Relativistic configuration-interaction calculations for the ground state and $n = 2$ singlet states of heliumlike ions

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(Received 23 December 1993)

Term energies are determined for the ground state and $n = 2$ singlet states of heliumlike ions with nuclear charges in the range $4 \leq Z \leq 92$. These calculations are based on the relativistic no-pair Hamiltonian which includes both the Coulomb interaction and the retarded Breit interaction. Single-particle wave functions are expanded in a B-spline basis constructed from Dirac-Coulomb orbitals restricted to a finite cavity. The Hamiltonian matrix is evaluated and Davidson's method is used to determine the lowest few eigenenergies and eigenfunctions for each angular symmetry. Quantum electrodynamic corrections are also calculated. We find good, but not precise, agreement between theory and experiment for the $K\alpha$ x-ray energies. It is argued that high-precision x-ray measurements for highly charged ions are needed to further test the theory.

PACS number(s): 31.10.+z, 31.20.Tz, 31.30.Jv

I. INTRODUCTION

Energy levels of two-electron ions have been the subject of intense investigation during the past two decades. Accad, Pekeris, and Schiff [1] carried out important benchmark calculations including relativistic, quantum electrodynamic (QED), and recoil corrections for the low-lying states of light heliumlike ions using variational techniques. Drake [2] performed extensive calculations of the term values for the $n = 1$ and 2 states of heliumlike ions in the range $Z = 2$–100 by combining variational methods and the relativistic $1/Z$ expansion approach. Drake's unified method accounts for electron correlations precisely at low Z and includes the dominant relativistic, QED, and recoil corrections. Drake estimates that the term values in the unified method are in error by $\pm 0.2\,\alpha^4 Z^4$ a.u. due to the neglect of higher-order relativistic and QED corrections. Discrepancies with the unified method were found by Johnson and Sapirstein using relativistic many-body perturbation theory (MBPT) for $Z = 10$–36 [3]. In fact, differences between the unified method and the relativistic MBPT energies for the $2\,^3P_0$ states were found to be two to three times higher than Drake's estimate. Similar differences with the unified method have also been found for the experimentally measured $2\,^3P_0$-$2\,^3S_1$ energy intervals [4,5] and for the $2\,^3P_0$-$2\,^3P_1$ fine structure splittings [6,7].

Recently, we have developed a large-scale relativistic configuration-interaction (CI) code for two-electron ions [8]. This code is based on the relativistic no-pair Hamiltonian and makes use of finite basis sets constructed from B splines [9]. This CI code was used to calculate the energy levels of the $n = 2$ triplet states of heliumlike ions for $Z = 5$–100 [8]. These calculations produced term energies in precise agreement with experiment throughout the periodic table. Furthermore, our results are in very good agreement with MBPT [3] and show systematic discrepancies with the unified method.

In this paper, we report relativistic CI calculations for the ground state and $n = 2$ singlet states of heliumlike ions. These calculations were undertaken to provide accurate term energies of the singlet states of highly-charged heliumlike ions and to shed light on possible systematic discrepancies between theory and experiment for the $K\alpha$ x-ray energies noted by Beiersdorfer *et al.* [10]. As in Ref. [8], our calculations are based on the no-pair Hamiltonian from QED [11–13]. Two-electron basis functions with fixed angular momentum J and parity π are constructed from products of one-electron orbitals. The one-electron orbitals are approximate solutions of the Dirac equation for an electron in a Coulomb field constrained to a finite cavity [9]. The resulting single-particle spectrum separates cleanly into positive- and negative-energy branches. The one-electron basis functions used in our work contain only positive-energy states as required by the presence of positive-energy projection operators in the no-pair Hamiltonian. The B-spline functions form a complete basis set for functions that can be approximated by piecewise polynomials of a fixed degree. As a result, correlation energy contributions from both bound and continuum states are automatically included in our CI calculations.

The Hamiltonian matrix is evaluated in the two-electron basis and the variational principle is applied to determine the eigenvalues and eigenvectors. The resulting Hamiltonian matrix is dense. In this work, the number of configurations used ranges from a few hundred to well over eight thousand. We use Davidson's method [14,15] to obtain the first few solutions to these large eigenvalue problems. The evaluation of the Hamiltonian

matrix is computer intensive. Although we have developed efficient algorithms to calculate angular momentum recoupling coefficients and Coulomb and Breit integrals, ten to twenty hours of CRAY-YMP supercomputer time are still needed for each of the heliumlike ions considered here. The evaluation of the retarded magnetic interaction is particularly time consuming and its convergence as a function of the highest angular momentum state is rather slow for the $1\,^1S_0$ ground state. Considerably more effort is spent in calculating the retarded Breit energies for the singlet states than for the triplet states.

We have also calculated QED corrections using the method described in Ref. [16]. Contributions from mass-polarization effect are taken from Drake [2]. Our term energies from the no-pair Hamiltonian are in very good agreement with the relativistic all-order many-body calculations of Plante, Johnson, and Sapirstein [17] throughout the isoelectronic sequence. For low-Z ions, the present results are in good, but not precise, agreement with Drake's unified method [2]. Deviations increase as Z increases. They come partly from no-pair energies and partly from QED corrections.

