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Relativistic all-order many-body calculations of the $n = 1$ and $n = 2$ states of heliumlike ions

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An all-order procedure is used to determine the energies of the $n = 1$ and $n = 2$ states of heliumlike ions with nuclear charges in the range Z =3–100. The Coulomb energies and wave functions are obtained from a no-pair Hamiltonian by an iterative scheme that sums all orders of many-body perturbation theory. The Breit energy is determined by taking the expectation value of the instantaneous Breit Hamiltonian between the Coulomb wave functions. Corrections for the frequency dependence of the Breit interaction and for two Breit interactions are included. Quantum-electrodynamic and mass-polarization corrections are taken from Drake's unified method [Can. J. Phys. **66**, 586 (1988)]. The resulting energies are complete through order $(Z\alpha)^3$ a.u. and include new terms of order $(Z\alpha)^4$ a.u. Comparisons are made with experiment and with recent configuration-interaction calculations.

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I. INTRODUCTION

The study of spectra of heliumlike ions has proven to be useful for understanding relativistic and quantum-electrodynamic (QED) effects in many-body systems. Because only two electrons are present, accurate solutions to the nonrelativistic Schrödinger equation are available. Again because there are only two electrons, it is possible to treat heliumlike ions in a QED framework using the Bethe-Salpeter equation [1], which allows the calculation of relativistic corrections of order $(Z\alpha)^2$ a.u. together with QED corrections of order $(Z\alpha)^3$ a.u. This approach has been applied to $n = 1$ and $n = 2$ states for the entire helium isoelectronic sequence by Drake [2] in his unified method.

The unified method is known to be incomplete at the level of $(Z\alpha)^4$ a.u. There are three sources of $(Z\alpha)^4$ a.u. terms. The one considered here will be referred to as a "structure" contribution. This contribution arises from the solution to the relativistic version of the Schrödinger equation (to be defined below). Any such solution must reproduce the nonrelativistic energy and the known $(Z\alpha)^2$ a.u. corrections, but will also include corrections of order $(Z\alpha)^4$ a.u. and higher. The second and third are QED corrections, the second being the order $Z\alpha$ corrections to the leading $(Z\alpha)^3$ a.u. two-body QED correction, and the third being the two-loop Lamb shift. For very-high-Z ions it is clearly preferable not to expand in powers of $Z\alpha$. Such expansions can be avoided by reevaluating the Feynman diagrams that lead to QED corrections using exact electron propagators. While some progress has been made in such calculations, as discussed in the conclusion, they are at present incomplete. For this reason we have chosen to use Drake's QED values in this work even for high Z with the understanding that they should eventually be replaced with more exact calculations.

There has been considerable theoretical interest in this problem. In addition to the unified method, there have been calculations using many-body perturbation theory (MBPT) [3], the configuration-interaction (CI) method [4], multiconfiguration Dirac-Fock (MCDF) [5,6], and the screened $1/Z$ expansion [7]. The present work is closest in approach to Refs. [3,4], and good agreement between the calculations is found.

The quantities calculated in this paper are the energies of $n = 1$ and $n = 2$ states of heliumlike ions in the range of nuclear charge $Z = 3 - 100$. The relativistic generalization of the Schrödinger Hamiltonian is the *no-pair* Hamiltonian, derived from QED [8]. We introduce an iterative method for determining the eigenvalues of this Hamiltonian based on an expansion of the wave function in terms of products of the positive energy components of a relativistic basis set [9]. The instantaneous Breit interaction is treated as a perturbation. Frequency-dependent corrections to the Breit energy are included to first order along with the second-order effect of two Breit interactions. Finite nuclear size effects are automatically included in the present calculation by replacing the nuclear Coulomb field by the field of a distributed nuclear charge. The nuclear charge distribution is modeled by a Fermi distribution as described by Johnson and Soff [10]. Reduced mass is accounted for by using the finite-mass Rydberg constant when converting from atomic units to cm^{-1}. Corrections for mass polarization and QED are taken from Drake [2].

For triplet states, the numerical accuracy of our calculations is 10^{-7} a.u. for $Z = 3 - 9$, 10^{-6} a.u. for $Z = 10 - 28$, 10^{-5} a.u. for $Z = 30 - 80$, and 10^{-4} a.u. for $Z = 82 - 100$. For singlet states, the numerical accuracy is the same as for triplet states for $Z \geq 10$; however, for $Z = 3 - 9$, the accuracy is reduced to 10^{-6} a.u.

The theory presented in this paper provides us with a method for determining the "structure" part of the energy accurately for ions along the helium isoelectronic sequence. After including the QED corrections calculated

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by Drake [2], the only missing corrections to order $(Z\alpha)^4$ a.u. are the $(Z\alpha)^4$ QED corrections mentioned above. As the precision of high-Z experiments improves, the present calculations should help in determining these as yet uncalculated terms.

The plan of this paper is as follows. In Sec. II we give a detailed description of the calculational method used. In Sec. III, the energies for the seven $n = 1$ and $n = 2$ states, namely the $1\,^1S_0$, $2\,^1S_0$ and $2\,^1P_1, 2\,^3S_1$, $2\,^3P_0$, $2\,^3P_1$ and $2\,^3P_2$ states, will be given along with a comparison with results obtained using the CI, MBPT, unified, and MCDF methods. Section IV concludes with a discussion of limitations of the present calculations and possible directions for future research.

