [12]. Agreement of the order of 0.005 a.u. is found for the states under consideration where $10 \leqslant Z \leqslant 36$. In comparison to the work of Safronova, Safronova, and Bruch [13], which is based on $1/Z$ expansion, and for the range $18 \leqslant Z \leqslant 42$, the difference from our calculation ranges between 0.002 and 0.03 a.u, while for $Z=54$ it rises to 0.1 a.u. Good agreement is found with the Dirac-Slater calculation of Sampson *et al.* [14]. Our difference from this calculation is between 0.0005 a.u. for $Z=26$ and 0.04 a.u. for $Z=92$. In comparison to the multiconfiguration Dirac-Fock (MCDF) calculations of Cogordan and Lunell [15] that cover the region $20 \leqslant Z \leqslant 54$,

TABLE V. Comparison of theoretical and experimental energies for the $[2p_{3/2}^{-1}3d_{5/2}]_1$ state of neonlike ions. Units: a.u.

Z	Theory	Expt.	Theor.−Expt.	Ref.	Z	Theory	Expt.	Theor.−Expt.	Ref.
10	0.7306	0.7365(1)	-0.0059	[20]	27	32.8608	32.865(6)	-0.005	[31,32]
11	1.5045	1.5115(1)	-0.0070	[21]	28	36.0077	36.006(7)	0.002	[29,31,32]
12	2.4255	2.4340(1)	-0.0085	[22]	29	39.2948	39.292(9)	0.003	[31,32]
13	3.4878	3.4944(1)	-0.0066	[22]	30	42.7222	42.729(11)	-0.007	[31,32]
14	4.6858	4.6903(1)	-0.0045	[23]	31	46.2898	46.295(24)	-0.005	[31]
15	6.0196	6.0236(5)	-0.0040	[24]	32	49.9976	50.014(10)	-0.016	[31,32]
16	7.4903	7.4933(1)	-0.0030	[25]	34	57.8345	57.864(14)	-0.029	[31,32]
17	9.0989	9.0992(2)	-0.0003	[26]	35	61.9637	61.983(42)	-0.019	[31]
18	10.8462	10.843(8)	0.003	[27]	36	66.2337	66.245(48)	-0.011	[33,34]
19	12.7325	12.7345(5)	-0.0020	[28]	40	84.7224	84.713(15)	0.009	[34,35]
20	14.7584	14.7612(5)	-0.0028	[28]	42	94.8167	94.839(17)	-0.022	[32,34,35]
21	16.9240	16.9255(6)	-0.0015	[28]	47	122.5459	122.551(4)	-0.005	[36]
22	19.2296	19.2267(8)	0.0029	[28]	54	167.4993	167.494(6)	0.005	[19]
23	21.6754	21.6783(10)	-0.0029	[28]	57	188.7392	188.754(8)	-0.015	[19]
24	24.2614	24.2592(12)	0.0022	[28,29]	60	211.4833	211.500(15)	-0.016	[19]
25	26.9876	26.9893(16)	-0.0017	[30]	79	386.8530	386.592(200)	0.261	[38]
26	29.8541	29.8516(38)	0.0025	[29,31,32]	83	430.8911	430.783(64)	0.108	[39]

TABLE VI. Comparison of theoretical and experimental energies for the $[2p_{3/2}^{-1}3d_{3/2}]_1$ state of neonlike ions. Units: a.u.

Z	Theory	Exp.	Theor.−Expt.	Ref.	Z	Theory	Expt.	Theor.−Expt.	Ref.
10	0.7303	0.7360(1)	-0.0057	[20]	25	26.6501	26.653(2)	-0.003	[30]
11	1.5017	1.5065(1)	-0.0048	[21]	26	29.4820	29.492(5)	-0.010	[29,31,32]
12	2.4120	2.4168(1)	-0.0048	[22]	27	32.4529	32.455(6)	-0.002	[31,32]
13	3.4566	3.4610(1)	-0.0044	[22]	28	35.5628	35.569(7)	-0.006	[29,31,32]
14	4.6353	4.6394(1)	-0.0041	[23]	29	38.8117	38.821(9)	-0.009	[31,32]
15	5.9490	5.9536(5)	-0.0046	[24]	30	42.1999	42.206(10)	-0.006	[31,32]
16	7.3988	7.4030(1)	-0.0042	[25]	31	45.7272	45.742(23)	-0.015	[31]
17	8.9855	8.9869(2)	-0.0014	[26]	32	49.3939	49.409(10)	-0.015	[31,32]
18	10.7097	10.7057(25)	0.0040	[27]	34	57.1454	57.188(14)	-0.043	[31,32]
19	12.5717	12.5764(5)	-0.0047	[28]	35	61.2304	61.274(41)	-0.044	[31]
20	14.5718	14.5771(5)	-0.0053	[28]	36	65.4551	65.472(5)	-0.017	[33,34]
21	16.7103	16.7144(6)	-0.0041	[28]	40	83.7521	83.894(15)	-0.142	[34,35]
22	18.9872	18.9919(8)	-0.0047	[28]	42	93.7406	93.914(19)	-0.173	[32,34,35]
23	21.4027	21.3973(50)	0.0054	[40]	47	121.1692	121.186(3)	-0.016	[36]
24	23.9570	23.9618(13)	-0.0048	[30,29]	79	380.8596	380.646(191)	0.214	[38]