For the $K\alpha$ x-ray energies, our results agree slightly better with the multiconfiguration Dirac-Fock (MCDF) predictions [18,19] and with experiment than the unified method does. However, for Ge^{30+} and Kr^{34+}, all theoretical results lie slightly outside experimental uncertainties. As differences in correlation energies between various calculations are small compared to those between theory and experiment in this Z range, we believe that residual discrepancies with experiment, if they can be verified, must arise from uncalculated higher-order QED corrections.

II. THEORETICAL METHOD

Details of our relativistic CI method are given in Ref. [8]. Here, we only outline the essential features. Briefly, the no-pair Hamiltonian is given in second-quantized form as

$$H = \sum_i \epsilon_i a_i^\dagger a_i + \frac{1}{2}\sum_{ijk\ell}(g_{ijk\ell} + b_{ijk\ell})\, a_i^\dagger a_j^\dagger a_\ell a_k \ , \qquad (1)$$

where ϵ_i is the ith energy eigenvalues of the single-particle Dirac equation for an electron in the Coulomb field of the nucleus and where $g_{ijk\ell}$ and $b_{ijk\ell}$ are two-particle matrix elements of the Coulomb and Breit interactions, respectively. The operators a_i and $a_i^\dagger$ are the annihilation and creation operators for an electron with quantum numbers $i = (n_i, \kappa_i, m_i)$, where n_i is the principal quantum number, κ_i is the relativistic angular quantum number related to the orbital angular momentum ℓ_i and total angular momentum j_i by $\kappa_i = (\ell_i - j_i)(2j_i + 1)$, and m_i is the projection quantum number of the total angular momentum. Nuclear finite-size corrections are taken into account by using a Fermi charge distribution with parameters given by Johnson and Soff [20].

We expand the atomic state function Ψ_{JM} in terms of two-electron configuration state functions ϕ_I as

$$\Psi_{JM} = \sum_I C_I \phi_I \ . \qquad (2)$$

Here, a single index I denotes the configuration state function $\phi_I = \phi(ij)$ with $i \le j$, and C_I are the expansion coefficients. The expectation value of the Hamiltonian is then given by

$$\langle \Psi_{JM}|H|\Psi_{JM}\rangle = \sum_I E_I C_I^2 + \sum_{I,K} C_I C_K V_{IK} \ . \qquad (3)$$

In Eq. (3), the single-particle energy E_I is given by $E_I = \epsilon_i + \epsilon_j$ for the configuration $I = (ij)$. The potential energy matrix element V_{IK} including Coulomb and retarded Breit interactions for the configurations $I = (ij)$ and $K = (k\ell)$ is defined in Ref. [8].

Applying the variational principle to the functional constructed from the Hamiltonian matrix and the wavefunction normalization condition with respect to the expansion coefficients leads to the CI equation

$$\sum_K (E_I \delta_{IK} + V_{IK}) C_K = \lambda C_I \ . \qquad (4)$$

Here, the eigenvalues λ are energies of various atomic states and the eigenvectors C_I are corresponding expansion coefficients.

III. NUMERICAL CALCULATIONS

The B-spline basis functions for a Dirac electron in a Coulomb field constrained to a cavity of finite radius were obtained using the method by Johnson, Blundell, and Sapirstein [9]. The radius of the cavity was chosen so that the first few s and p states agree precisely with the actual Dirac-Coulomb eigenvalues. A radius of 8 a.u. was used for orbitals with $\ell \le 3$ for Ne^{8+} and the radius was gradually increased to 16 a.u. for $\ell = 8$ orbitals. A $1/Z$ scaling rule was used to determine the cavity radius for other ions. The choice of the cavity radius is not critical.

In this work, 40 positive-energy B-spline orbitals are generated for each of the $s, p, d, \ldots$, states inside the cavity. For the $^1S_0$ states, we included orbitals with $\ell = 0$–8 in our calculations. For $Z \le 10$, we used 25 orbitals from a complete set of 40 B-spline basis functions for each of the angular symmetries in our CI expansion. For higher-Z ions where correlation corrections are less important, a smaller basis set consisting of 25 s, 24 p, 23 d, ..., 22 l orbitals was used to reduce the computational effort. There are many more configurations for the $^1P_1$ state than for the $^1S_0$ state and so the basis set is further reduced to 23 s, 22 p, 21 d, ..., 20 i orbitals. As in Ref. [8], the use of these truncated B-spline basis sets was found to have negligible effect on the accuracy of our calculations. Much larger basis sets are used here as compared to Ref. [8], where we included only orbitals with $\ell \le 5$. These larger basis sets are required because of the slow convergence of the partial wave sequences for singlet states. Once the Hamiltonian matrix is set up,

Davidson's method permits us to solve the large eigenvalue problem, which for the $2\,^1P_1$ state contains more than 8000 configurations, in a relatively short time.

As in our previous work on the $n = 2$ triplet states, the full frequency-dependent magnetic and retardation corrections were calculated using a two-step approach. First, the off-diagonal Hamiltonian matrix was calculated with the unretarded Breit operator while the diagonal matrix was evaluated with the retarded Breit operator to obtain the leading frequency-dependent Breit energies. Next, the corrections $\Delta B(\omega)$ from the off-diagonal matrix elements of the retarded Breit interaction were obtained by repeating the CI calculation described above with a smaller set of B-spline orbitals and subtracting this result from a similar calculation with the full, frequency-symmetrized Breit operator [13]. For the $^1P_1$ states, we include up to the f orbitals in calculating the $\Delta B(\omega)$ corrections. For the $^1S_0$ states, we have to include states with angular momentum up to $\ell = 7$ because of the slow convergence of the Breit interaction, which decreases as $1/\ell^2$ asymptotically.