II. CALCULATION

A. Preliminaries

The starting point for relativistic many-body calculations is the no-pair Hamiltonian discussed by Sucher [8]. For a many-electron system, in atomic units ($\hbar = m = e/\sqrt{4\pi\epsilon_0} = 1$), the no-pair Hamiltonian may be written $H = H_0 + V + B$. Here, H_0 is the unperturbed Hamiltonian given in second quantized form by

$$H_0 = \sum_i \epsilon_i \, a_i^\dagger a_i \,, \tag{2.1}$$

where ϵ_i is an eigenvalue of the Dirac equation

$$h\,\phi_i = \epsilon_i\,\phi_i \,, \tag{2.2}$$

with

$$h = c\,\boldsymbol{\alpha}\cdot\boldsymbol{p} + (\beta - 1)c^2 + V_{\rm nuc}(r) \,. \tag{2.3}$$

In this equation, $V_{\rm nuc}(r)$ is the Coulomb potential of the nucleus incorporating the effect of its finite size. The index i represents the set of one-electron quantum numbers: the principal quantum number n_i, the angular momentum quantum number κ_i [$\kappa_i = \mp(j_i + 1/2)$ for $j_i = (l_i \pm 1/2)$], and the magnetic quantum number m_i. The Coulomb interaction V is given by

$$V = \frac{1}{2}\sum_{ijkl} g_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k \,, \tag{2.4}$$

where the sum is over positive energy states only. This restriction implements the positive energy projection operators used in Ref. [8]. The quantities g_{ijkl} in Eq. (2.4) are two-electron Coulomb matrix elements:

$$g_{ijkl} = \left\langle ij \left| \frac{1}{r_{12}} \right| kl \right\rangle . \tag{2.5}$$

The Breit interaction B is given by

$$B = \frac{1}{2}\sum_{ijkl} b_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k \,, \tag{2.6}$$

where again the summation is restricted to positive energy states. Here b_{ijkl} are two-electron Breit matrix elements

$$b_{ijkl} = \langle ij|\, b_{12}\, |kl\rangle \,, \tag{2.7}$$

where

$$b_{12} = -\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2 + \boldsymbol{\alpha}_1\cdot\hat{\mathbf{r}}_{12}\,\boldsymbol{\alpha}_2\cdot\hat{\mathbf{r}}_{12}}{2r_{12}} \,. \tag{2.8}$$

The no-pair Hamiltonian includes all corrections of order $(Z\alpha)^2$ a.u. However, QED corrections of order $(Z\alpha)^3$ a.u. arising from negative energy states are omitted; such corrections must be calculated separately, as discussed in [11].

A two-electron state vector describing an atomic state with angular momentum J, M may be written

$$\Psi_{JM} = \sum_{i\leq j} \rho_{ij}\Phi_{ij} \,, \tag{2.9}$$

where the quantities ρ_{ij} are expansion coefficients and where the configuration state vectors Φ_{ij} are defined by

$$\Phi_{ij} = \eta_{ij} \sum_{m_i m_j} \langle j_i m_i, j_j m_j | JM\rangle \; a_i^\dagger a_j^\dagger |0\rangle \,, \tag{2.10}$$

with

$$\eta_{ij} = \begin{cases} 1 & \text{if } i \neq j \\ 1/\sqrt{2} & \text{if } i = j \,. \end{cases} \tag{2.11}$$

The quantities ρ_{ij}, Φ_{ij}, and η_{ij} are all independent of magnetic quantum numbers. Therefore, a particular i is uniquely determined by n_i and κ_i. To construct a state of even or odd parity, one must require the sum $l_i + l_j$ to be either even or odd, respectively.

From the symmetry properties of the Clebsch-Gordan coefficients, it can be shown that

$$\Phi_{ij} = (-1)^{j_i + j_j + J + 1}\Phi_{ji} . \tag{2.12}$$

From this relation it follows that Φ_{ii} vanishes unless J is even. The normalization condition has the form

$$\langle\Psi_{JM}|\Psi_{JM}\rangle = \sum_{i\leq j} \rho_{ij}^2 = 1. \tag{2.13}$$

Substituting Ψ_{JM} into the Schrödinger equation $(H_0 + V)\Psi_{JM} = E\Psi_{JM}$, one obtains the following set of linear equations for the expansion coefficients ρ_{ij}:

$$(\epsilon_i + \epsilon_j)\rho_{ij} + \sum_{k\leq l} \eta_{ij} V(ij;kl)\,\eta_{kl}\,\rho_{kl} = E\rho_{ij} \,. \tag{2.14}$$

Here

$$\begin{aligned} V(ij;kl) = {} & \sum_L (-1)^{j_j + j_k + L + J} \begin{Bmatrix} j_i & j_j & J \\ j_l & j_k & L \end{Bmatrix} X_L(ijkl) \\ & + \sum_L (-1)^{j_j + j_k + L} \begin{Bmatrix} j_i & j_j & J \\ j_k & j_l & L \end{Bmatrix} \\ & \times X_L(ijlk), \end{aligned} \tag{2.15}$$

where the quantities $X_L(ijkl)$ are given by

$$X_L(ijkl) = (-1)^L \langle\kappa_i\|C_L\|\kappa_k\rangle\langle\kappa_j\|C_L\|\kappa_l\rangle R_L(ijkl)\,. \tag{2.16}$$

The quantities $\langle\kappa_i\|C_L\|\kappa_j\rangle$ are reduced matrix elements of normalized spherical harmonics; they are given by

$$\langle\kappa_i\|C_L\|\kappa_j\rangle = (-1)^{j_i+1/2}\sqrt{[j_i][j_j]}\begin{pmatrix} L & j_i & j_j \\ 0 & -\frac{1}{2} & \frac{1}{2}\end{pmatrix} \times\Pi(l_i,l_j,L)\,, \tag{2.17}$$

where $[j] = 2j+1$, and where Π is a parity factor

$$\Pi(l_i,l_j,L) = \begin{cases} 1 & \text{if } l_i+l_j+L \text{ is even} \\ 0 & \text{if } l_i+l_j+L \text{ is odd}\,. \end{cases} \tag{2.18}$$

The quantity $R_L(ijkl)$ in Eq. (2.16) is a Slater integral given by

$$R_L(ijkl) = \int_0^\infty\int_0^\infty dr_1 dr_2 \frac{r_<^L}{r_>^{L+1}} \times[G_i(r_1)G_k(r_1)+F_i(r_1)F_k(r_1)] \times[G_j(r_2)G_l(r_2)+F_j(r_2)F_l(r_2)], \tag{2.19}$$

where $G_i(r)$ and $F_i(r)$ are the large and small components of the radial Dirac wave function, respectively.