we agree at the level of 0.01 a.u.. Especially for $30 \leqslant Z \leqslant 48$, we have excellent agreement on the order of 0.002 a.u.. The difference with the relativistic configuration-interaction calculations of Kagawa, Honda, and Kiyokawa [16] ranges between 0.05 and 0.1 a.u. for $18 \leqslant Z \leqslant 42$. In comparison with the CI calculations of Biémont and Hansen [17], we differ by 0.001–0.05 a.u. over their range of values $19 \leqslant Z \leqslant 34$. Relative to the calculation of Zhang *et al.* [18], we find differences starting from order of 0.003 a.u. for Z around 18, and rising to the order of 0.2 a.u for Z around 54. For $Z=70$ and 74, we differ by 1.5 a.u. A detailed comparison with the above-mentioned theories is presented in Fig. 8.

Finally, for high Z, we compare our values with the MCDF calculations of Ref. [19]. Individual comparisons for the electrostatic Coulomb, Breit and QED contributions are shown in Table III. We see that the Coulomb corrections differ by less than 0.006 a.u. As for the QED corrections, they differ by 0.010 a.u., while the Breit corrections differ by the same amount but by different sign. Because of the near cancellation of Breit and QED corrections and the relative insignificance of electrostatic correlations at these high Z, the two calculations practically agree within the experimental error.

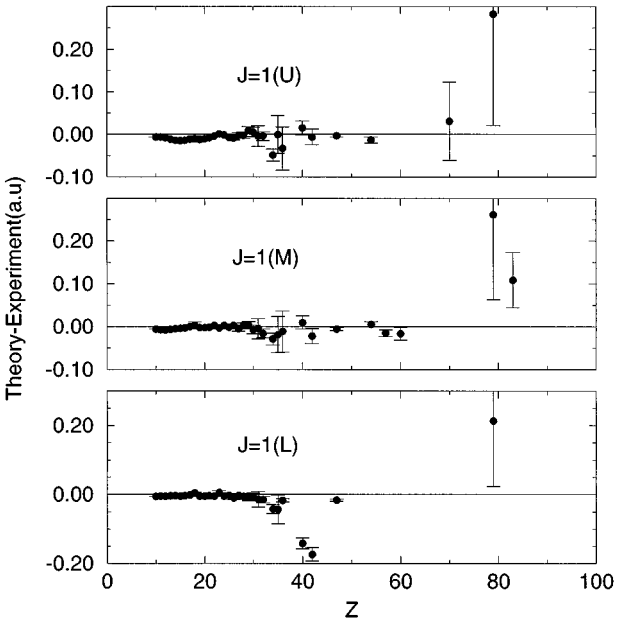

FIG. 9. Differences between theoretical and experimental energies for the $[2p^{-1}3d]_1$ states of neonlike ions.

A detailed comparison between theory and experiment for the three states under consideration is presented in Tables IV–VI, while in Fig. 9 we plot the differences between theory and experiment along with the estimated error bars. For the quoted experimental values we took the weighted average whenever we had more than one references for the same ion. Experimental energies are almost always smaller than the theoretical ones except for $Z \geqslant 70$. The difference between theory and experiment starts from 0.005 a.u in the beginning of the isoelectronic sequence, drops to ≈ 0.002 a.u. for medium Z (i.e, $20 \leqslant Z \leqslant 40$), and remains at ≈ 0.01 a.u. for the rest of the sequence up to $Z=60$. We do not have an explanation for the large discrepancy with the experimental values at $Z=40$ and 42 of the $[2p_{3/2}^{-1}3d_{3/2}]_1$ state.

Very few experimental values exist for $Z>60$, all of them quoted with large error bars of order 0.1 a.u. Our approximate treatment of the QED corrections might well account for this discrepancy.

ACKNOWLEDGMENTS

We would like to acknowledge useful conversations with Professor W. Johnson and Profesor J. Sapirstein. We also like to thank Professor E. Livingston for helpful discussions over the evaluation of the experimental results. This research was supported in part by NSF Grant No. PHY-92-04089.

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