For the $n = 2$ to 1 transitions, QED corrections are significant. Drake carried out two-electron QED calculations in his unified method [2] based on works of Araki [21], Sucher [22], and Kabir and Salpeter [23] and included all the known one- and two-electron terms. In the MCDF calculations by Indelicato and co-workers [18,19], the self-energy was estimated by the Welton method [24]. In the present work, self-energy corrections for the highly-charged ions are calculated using the scheme of Cheng, Johnson, and Sapirstein [16] based on a method by Brown, Langer, and Schafer [25]. The effects of screening and relaxation on the self-energy are included by using appropriate Dirac-Slater (DS) potentials for different low-lying states in calculating one-electron self-energies. Thus, for example, the self-energy corrections for $1s2s$ states would be calculated as the sum of the $1s$ and $2s$ one-electron self-energies in a $1s2s$ DS potential, whereas the ground state correction would be calculated in the $1s^2$ DS potential. Nuclear finite-size effects on the self-energy are also included by using a uniformly charged sphere nuclear model in the DS potential. The one-electron vacuum polarizations and higher-order QED corrections are taken from the tabulation by Johnson and Soff [20]. Their sum is then adjusted by a screening factor taken as the ratio of the expectation values of the Uehling potential between the Dirac-Fock and the corresponding hydrogenic results calculated using Grant's MCDF code [26]. Total QED corrections are given by the sum of the calculated single-particle self-energies and the adjusted vacuum polarization and higher-order QED contributions, weighted by the fractional occupation number of each orbital as obtained from the eigenvectors of the CI calculation. We include QED corrections from the $1s, 2s$, and $2p$ orbitals only, as contributions from higher-n orbitals are found to be quite negligible. Details of our QED calculations will be published elsewhere.

IV. RESULTS AND DISCUSSION

Typical results of the Coulomb and Breit energies for O^{6+} as functions of the angular momentum of orbitals included in the calculation are listed in Table I. In the first two columns, the orbitals and number of configurations included up to the indicated angular momentum are listed. In the third to fifth columns of the first row, we list under E_C, E_B, and $E_{\text{no-pair}}$ the Coulomb, Breit, and no-pair energies, respectively, obtained by using $nsn's$ basis states. The contribution E_C is found by restricting the interaction to the Coulomb interaction and $E_{\text{no-pair}}$ is the value from the full no-pair Hamiltonian. The contribution E_B is the difference between the latter two terms. From a perturbation theory point of view, E_B contains contributions not only from the usual first-order Breit corrections but also from higher-order Breit-Breit and Coulomb-Breit interactions.

In the second to the ninth row, we list the increments of the Coulomb, Breit, and no-pair energies obtained by successively adding more angular momentum states.

TABLE I. Contributions to the ionization energy (a.u.) of the ground state of heliumlike oxygen, $Z = 8$. E_C is the Coulomb energy, E_B is the Breit energy, and $E_{\text{no-pair}}$ is the energy from the no-pair Hamiltonian. The values listed in the second through ninth rows are the increments obtained on adding successive configurations. The second column lists the number of configuration state functions included up to the indicated orbital symmetry.

Configuration	No. of configurations	E_C	E_B	$E_{\text{no-pair}}$
ss	325	-27.147405	0.005825	-27.141580
pp	975	-0.025393	-0.000460	-0.025853
dd	1625	-0.003454	-0.000098	-0.003552
ff	2275	-0.000922	-0.000043	-0.000965
gg	2925	-0.000340	-0.000024	-0.000364
hh	3575	-0.000152	-0.000015	-0.000167
ii	4225	-0.000078	-0.000010	-0.000088
kk	4875	-0.000043	-0.000007	-0.000050
ll	5525	-0.000026	-0.000005	-0.000031
Tail		-0.000060(3)	-0.000029(4)	-0.000089(5)
Total		-27.177873(3)	0.005134(4)	-27.172739(5)

TABLE II. Coulomb and Breit contributions to the ionization energies (a.u.) of the ground and $n = 2$ singlet states of heliumlike ions are given, together with frequency-dependent Breit corrections $\Delta B(\omega)$, mass-polarization corrections MP [2], and QED corrections.