We solve the eigenvalue problem in Eq. (2.14) iteratively, as described in the next section. Once the iteration procedure has converged, the corresponding state vector is used to determine the correction to the energy from the Breit interaction:

$$E_B = \langle\Psi_{JM}|B|\Psi_{JM}\rangle = \sum_{\substack{i\le j\\ k\le l}} \eta_{ij}\,\rho_{ij} V_B(ij;kl)\,\eta_{kl}\,\rho_{kl}, \tag{2.20}$$

where $V_B(ij;kl)$ is given by the formula for $V(ij;kl)$ in Eq. (2.15) with

$$X_L(ijkl) \to M_L(ijkl) + N_L(ijkl) + O_L(ijkl)\,, \tag{2.21}$$

where $M_L(ijkl)$, $N_L(ijkl)$, and $O_L(ijkl)$ are the magnetic Slater integrals defined in Ref. [12]. The energy determined by Eq. (2.20) includes only the contributions from a single instantaneous Breit interaction. Corrections for frequency dependence of the Breit interaction and for multiple Breit interactions are made separately.

B. Iteration procedure

For simplicity, we replace the pair of indices ij used in the preceding subsection by the single channel index I, and we denote Φ_{ij} and ρ_{ij} by Φ_I and c_I, respectively. The two-electron state vector may then be rewritten as

$$\Psi_{JM} = \sum_I c_I \Phi_I\,, \tag{2.22}$$

and the eigenvalue equation (2.14) can be rewritten as

$$E_I\, c_I + \sum_K V_{IK}\, c_K = E\, c_I\,, \tag{2.23}$$

where $E_I = \epsilon_i + \epsilon_j$, and where $V_{IK} = \eta_{ij} V(ij;kl)\,\eta_{kl}$. The sum over K includes all positive energy bound and continuum states. To bring this equation into a form suitable for iteration, we separate out one or more "dominant" channels to serve as an initial approximation, ordering the channels so that they occur first. Of the seven $n=1$ and $n=2$ states considered, five are comprised of a single dominant channel, namely, $1\,^1S_0$, $2\,^1S_0$, $2\,^3S_1$, $2\,^3P_0$, and $2\,^3P_2$ for which a $1s_{1/2}$ electron is coupled to a $1s_{1/2}$, $2s_{1/2}$, $2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$ electron, respectively. The two remaining states, $2\,^1P_1$ and $2\,^3P_1$, are mixed and consist of two dominant channels, with a $1s_{1/2}$ electron coupling to both a $2p_{1/2}$ and $2p_{3/2}$ electron.

We first consider the case of a single dominant channel, $I=1$. We choose $c_1 = 1$ and $c_I = 0$ for $I > 1$ as a starting approximation and normalize our state vector using intermediate normalization [13], so that $c_1 = 1$ at all stages of iteration. The set of equations (2.23) may be broken up into an equation for the dominant channel,

$$(E_1 - E) + V_{11} = -\sum_{K>1} V_{1K}\, c_K\,, \tag{2.24}$$

and a set of equations for the remaining channels,

$$(E_I - E)\, c_I = -V_{I1} - \sum_{K>1} V_{IK}\, c_K\,, \qquad I > 1. \tag{2.25}$$

The iterative solution of these equations follows a pattern similar to Rayleigh-Schrödinger perturbation theory. In the nth iteration we will have $E^{(n)} = E_1 + \Delta E^{(n)}$, where E_1 is the sum of the single-particle energies of the two electrons of the dominant channel. The iterative solution is begun by dropping the right-hand side of Eq. (2.24) to obtain $E^{(1)} = E_1 + \Delta E^{(1)}$, where $\Delta E^{(1)} = V_{11}$. We continue the iteration with $c_I^{(1)} = -V_{I1}/(E_I - E_1)$, for $I > 1$, from Eq. (2.25) as a first-order approximation for the expansion coefficients. Generally, in the nth approximation, we obtain from Eq. (2.24)

$$\Delta E^{(n)} = \Delta E^{(1)} + \sum_{K>1} V_{1K}\, c_K^{(n-1)}\,, \tag{2.26}$$

and from Eq. (2.25)

$$c_K^{(n)} = \frac{1}{E_K - E_1}\left\{\Delta E^{(n-1)} c_K^{(n-1)} - V_{K1} - \sum_{L>1} V_{KL} c_L^{(n-1)}\right\},\; K > 1. \tag{2.27}$$

This scheme differs somewhat from the Rayleigh-Schrödinger perturbation expansion, in that terms of nth order are not proportional to V^n. Therefore $E^{(n)}$ does not correspond to the nth-order correction to the energy as defined by perturbation theory. Nevertheless, the scheme converges rapidly to give a solution to Eqs. (2.24) and (2.25). We continue the iteration above until the energy converges to an accuracy of one decimal place more than is quoted in the tables. When n is sufficiently large so that this level of convergence has been reached we set $\Delta E = \Delta E^{(n)}$, and refer to the sum $E_1 + \Delta E$ as the all-order Coulomb energy in the following.

For cases in which there are two dominant channels, the first two of Eqs. (2.23) corresponding to the dominant channels are written

$$(E_1 - E)c_1 + V_{11}\, c_1 + V_{12}\, c_2 = -\sum_{K>2} V_{1K} c_K\,, \quad (2.28)$$

and

$$(E_2 - E)c_2 + V_{21}\, c_1 + V_{22}\, c_2 = -\sum_{K>2} V_{2K} c_K\,, \quad (2.29)$$

while the equations corresponding to the remaining channels are written

$$(E_I - E)c_I + V_{I1}\, c_1 + V_{I2}\, c_2 = -\sum_{K>2} V_{IK} c_K\,, \qquad I > 2. \quad (2.30)$$

Ignoring the contributions from the subdominant channels on the right-hand sides of Eqs. (2.28) and (2.29) leads to a 2×2 eigenvalue equation for the expansion coefficients c_1 and c_2 and the energy E. We designate the two eigenvalues of this equation by E_a and E_b and the corresponding orthonormal eigenvectors by $a = (a_1, a_2)$ and $b = (b_1, b_2)$, respectively.