Z	State	Coulomb	Breit	$\Delta B(\omega)$	MP	QED	Total
4	$1\,^1S_0$	-5.656547	0.000468	-0.000001	0.000026	0.000089	-5.655965
	$2\,^1S_0$	-1.1850941	0.0000678	-0.0000001	0.0000021	-0.0000039	-1.1850282
	$2\,^1P_1$	-1.1108574	-0.0000212	0.0000000	0.0000378	-0.0000348	-1.1108756
	$2\,^3P_1$	-1.1751078	0.0000595	0.0000000	-0.0000430	-0.0000289	-1.1751202
6	$1\,^1S_0$	-14.412373	0.001955	-0.000004	0.000031	0.000542	-14.409849
	$2\,^1S_0$	-3.2235592	0.0003204	-0.0000010	0.0000027	0.0000267	-3.2232104
	$2\,^1P_1$	-3.0939876	-0.0000857	0.0000001	0.0000843	-0.0000891	-3.0940780
	$2\,^3P_1$	-3.2227454	0.0002562	-0.0000001	-0.0000905	-0.0000795	-3.2226593
8	$1\,^1S_0$	-27.177873	0.005134	-0.000016	0.000033	0.001739	-27.170983
	$2\,^1S_0$	-6.2644199	0.0008874	-0.0000033	0.0000028	0.0001365	-6.2633965
	$2\,^1P_1$	-6.0772025	-0.0002114	0.0000003	0.0001267	-0.0001730	-6.0774599
	$2\,^3P_1$	-6.2733594	0.0006735	-0.0000006	-0.0001330	-0.0001628	-6.2729823
10	$1\,^1S_0$	-43.961648	0.010657	-0.000032	0.000033	0.004122	-43.946868
	$2\,^1S_0$	-10.310427	0.001898	-0.000006	0.000003	0.000383	-10.308149
	$2\,^1P_1$	-10.062286	-0.000405	0.000001	0.000169	-0.000288	-10.062809
	$2\,^3P_1$	-10.328201	0.001384	-0.000002	-0.000175	-0.000283	-10.327277
14	$1\,^1S_0$	-89.631016	0.031334	-0.000099	0.000034	0.014435	-89.585312
	$2\,^1S_0$	-21.432270	0.005768	-0.000019	0.000003	0.001560	-21.424958
	$2\,^1P_1$	-21.044501	-0.000936	0.000007	0.000253	-0.000613	-21.045790
	$2\,^3P_1$	-21.461025	0.003890	-0.000010	-0.000259	-0.000655	-21.458059
18	$1\,^1S_0$	-151.54093	0.06926	-0.00020	0.00003	0.03571	-151.43613
	$2\,^1S_0$	-36.625924	0.012982	-0.000038	0.000003	0.004146	-36.608831
	$2\,^1P_1$	-36.053818	-0.001247	0.000025	0.000297	-0.001041	-36.055784
	$2\,^3P_1$	-36.651675	0.007870	-0.000034	-0.000302	-0.001233	-36.645374
22	$1\,^1S_0$	-229.85580	0.12970	-0.00044	0.00003	0.07245	-229.65405
	$2\,^1S_0$	-55.941848	0.024610	-0.000083	0.000003	0.008812	-55.908506
	$2\,^1P_1$	-55.102216	-0.000273	0.000063	0.000357	-0.001514	-55.103583
	$2\,^3P_1$	-55.948091	0.012781	-0.000083	-0.000362	-0.002057	-55.937812
24	$1\,^1S_0$	-275.22905	0.17009	-0.00057	0.00003	0.09810	-274.96140
	$2\,^1S_0$	-67.165363	0.032431	-0.000108	0.000003	0.012152	-67.120885
	$2\,^1P_1$	-66.144038	0.001169	0.000090	0.000378	-0.001741	-66.144142
	$2\,^3P_1$	-67.156365	0.015280	-0.000118	-0.000384	-0.002571	-67.144158
26	$1\,^1S_0$	-324.78620	0.21813	-0.00088	0.00003	0.12939	-324.43952
	$2\,^1S_0$	-79.444960	0.041771	-0.000168	0.000003	0.016294	-79.387060
	$2\,^1P_1$	-78.198991	0.003480	0.000120	0.000393	-0.001944	-78.196942
	$2\,^3P_1$	-79.417990	0.017655	-0.000159	-0.000399	-0.003157	-79.404050
32	$1\,^1S_0$	-498.91779	0.41566	-0.00150	0.00003	0.26335	-498.24025
	$2\,^1S_0$	-122.73079	0.08050	-0.00029	0.00000	0.03458	-122.61601
	$2\,^1P_1$	-120.45536	0.01678	0.00022	0.00038	-0.00226	-120.44023
	$2\,^3P_1$	-122.64093	0.02362	-0.00031	-0.00039	-0.00532	-122.62332
36	$1\,^1S_0$	-636.63910	0.59905	-0.00231	0.00003	0.39243	-635.64991
	$2\,^1S_0$	-157.09004	0.11678	-0.00046	0.00000	0.05279	-156.92092
	$2\,^1P_1$	-153.72059	0.03141	0.00027	0.00037	-0.00204	-153.69057
	$2\,^3P_1$	-156.95589	0.02683	-0.00041	-0.00038	-0.00703	-156.93688
44	$1\,^1S_0$	-965.84261	1.11783	-0.00413	0.00003	0.77028	-963.95859
	$2\,^1S_0$	-239.58755	0.22066	-0.00085	0.00000	0.10835	-239.25937
	$2\,^1P_1$	-232.57025	0.07542	0.00033	0.00037	0.00039	-232.49375
	$2\,^3P_1$	-239.36587	0.03283	-0.00066	-0.00037	-0.01065	-239.34472

TABLE II. *(Continued).*

Z	State	Coulomb	Breit	$\Delta B(\omega)$	MP	QED	Total
54	$1\,^1S_0$	-1483.6398	2.1210	-0.0093	0.0000	1.5275	-1480.0006
	$2\,^1S_0$	-370.26864	0.42550	-0.00186	0.00000	0.22632	-369.61868
	$2\,^1P_1$	-354.51341	0.16155	0.00020	0.00037	0.01017	-354.34112
	$2\,^3P_1$	-369.93985	0.04169	-0.00089	-0.00038	-0.01367	-369.91310
64	$1\,^1S_0$	-2129.9058	3.6309	-0.0157	0.0000	2.6989	-2123.5916
	$2\,^1S_0$	-534.84762	0.74164	-0.00321	0.00000	0.42163	-533.68756
	$2\,^1P_1$	-502.93046	0.28906	-0.00025	0.00040	0.03333	-502.60791
	$2\,^3P_1$	-534.41785	0.05254	-0.00108	-0.00040	-0.00916	-534.37596
80	$1\,^1S_0$	-3472.3394	7.4795	-0.0271	0.0000	5.7982	-3459.0888
	$2\,^1S_0$	-881.87825	1.58226	-0.00576	0.00001	0.99021	-879.31154
	$2\,^1P_1$	-797.15100	0.59928	-0.00202	0.00046	0.12184	-796.43145
	$2\,^3P_1$	-881.40670	0.07170	-0.00120	-0.00046	0.04685	-881.28981
92	$1\,^1S_0$	-4783.2993	11.9683	-0.0365	0.0000	9.5107	-4761.8567
	$2\,^1S_0$	-1227.7330	2.6185	-0.0081	0.0000	1.7486	-1223.3740
	$2\,^1P_1$	-1065.4797	0.9336	-0.0045	0.0005	0.2577	-1064.2924
	$2\,^3P_1$	-1227.7708	0.0802	-0.0010	-0.0005	0.1901	-1227.5020

These tabulated values are extrapolated to infinity by assuming that the increments decrease as $a(\ell + 1/2)^{-k} + b(\ell + 1/2)^{-k-1}$, where $k = 4$ for E_C and $k = 2$ for E_B. Comparing with the $n = 2$ triplet states where $k = 6$ and 4 for E_C and E_B [8], respectively, it is clear that the convergence of the Coulomb and Breit energies as functions of ℓ are substantially slower for the singlet states than for the triplet states. Results of the extrapolated tails, including estimated extrapolation errors, are listed in the tenth row. The final Coulomb, Breit, and no-pair energies, including the extrapolated values, are listed in the last row of the table. The computational procedure described above was applied to all ions covered in this study.

In Table II, we present the ionization energies of the ground and $n = 2$ singlet states for sixteen heliumlike ions with Z in the range $4 \leq Z \leq 92$. Data for the $1s2p\,^3P_1$ state, which decays to the $1s^2\,^1S_0$ ground state as the $K\alpha_2$ line, are also included. The values of mass-polarization corrections are taken from Drake [2]. For $Z \geq 18$, we use the calculated QED corrections described above. For $Z < 18$, the accuracy of our QED results is affected by severe numerical cancellations in our method for calculating electron self-energies. In this Z range, we subtract our QED results from those of Drake [2] and extrapolate the difference to low-Z ions. We then use Drake's QED values, corrected for the extrapolated difference, for ions with $Z < 18$.

In general, our QED corrections are smaller than those given by Drake. This difference is, in part, due to the way in which the QED corrections are calculated, and, for singlet states, to a difference in the definition of the QED corrections. As pointed out by Blundell *et al.* [27], singlet state energies calculated using the no-pair Hamiltonian contain $(\alpha Z)^3$ terms from perturbation theory which are given by

$$\Delta E[(\alpha Z)^3] = \left(\frac{19}{3} - \frac{\pi}{2}\right) \langle \delta^3(\mathbf{r}_{12}) \rangle \,, \tag{5}$$

where

$$\langle \delta^3(\mathbf{r}_{12}) \rangle = \begin{pmatrix} 1/8\pi \\ 6/243\pi \\ 2/243\pi \end{pmatrix} \times (\alpha Z)^3 \quad \text{for} \quad \begin{pmatrix} 1\,^1S_0 \\ 2\,^1S_0 \\ 2\,^1P_1 \end{pmatrix} . \tag{6}$$

For triplet states, $\langle \delta^3(\mathbf{r}_{12}) \rangle = 0$, and there are no corresponding $(\alpha Z)^3$ terms. In Ref. [2], Drake includes these $(\alpha Z)^3$ terms with his QED contributions. As these terms actually come from the no-pair Hamiltonian, they show up in our CI energies but not in our QED corrections. In subsequent comparisons with Drake's results, these terms are subtracted from his QED data and added to his correlation energies. This does not affect Drake's total and transition energy results, but gives more appropriate QED and correlation energy comparisons between our two calculations.

In Figs. 1–4, correlation energies from the present work are compared with those from the unified method [2] and the all-order theory [17] for the $1\,^1S_0$, $2\,^1S_0$, $2\,^1P_1$, and $2\,^3P_1$ states, respectively. Here, comparing correlation energies is the same as comparing term energies without QED corrections. Also shown are differences between the present results and those of Drake's on QED corrections. [Plante *et al.* [17] use Drake's QED data, corrected for the $(\alpha Z)^3$ terms for the singlet states, in their all-order calculations.] In general, correlation energies from our CI calculations are in very good agreement with those from the all-order theory. Small discrepancies arise mainly from the off-diagonal frequency-dependent Breit corrections, $\Delta B(\omega)$, which are included in this work but not in Ref. [17]. Drake's correlation energies are in good agreement with our present results for the $^{1,3}P_1$ states, but are much higher than our CI values for the two $^1S_0$ states.