We may choose either of these two eigenstates to start our iteration. To be specific, let us start with state a. We then have as a lowest approximation $c_1 = a_1$ and $c_2 = a_2$. At each step of the iteration, we expand the coefficients c_1 and c_2 in terms of the eigenvectors a and b as

$$c_I^{(n)} = a_I + \lambda^{(n)} b_I\,, \qquad I = 1, 2. \quad (2.31)$$

This form is dictated by the intermediate normalization requirement for the wave function. We set $E_0 = (E_1 + E_2)/2$ and define $\Delta E = E - E_0$. Then, we have as a first approximation to the energy, $\Delta E^{(1)} = E_a - E_0$ from Eqs. (2.28) and (2.29). Similarly, the first approximation to the expansion coefficients is given by

$$c_K^{(1)} = -\frac{1}{E_K - E_0} \sum_{J=1,2} V_{KJ} a_J \quad \text{for } K > 2\,. \quad (2.32)$$

In the nth approximation, inserting Eq. (2.31) into Eqs. (2.28) and (2.29) and using the orthogonality of the eigenvectors a and b, it follows that

$$\Delta E^{(n)} = \Delta E^{(1)} + \sum_{\substack{I=1,2\\ K>2}} a_I V_{IK}\, c_K^{(n-1)} \quad (2.33)$$

and

$$\lambda^{(n)} = \frac{1}{E^{(n-1)} - E_b} \sum_{\substack{I=1,2\\ K>2}} b_I V_{IK}\, c_K^{(n-1)}\,, \quad (2.34)$$

where

$$c_K^{(n)} = \frac{1}{E_K - E_0} \Bigg\{ \Delta E^{(n-1)} c_K^{(n-1)} - \sum_{J=1,2} V_{KJ} a_J - \lambda^{(n-1)} \sum_{J=1,2} V_{KJ} b_J - \sum_{L>2} V_{KL} c_L^{(n-1)} \Bigg\}\,, \qquad K > 2\,. \quad (2.35)$$

Again, the iteration was continued until the energy converged to one decimal place beyond what is quoted in the tables. In this case the all-order Coulomb energy is equal to $E_0 + \Delta E$.

C. Numerical procedure

For our calculations, we begin by using 50 positive energy basis functions formed from B splines to obtain our single-particle orbitals as described in Ref. [9]. We choose a cavity radius of $60/Z$ a.u., and find that small changes to the size of the cavity produce negligible differences to the energy at the accuracy desired. We then compute the energy $\Delta E^{(2)}$ using the procedure described in the preceding section using the full basis set. The choice of 50 basis functions was the minimum needed to reduce basis set dependence to below our quoted numerical accuracy. However, to reduce computing time, a finite basis set with 40 basis functions was used to iterate the all-order equations to convergence. We then formed the energy $E_+^{(3)} \equiv \Delta E - \Delta E^{(2)}$, with the expectation that the basis set dependence of this quantity is not as sensitive as the full energy. This was verified by evaluating $E_+^{(3)}$ with both the larger and smaller basis sets for several cases and finding negligible differences in the results. The total Coulomb energy is then obtained by adding $\Delta E^{(2)}$ evaluated with the large basis set to $E_+^{(3)}$ and the lowest-order energy, E_1 or E_0, for the one- or two-channel cases, respectively.

Even when using the smaller basis set, solving the all-order equations is still computationally demanding, with a single iteration taking as long as 10 CPU hours on a Hewlett-Packard 720 workstation. A variety of approximations were made to reduce computer time. We find, for example, that channels in which the orbital angular momentum quantum numbers of the two electrons differ by two or more, for example, an $s_{1/2}$ electron coupled to a $d_{1/2}$ electron, contribute little to the energy, so these channels are excluded from our computations. Also, since only $\Delta E^{(2)}$ and ΔE are needed in determining $E_+^{(3)}$, we may greatly decrease the computer time needed by including all of the channels to obtain $\Delta E^{(2)}$ but then only using the first few channels for the next several iterations. We then include all of the channels again for the final iterations until convergence. Also, in obtaining $E_+^{(3)}$, it is often found that the contribution from the last five or ten basis functions is negligible, depending on the state and value of Z being calculated. For example, for $2\,^3S_1$ and $2\,^3P_2$ only 30 of the 40 basis states are needed for Z = 10–40 while 35 to 40 states are needed for all of the singlet states in the same range of Z. For all states, the full basis set is needed for $Z > 50$.

The number of partial waves needed in summing over L to determine $V(ijkl)$ and $V_B(ijkl)$ also depends on the state and the value of Z. Motivated by the work of Schwartz [14], we assume that the successive terms in the sum over angular momentum converge as $(L + 1/2)^{-n}$. The partial wave summation is carried out by summing explicitly to a value $L_{\rm max}$, chosen high enough that the asymptotic form is taken on, then using that form to estimate the remainder from $L = L_{\rm max} + 1$ to $L = \infty$. For the Coulomb energy, we find that $n \approx 5$ or 6 for the triplet states while $n \approx 4$ for the singlet states. For the Breit energy, we find that $n \approx 3.5$–5 for the triplet states while $n \approx 2$–3.5 for the singlet states.

Because the partial wave expansions for singlet states converge more slowly than those for triplet states, more partial waves are needed for singlet states. We need $L_{\rm max} = 7$ for all states in the range $70 \leq Z \leq 80$, and $L_{\rm max} = 6$ for all states in the range $80 < Z \leq 100$. Moreover, it is necessary to use $L_{\rm max} = 7$ or 8 for singlet states in the range $10 \leq Z < 70$, whereas $L_{\rm max} = 5$, 6, or 7 suffices for triplet states in this same range. For $Z < 10$, we need $L_{\rm max} = 7$ or 8 for all states.