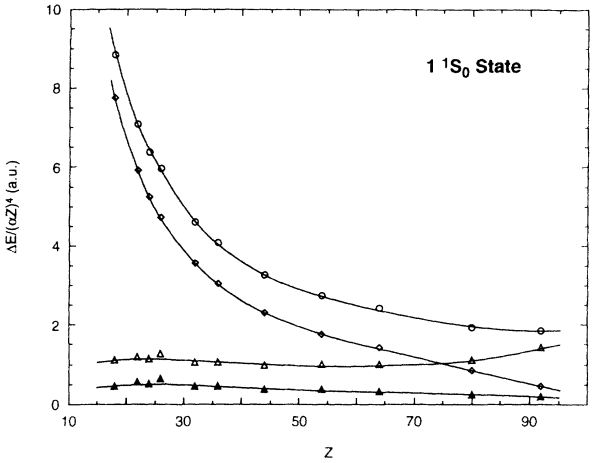

FIG. 1. The $1\,^1S_0$ term energies (a.u.) relative to the present results scaled by $(\alpha Z)^4$ as functions of the atomic number. Open diamonds are Drake's QED corrections. Open circles and open triangles are Drake's term energies with and without QED corrections, respectively. Solid triangles are term energies without QED corrections from the all-order theory.

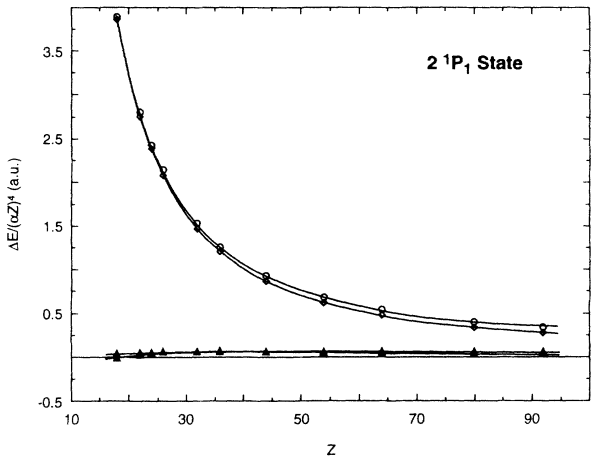

FIG. 3. The $2\,^1P_1$ term energies (a.u.) relative to the present results scaled by $(\alpha Z)^4$ as functions of the atomic number. Symbols are the same as in Fig. 1.

At $Z = 36$, CI correlation energies differ from Drake's by $\lambda\alpha^4Z^4$ a.u., where $\lambda = 1$, 0.5, 0.05, and 0.15 for the $1\,^1S_0$, $2\,^1S_0$, $2\,^1P_1$, and $2\,^3P_1$ states, respectively. These differences are largely due to the neglect of higher-order relativistic corrections in Drake's calculations which are dominated by the leading α^4Z^4 term.

Differences in correlation energies between the present work and the unified method are, however, small compared to differences in QED corrections between the two calculations. Exceptions are the two $^1S_0$ states at very high Z, where differences in correlations energies, which scale like $(\alpha Z)^4$, overtake differences in QED corrections, which scale like $(\alpha Z)^{2.5}$. Drake's QED corrections are consistently larger than the present results. For the ground state at $Z = 18$, 36, 54, and 92, our QED corrections are smaller than Drake's values by 0.063, 0.39, 1.15, and 2.45 eV, respectively, while our correlation energies are smaller than his values by 0.009, 0.14, 0.66, and 7.79 eV, respectively. At the same time, discrepancies on correlation energies between our CI and the all-order theory are smaller at 0.004, 0.06, 0.24, and 0.97 eV, respectively.

The calculations described above are used to give the $K\alpha_1$ and $K\alpha_2$ x-ray energies presented in Tables III and IV, respectively. These x-ray energies are compared with results from the unified method [2], from the all-order theory [17], from MCDF [18,19], and from experiment. For low-Z ions, the present CI values differ from the unified method by less than 0.001 eV. As Z increases, the differences become much more pronounced. For example, at $Z = 92$, the CI value for $K\alpha_1$ energy is larger than the unified model by 8.4 eV, which is about 83 ppm of the $K\alpha_1$ energy. The size of the discrepancy may be observable using modern spectroscopic techniques.

In Table V, theoretical contributions to $K\alpha$ x-ray energies from electron correlation and QED corrections rel-

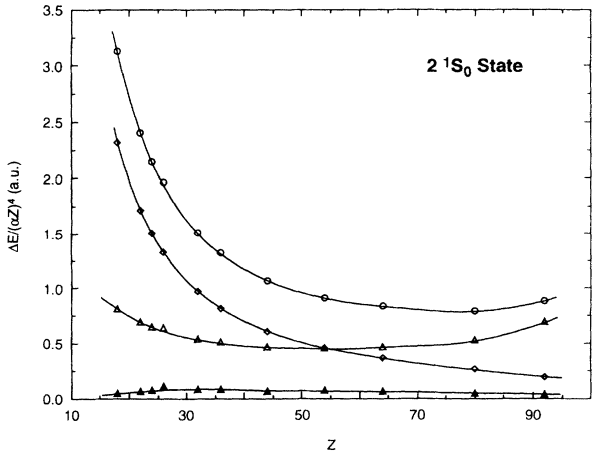

FIG. 2. The $2\,^1S_0$ term energies (a.u.) relative to the present results scaled by $(\alpha Z)^4$ as functions of the atomic number. Symbols are the same as in Fig. 1.

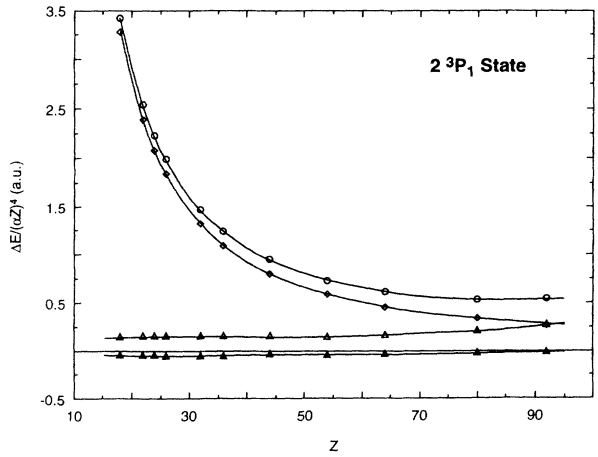

FIG. 4. The $2\,^3P_1$ term energies (a.u.) relative to the present results scaled by $(\alpha Z)^4$ as functions of the atomic number. Symbols are the same as in Fig. 1.

TABLE III. Theoretical and experimental $K\alpha_1$ x-ray energies (eV) for heliumlike ions.

Z	Present work	Drake[a]	All-order[b]	MCDF[c]	Experiment	Reference
4	123.6707	123.6704				
6	307.9038	307.9026				
8	573.9645	573.9612	573.9616			
10	922.0072	922.0006	922.0009			
14	1865.020	1865.000	1865.002			
18	3139.617	3139.577	3139.582	3139.649	3139.55 (0.04)	[28]
					3139.57 (0.25)	[29]
22	4749.708	4749.630	4749.641		4749.74 (0.17)	[10]
24	5682.149	5682.048	5682.064		5682.32 (0.40)	[10]
26	6700.539	6700.404	6700.427	6700.603	6700.73 (0.20)	[10]
					6700.90 (0.25)	[30]
32	10280.39	10280.14	10280.19		10280.70 (0.22)	[31]
36	13114.70	13114.34	13114.42	13114.80	13115.31 (0.30)	[32]
44	19904.07	19903.40	19903.57			
54	30630.64	30629.28	30629.68	30630.76	30629.1 (3.5)	[33]
64	44109.08	44106.64	44107.49			
80	72454.43	72449.62	72452.26			
92	100615.7	100607.3	100614.0		100626 (35)	[34]

[a]Drake, Ref. [2].
[b]Plante *et al.*, Ref. [17].
[c]Indelicato *et al.*, Ref. [18].

ative to results of the present work are shown for selected ions. For the unified method, discrepancies with our results are dominated by differences in QED corrections at low Z to mid Z and by differences in correlation energies at high Z. Discrepancies between our results and the all-order theory, on the other hand, are due mainly to differences in QED corrections. In general, our results agree well with the MCDF predictions [18,19] for $Z = 18$ to 54. For Xe^{52+}, for example, our CI value for the x-ray energy is smaller than the MCDF result by only 0.12 eV. However, this is partly because of cancellation of differences between contributions from correlation energies and QED corrections. For low-Z ions, MCDF correlation energies are much higher than those from other theories considered here. It is nevertheless interesting to note that the present QED results are in very good agreement with those from MCDF which are obtained using a modification of Welton's method [24].

In Figs. 5 and 6, the present $K\alpha$ transition energies are compared with other theories and with experiment. The CI and MCDF results agree with measured values to within experimental uncertainties except for Ar^{16+} and

TABLE IV. Theoretical and experimental $K\alpha_2$ x-ray energies (eV) for heliumlike ions.

Z	Present work	Drake[a]	All-order[b]	MCDF[c]	Experiment	Reference
4	121.9226	121.9222				
6	304.4051	304.4035				
8	568.6443	568.6401	568.6408			
10	914.8109	914.8029	914.8034			
14	1853.801	1853.780	1853.781			
18	3123.574	3123.530	3123.534	3123.567	3123.52 (0.04)	[28]
					3123.60 (0.25)	[29]
22	4727.007	4726.925	4726.933			
24	5654.938	5654.831	5654.843			
26	6667.692	6667.552	6667.567	6667.669	6667.50 (0.25)	[30]
32	10220.98	10220.73	10220.76		10221.80 (0.35)	[31]
36	13026.36	13026.00	13026.05	13026.31	13026.8 (0.3)	[32]
44	19717.65	19716.98	19717.10			
54	30206.91	30205.58	30205.87	30206.53	30209.6 (3.5)	[33]
64	43244.63	43242.29	43242.92			
80	70145.32	70140.93	70142.94			
92	96174.5	96167.2	96172.5		96171 (52)	[34]

[a]Drake, Ref. [2].
[b]Plante *et al.*, Ref. [17].
[c]Indelicato, Ref. [19].

TABLE V. $K\alpha$ transition energies (eV) from the unified model, all-order theory, and MCDF relative to the present results. Total and no QED are transition energy differences with and without QED corrections.