III. RESULTS

In Table I, we present a detailed breakdown of our results for the ionization energies of the seven $n = 1$ and $n = 2$ states for heliumlike ions with $Z = 10, 20, 30, \ldots, 100$. The third column gives the all-order Coulomb energy, and the fourth column gives the all-order Breit energy determined from Eq. (2.20). The correction for frequency dependence of the Breit interaction, $\Delta B^{(1)}$ is given in the fifth column. In the sixth column, the effect of two instantaneous Breit interactions $[B \times B]$ is presented. For the single-channel cases, $\Delta B^{(1)}$ is calculated as described in Ref. [16], and $[B \times B]$ is evaluated in a manner similar to that used to evaluate $E^{(2)}$, with the Coulomb matrix elements g_{ijkl} replaced with Breit matrix elements b_{ijkl}. The seventh and eighth columns show the mass polarization and QED effects, respectively, as tabulated by Drake [2], where the QED value for singlet states has been modified in a way described below. Reduced mass is *not* included in the tables, but rather is incorporated in the conversion to cm^{-1} or eV.

In the two-channel case, $\Delta B^{(1)}$ and $[B \times B]$ require further discussion. We recall that in lowest order the Coulomb energy is obtained by diagonalizing a 2 × 2 matrix. The off-diagonal matrix elements determine how strongly the two channels are mixed. In order to treat frequency dependence of the Breit interaction for the two-channel case we first construct a 2 × 2 Breit matrix analogous to that for the Coulomb interaction. The lowest-order instantaneous Breit energies for the two channels are given by $B_a = a^\dagger B a$ and $B_b = b^\dagger B b$, where B is the 2 × 2 instantaneous Breit matrix, and where $a = (a_1, a_2)$ and $b = (b_1, b_2)$ are the lowest-order Coulomb eigenvectors in the respective channels. When the generalized

TABLE I. Ionization energies (in a.u.) for $n = 1$ and $n = 2$ singlet and triplet states of heliumlike ions. Coulomb and Breit energies are all-order values, $\Delta B^{(1)}$ is the first-order correction for frequency dependence to the Breit energy, $[B \times B]$ is the second-order correction for two Breit interactions, MP is mass polarization as taken from Drake [2], and QED is also from Ref. [2] with $(\alpha Z)^3$ corrections already accounted for in the structure part of the energy subtracted.

Z	State	Coulomb	Breit	$\Delta B^{(1)}$	$[B \times B]$	MP	QED	Total
10	$2\,^3S_1$	-10.685610	-0.000009	0.000000	0.000000	0.000003	0.000599	-10.685017
	$2\,^3P_0$	-10.332144	0.003962	0.000000	-0.000005	-0.000176	-0.000051	-10.328414
	$2\,^3P_1$	-10.328202	0.001387	-0.000002	-0.000004	-0.000176	-0.000047	-10.327044
	$2\,^3P_2$	-10.319959	0.000223	-0.000004	0.000000	-0.000176	-0.000029	-10.319945
	$1\,^1S_0$	-43.961664	0.010708	0.000000	-0.000048	0.000033	0.004610	-43.946361
	$2\,^1S_0$	-10.310434	0.001906	0.000000	-0.000011	0.000003	0.000543	-10.307993
	$2\,^1P_1$	-10.062304	-0.000406	0.000003	0.000000	0.000169	0.000004	-10.062534
20	$2\,^3S_1$	-46.593321	-0.000045	0.000005	-0.000002	0.000003	0.007396	-46.585964
	$2\,^3P_0$	-45.843221	0.035760	-0.000013	-0.000077	-0.000390	-0.000409	-45.808350
	$2\,^3P_1$	-45.782897	0.010383	-0.000057	-0.000130	-0.000368	-0.000353	-45.773422
	$2\,^3P_2$	-45.611682	0.002042	-0.000129	-0.000002	-0.000390	0.000040	-45.610121
	$1\,^1S_0$	-188.635728	0.096696	0.000000	-0.000433	0.000035	0.054905	-188.484525
	$2\,^1S_0$	-45.764903	0.018240	0.000014	-0.000100	0.000003	0.007072	-45.739674
	$2\,^1P_1$	-45.072511	-0.001142	0.000105	0.000092	0.000363	0.000189	-45.072904
30	$2\,^3S_1$	-108.52615	-0.00015	0.00004	-0.00001	0.00000	0.03068	-108.49559
	$2\,^3P_0$	-107.34636	0.12707	-0.00009	-0.00039	-0.00057	-0.00127	-107.22161
	$2\,^3P_1$	-107.14754	0.02262	-0.00031	-0.00086	-0.00041	-0.00118	-107.12768
	$2\,^3P_2$	-106.09106	0.00726	-0.00098	-0.00001	-0.00057	0.00110	-106.08426
	$1\,^1S_0$	-436.59161	0.34170	0.00000	-0.00161	0.00003	0.22029	-436.03120
	$2\,^1S_0$	-107.21557	0.06589	0.00011	-0.00039	0.00000	0.02986	-107.12010
	$2\,^1P_1$	-105.35310	0.01020	0.00068	0.00070	0.00041	0.00154	-105.33957

TABLE I. (*Continued*).

Z	State	Coulomb	Breit	$\Delta B^{(1)}$	$[B \times B]$	MP	QED	Total
40	$2\,^3S_1$	-197.83315	-0.00042	0.00015	-0.00003	0.00000	0.08355	-197.74990
	$2\,^3P_0$	-196.16979	0.31372	-0.00033	-0.00121	-0.00073	-0.00222	-195.86056
	$2\,^3P_1$	-195.81552	0.03169	-0.00076	-0.00196	-0.00039	-0.00214	-195.78908
	$2\,^3P_2$	-192.00077	0.01781	-0.00412	-0.00003	-0.00073	0.00518	-191.98266
	$1\,^1S_0$	-792.12605	0.83482	0.00000	-0.00409	0.00003	0.57860	-790.71669
	$2\,^1S_0$	-195.99379	0.16352	0.00044	-0.00104	0.00000	0.08204	-195.74883
	$2\,^1P_1$	-191.08410	0.04780	0.00232	0.00155	0.00038	0.00611	-191.02594
50	$2\,^3S_1$	-316.58764	-0.00106	0.00044	-0.00008	0.00000	0.18264	-316.40570
	$2\,^3P_0$	-314.36275	0.63869	-0.00085	-0.00296	-0.00086	-0.00139	-313.73012
	$2\,^3P_1$	-313.86372	0.04100	-0.00134	-0.00317	-0.00037	-0.00130	-313.82890
	$2\,^3P_2$	-303.69226	0.03586	-0.01259	-0.00006	-0.00086	0.01583	-303.65408
	$1\,^1S_0$	-1261.80395	1.67421	0.00000	-0.00846	0.00003	1.21558	-1258.92259
	$2\,^1S_0$	-314.14992	0.33279	0.00132	-0.00222	0.00000	0.18036	-313.63767
	$2\,^1P_1$	-302.59145	0.11536	0.00619	0.00228	0.00037	0.01742	-302.44983
60	$2\,^3S_1$	-467.80924	-0.00247	0.00108	-0.00015	0.00000	0.35005	-467.46073
	$2\,^3P_0$	-464.91678	1.15655	-0.00155	-0.00622	-0.00105	0.00582	-463.76323
	$2\,^3P_1$	-464.28074	0.05257	-0.00201	-0.00460	-0.00041	0.00592	-464.22927
	$2\,^3P_2$	-441.63266	0.06388	-0.03133	-0.00012	-0.00105	0.03863	-441.56265
	$1\,^1S_0$	-1855.11862	2.97236	0.00000	-0.01528	0.00003	2.22984	-1849.93167
	$2\,^1S_0$	-464.67248	0.60029	0.00323	-0.00414	0.00000	0.34699	-463.72611
	$2\,^1P_1$	-440.34795	0.21708	0.01434	0.00289	0.00040	0.04109	-440.07215
70	$2\,^3S_1$	-655.82894	-0.00531	0.00228	-0.00029	0.00000	0.61626	-655.21600
	$2\,^3P_0$	-652.14022	1.94032	-0.00178	-0.01180	-0.00118	0.02875	-650.18591
	$2\,^3P_1$	-651.37055	0.06608	-0.00252	-0.00633	-0.00042	0.02885	-651.28489
	$2\,^3P_2$	-606.41466	0.10467	-0.06770	-0.00021	-0.00118	0.08161	-606.29747
	$1\,^1S_0$	-2585.54043	4.86393	0.00000	-0.02523	0.00003	3.74008	-2576.96162
	$2\,^1S_0$	-651.84714	1.00042	0.00683	-0.00707	0.00000	0.61254	-650.23442
	$2\,^1P_1$	-604.95462	0.35771	0.02989	0.00340	0.00042	0.08524	-604.47796
80	$2\,^3S_1$	-886.91950	-0.01069	0.00431	-0.00049	0.00001	1.02469	-885.90167
	$2\,^3P_0$	-882.30941	3.09356	0.00044	-0.02088	-0.00133	0.08501	-879.15261
	$2\,^3P_1$	-881.40698	0.07918	-0.00219	-0.00840	-0.00046	0.08512	-881.25373
	$2\,^3P_2$	-798.76963	0.16140	-0.13189	-0.00035	-0.00133	0.15572	-798.58608
	$1\,^1S_0$	-3472.33934	7.51789	0.00000	-0.03914	0.00003	5.89519	-3458.96537
	$2\,^1S_0$	-881.87824	1.58028	0.01294	-0.01139	0.00001	1.02052	-879.27588
	$2\,^1P_1$	-797.15101	0.54102	0.05723	0.00369	0.00046	0.16087	-796.38774
90	$2\,^3S_1$	-1170.3770	-0.0205	0.0075	-0.0008	0.0000	1.6372	-1168.7536
	$2\,^3P_0$	-1164.8609	4.7728	0.0099	-0.0353	-0.0015	0.2070	-1159.9080
	$2\,^3P_1$	-1163.8255	0.0864	0.0006	-0.0108	-0.0005	0.2072	-1163.5426
	$2\,^3P_2$	-1019.5847	0.2376	-0.2371	-0.0006	-0.0015	0.2752	-1019.3111
	$1\,^1S_0$	-4543.5514	11.1581	0.0000	-0.0580	0.0000	8.8826	-4523.5687
	$2\,^1S_0$	-1163.9506	2.4084	0.0224	-0.0176	0.0000	1.6329	-1159.9045
	$2\,^1P_1$	-1017.8336	0.7685	0.1022	0.0038	0.0005	0.2824	-1016.6762
100	$2\,^3S_1$	-1520.5421	-0.0377	0.0120	-0.0013	0.0000	2.5473	-1518.0218
	$2\,^3P_0$	-1514.7521	7.2338	0.0368	-0.0581	-0.0017	0.4530	-1507.0883
	$2\,^3P_1$	-1513.5830	0.0759	0.0094	-0.0141	-0.0006	0.4532	-1513.0592
	$2\,^3P_2$	-1269.9244	0.3366	-0.3996	-0.0009	-0.0017	0.4576	-1269.5324
	$1\,^1S_0$	-5841.4994	16.0999	0.0000	-0.0836	0.0000	12.9704	-5812.5127
	$2\,^1S_0$	-1512.2125	3.5914	0.0361	-0.0268	0.0000	2.5433	-1506.0685
	$2\,^1P_1$	-1268.0793	1.0375	0.1721	0.0035	0.0006	0.4673	-1266.3983

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[a] Ref. [2].

TABLE II. Total ionization energies (in a.u.) for $n = 1$ and $n = 2$ singlet and triplet states of heliumlike ions.