Theory	Type	$K\alpha_1$ line				$K\alpha_2$ line			
		Ar^{16+}	Kr^{34+}	Xe^{52+}	U^{90+}	Ar^{16+}	Kr^{34+}	Xe^{52+}	U^{90+}
Drake[a]	no QED	-0.009	-0.13	-0.61	-7.4	-0.008	-0.12	-0.56	-6.3
	QED	-0.031	-0.24	-0.75	-0.9	-0.036	-0.25	-0.77	-1.0
	Total	-0.040	-0.36	-1.36	-8.4	-0.044	-0.37	-1.33	-7.3
All-order[b]	no QED	-0.004	-0.05	-0.21	-0.8	-0.004	-0.06	-0.27	-1.0
	QED	-0.031	-0.24	-0.75	-0.9	-0.036	-0.25	-0.77	-1.0
	Total	-0.035	-0.28	-0.96	-1.7	-0.040	-0.31	-1.04	-2.0
MCDF[c]	no QED	0.032	0.15	0.31		0.020	0.12	0.21	
	QED	0.000	-0.05	-0.19		-0.027	-0.18	-0.58	
	Total	0.032	0.10	0.12		-0.007	-0.06	-0.37	

[a]Drake, Ref. [2].
[b]Plante *et al.*, Ref. [17].
[c]$K\alpha_1$ data from Indelicato *et al.*, Ref. [18], $K\alpha_2$ data from Indelicato, Ref. [19].

Kr^{34+}. For the $K\alpha_1$ line, CI results are larger than experiment by 0.08 eV for Ar^{16+} and smaller by 0.6 eV for Kr^{34+}. On the other hand, the unified method and the all-order theory are below the present values and seem to show slightly worse agreement with experiment in the range $Z = 22$–36. Differences between the present work and the latter two calculations are due mainly to different treatments of QED corrections in this Z range. Furthermore, according to Table V, correlation energies from the CI and the all-order theory agree to within 0.05 eV for the $K\alpha_1$ line of Kr^{34+}. Even those from the unified method and MCDF are no more than 0.15 eV from the CI value. Considering that experiment is higher than the CI by 0.6 eV with an experimental uncertainty of ± 0.3 eV, it seems unlikely that residual errors in correlation energies are responsible for this discrepancy. Better experimental results on the $K\alpha$ x-ray energies may provide important tests of higher-order QED corrections in many-electron systems.

In summary, we have calculated the term energies for the ground state and $n = 2$ singlet states of heliumlike ions using the relativistic CI method with B-spline basis functions. Our term energies without QED corrections are in good agreement with the all-order theory and are slightly lower than the unified method. The QED corrections from the present work are consistently smaller than Drake's results throughout the isoelectronic sequence. We find good but not precise agreement between theory and experiment for the $K\alpha$ x-ray energies. Discrepancies between theory and experiment on the order of 0.6 eV for Kr^{34+} may exist but are rather difficult to quantify precisely due to the lack of accurate experimental data for highly-charged ions.

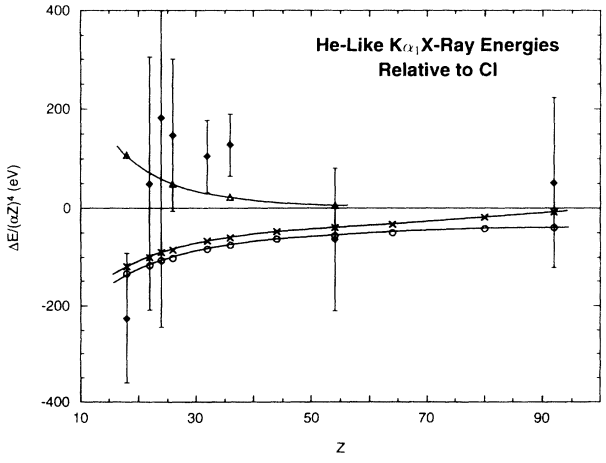

FIG. 5. The $K\alpha_1$ transition energies (eV) relative to the present CI values scaled by $(\alpha Z)^4$ as functions of the atomic number. Crosses, circles, and triangles represent results of all-order theory (Ref. [17]), unified theory (Ref. [2]), and MCDF (Refs. [18,19]), respectively. Diamonds with error bars are experimental measurements.

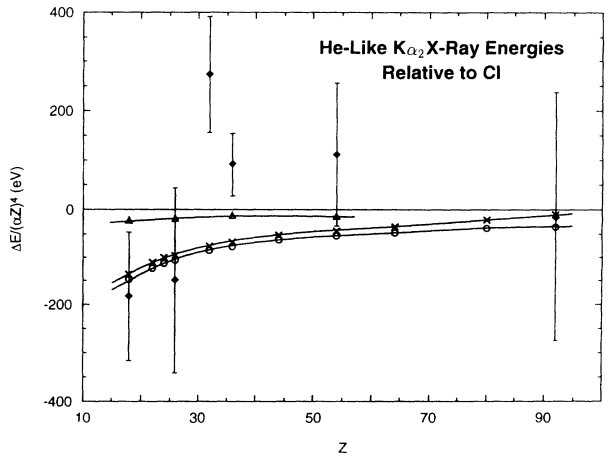

FIG. 6. The $K\alpha_2$ transition energies (eV) relative to the present CI values scaled by $(\alpha Z)^4$ as functions of the atomic number. Symbols are the same as in Fig. 5.

ACKNOWLEDGMENTS

The work of K.T.C. and M.H.C. were performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. The work of W.R.J. and J.S. was supported by NSF Grant No. PHY-92-04089. We thank Dan Plante for providing all-order many-body results prior to publication.

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