Z	$2\,^3S_1$	$2\,^3P_0$	$2\,^3P_1$	$2\,^3P_2$	$1\,^1S_0$	$2\,^1S_0$	$2\,^1P_1$
3	-0.6107986	-0.5277241	-0.5277479	-0.5277383	-2.779961	-0.540908	
4	-1.2974536	-1.1750420	-1.1750946	-1.1750270	-5.655943	-1.185020	
5	-2.2346975	-2.0734244	-2.0734983	-2.0732582	-9.532325	-2.078995	
6	-3.4225604	-3.2225342	-3.2225911	-3.2219723	-14.409738	-3.223173	
7	-4.8612263	-4.6223725	-4.6223327	-4.6210068	-20.288915	-4.617846	-4.460516
8	-6.5509613	-6.2731130	-6.2728452	-6.2703318	-27.170717	-6.263310	-6.077303
9	-8.4920953	-8.1750086	-8.1743193	-8.1699548	-35.056151	-8.159902	-7.944584
10	-10.685017	-10.328414	-10.327044	-10.319945	-43.946361	-10.307993	-10.062534
11	-13.130165	-12.733687	-12.731304	-12.720336	-53.842700	-12.708008	-12.431376
12	-15.828034	-15.391312	-15.387516	-15.371240	-64.746633	-15.360422	-15.051280
13	-18.779174	-18.301761	-18.296079	-18.272720	-76.659815	-18.265756	-17.922486
14	-21.984185	-21.465625	-21.457531	-21.424918	-89.584050	-21.424583	-21.045164
15	-25.443719	-24.883485	-24.872403	-24.827916	-103.521316	-24.837528	-24.419541
16	-29.158486	-28.556044	-28.541370	-28.481877	-118.473770	-28.505270	-28.045781
17	-33.129248	-32.483990	-32.465106	-32.386907	-134.443729	-32.428542	-31.924093
18	-37.356821	-36.668101	-36.644409	-36.543159	-151.433691	-36.608128	-36.054640
19	-41.842085	-41.109281	-41.080218	-40.950863	-169.446344	-41.044873	-40.437518
20	-46.585964	-45.808350	-45.773422	-45.610121	-188.484525	-45.739674	-45.072904
21	-51.589448	-50.766235	-50.725046	-50.521094	-208.551266	-50.693484	-49.960959
22	-56.853580	-55.984001	-55.936255	-55.684033	-229.649770	-55.907329	-55.101732
23	-62.379507	-61.462771	-61.407918	-61.099123	-251.783499	-61.382247	-60.495525
24	-68.168286	-67.203442	-67.142247	-66.766592	-274.955995	-67.119401	-66.141860
26	-80.539636	-79.475864	-79.401745	-78.859506	-324.432617	-79.385200	-78.194158
28	-93.978220	-92.811520	-92.726141	-91.964718	-378.112524	-92.715019	-91.259614
30	-108.49559	-107.22161	-107.12768	-106.08426	-436.03120	-107.12010	-105.33957
32	-124.10447	-122.71846	-122.61957	-121.22040	-498.22835	-122.61289	-120.43566
34	-140.81872	-139.31554	-139.21593	-137.37562	-564.74687	-139.20685	-136.54984
36	-158.65330	-157.02749	-156.93192	-154.55253	-635.63339	-156.91668	-153.68449
38	-177.62453	-175.87011	-175.78380	-172.75389	-710.93857	-175.75828	-171.84225
40	-197.74990	-195.86056	-195.78908	-191.98266	-790.71669	-195.74883	-191.02594
42	-219.04827	-217.01728	-216.96658	-212.24196	-875.02561	-216.90675	-211.23875
44	-241.54027	-239.36028	-239.33664	-233.53514	-963.93030	-239.25228	-232.48394
46	-265.24780	-262.91108	-262.92109	-255.86575	-1057.49844	-262.80688	-254.76501
47	-277.56472	-275.14655	-275.17600	-267.42122	-1106.05415	-275.04479	-266.29516
48	-290.19440	-287.69270	-287.74342	-279.23740	-1155.80244	-287.59364	-278.08570
50	-316.40570	-313.73012	-313.82890	-303.65408	-1258.92259	-313.63767	-302.44983
52	-343.90838	-341.05000	-341.20466	-329.11982	-1366.93888	-340.96521	-327.86154
54	-372.73282	-369.68122	-369.90002	-355.63899	-1479.94933	-369.60598	-354.32503
56	-402.91012	-399.65455	-399.94626	-383.21597	-1598.04815	-399.59056	-381.84486
58	-434.47392	-431.00333	-431.37724	-411.85556	-1721.33798	-430.95196	-410.42559
60	-467.46073	-463.76323	-464.22927	-441.56265	-1849.93167	-463.72611	-440.07215
62	-501.90862	-497.97269	-498.54136	-472.34450	-1983.94179	-497.95003	-470.78968
64	-537.86132	-533.67325	-534.35574	-504.19993	-2123.50855	-533.66699	-502.58336
66	-575.36492	-570.90957	-571.71785	-537.14109	-2268.77497	-570.92210	-535.45877
68	-614.46612	-609.72981	-610.67661	-571.17160	-2419.87609	-609.76122	-569.42164
70	-655.21600	-650.18591	-651.28489	-606.29747	-2576.96162	-650.23442	-604.47796
72	-697.67541	-692.33437	-693.60008	-642.52501	-2740.22939	-692.40143	-640.63398
74	-741.90323	-736.23610	-737.68419	-679.86075	-2909.84877	-736.32000	-677.89610
76	-787.96979	-781.95744	-783.60474	-718.31140	-3086.04309	-782.05910	-716.27108
78	-835.94321	-829.57017	-831.43468	-757.88408	-3269.00407	-829.68551	-755.76588
80	-885.90167	-879.15261	-881.25373	-798.58608	-3458.96537	-879.27588	-796.38774
82	-937.9599	-930.7906	-933.1492	-840.4250	-3656.2039	-930.9176	-838.1441
84	-992.1313	-984.5774	-987.2162	-883.4085	-3860.9789	-984.6988	-881.0431
86	-1048.5837	-1040.6146	-1043.5582	-927.5451	-4073.5338	-1040.7093	-925.0922
88	-1107.4216	-1099.0172	-1102.2920	-972.8430	-4294.3025	-1099.0756	-970.3004
90	-1168.7536	-1159.9080	-1163.5426	-1019.3111	-4523.5687	-1159.9045	-1016.6762
92	-1232.7146	-1223.4249	-1227.4511	-1066.9583	-4761.7311	-1223.3279	-1064.2287
94	-1299.4507	-1289.7206	-1294.1727	-1115.7940	-5009.2119	-1289.4886	-1112.9674
96	-1369.1323	-1358.9663	-1363.8820	-1165.8282	-5266.5222	-1358.5532	-1162.9017
98	-1441.9265	-1431.3506	-1436.7719	-1217.0707	-5533.9779	-1430.6851	-1214.0419
100	-1518.0218	-1507.0883	-1513.0592	-1269.5324	-5812.5127	-1506.0685	-1266.3983

Breit interaction [16] is used to include frequency dependence, there is an ambiguity as to which frequency to use for the off-diagonal elements. The general Breit operator, $b_{12}(\omega)$, used in place of the instantaneous Breit operator, Eq. (2.8), leads to a 2 × 2 Breit matrix whose off-diagonal elements depend on the energy differences of the $2p_{1/2}$ and $2p_{3/2}$ electrons with the $1s_{1/2}$ electron, which we refer to as ω_1 and ω_2. We resolve this ambiguity by using the formulation suggested by Mittleman [17]:

$$b_{12}(\omega) \rightarrow \frac{1}{2}[b_{12}(\omega_1) + b_{12}(\omega_2)]\,. \qquad (3.1)$$

We use the transformation given above for the instantaneous Breit interaction to obtain $B_a(\omega)$ and $B_b(\omega)$, and we subtract the instantaneous contributions to obtain $\Delta B^{(1)}$.

For the $[B \times B]$ contribution, we refer to Eqs. (2.32) and (2.33). Replacing the Coulomb matrix elements with Breit matrix elements in these equations and neglecting $\Delta E^{(1)}$, we obtain the leading approximation for two Breit interactions, namely,

$$[B \times B] = \sum_{\substack{IJ=1,2\\ K>2}} \frac{a_I B_{IK} B_{KJ} a_J}{E_0 - E_K}\,, \qquad (3.2)$$

where $B_{IK} = V_B(ij;kl)$ with $V_B(ij;kl)$ defined as for Eq. (2.20). The eigenvalues E_0 and E_K and the eigenvectors $a = (a_1, a_2)$ are the same as for Eqs. (2.32) and (2.33).

In calculating $[B \times B]$ for one-channel cases, $I = 1$ and $J = 1$ in Eq. (3.2) and K ranges over values $K > 1$. For one-channel cases, all leading-order contributions are given by Eq. (3.2). However, for two-channel cases, contributions to the $[B \times B]$ energy from states with $K < 2$ are not included in Eq. (3.2) and must be calculated separately. These contributions are obtained by including the Breit potential in Eqs. (2.28) and (2.29) when solving the 2×2 eigenvalue problem. The difference in energy obtained using the complete no-pair Hamiltonian in this 2 × 2 problem, and that obtained using the Coulomb interaction and treating the Breit interaction as a perturbation, gives the $[B \times B]$ contributions from states with $K < 2$. These corrections have been included along with those from Eq. (3.2) in the tabulated values of $[B \times B]$.

While the numerical value of the $[B \times B]$ term is small, its partial wave expansion converges too slowly to permit reliable estimates of remainders for the $1\,{}^1S_0$ and the $2\,{}^1P_1$ states at low values of Z. To overcome this difficulty we use the fact that the dominant contributions to these energies are of order $(Z\alpha)^3$ and $(Z\alpha)^4$. From the $[B \times B]$ energies computed at higher values of Z we determine the coefficients of these dominant contributions using a least-squares fit. The low-Z $[B \times B]$ energies are extrapolated using the coefficients from this fit. In Table I, the $[B \times B]$ terms for $Z < 18$ and $Z < 42$ for the states $1\,{}^1S_0$ and $2\,{}^1P_1$, respectively, have been determined by extrapolation from higher Z.

Turning to QED corrections, we note that the present calculation includes $(Z\alpha)^3$ a.u. corrections for singlet states. These arise from the second-order Coulomb energy, first-order Coulomb corrections to the instantaneous Breit interaction, and the term $[B \times B]$. However,

TABLE III. $2\,{}^3P_0$–$2\,{}^3S_1$ transition energies (in cm^{-1} except for $Z = 92$ which are given in eV). The quoted errors for the all-order (AO) energies do not include Drake's revised QED error estimate [24] for $Z = 3$, 4, and 5.

Z	AO	CI Ref. [4]	Drake Ref. [2]	MBPT Ref. [3]	MCDF Ref. [6]	Experiment	Ref.
3	18231.32(3)		18231.303(32)[a]			18231.303(1)	[25]
						18231.30188(19)	[26]
4	26864.61(3)		26864.617(89)[a]			26864.6120(4)	[27]
5	35393.59(3)	35393.608(30)	35393.666(207)[a]			35393.627(13)	[28]
6	43898.7	43898.7	43899.0			43899(1)	[29]
7	52420.3	52420.4	52421.0			52420.0(1.1)	[30]
8	60978.6	60978.7	60979.6			60978.4(0.5)	[30]
9	69590.5	69590.8	69592.5			69590.9(3.4)	[31]
						69586.0(2.9)	[32]
10	78263.2	78263.4	78265.9	78263.3	78244.6	78265.0(1.2)	[30]
						78263.2(2.4)	[33]
						78262.6(3.0)	[34]
12	95847	95848	95853	95848	95825	95850.6(7.3)	[31]
14	113809	113809	113820	113809	113785	113815(4)	[35]
16	132219	132219	132238	132219	132195	132218(4)	[36]
						132198(10)	[35]
18	151155	151156	151186	151155	151130	151160(7)	[38]
						151204(9)	[37]
26	233469	233471	233604			323558(550)	[39]
36	356822	356828	357330	356823	356911	357400(260)	[40]
92	252.79 eV	252.77 eV	256.63 eV		254.58 eV	260.0(7.9) eV	[41]

[a] The values for Z=3, 4, and 5 have been updated [24].

TABLE IV. $2\,^3P_1$–$2\,^3S_1$ transition energies (in cm^{-1}). The quoted errors for the AO energies do not include Drake's revised QED error estimate [24] for Z = 3, 4, and 5.

Z	AO	CI Ref. [4]	Drake Ref. [2]	Experiment	Ref.
3	18226.10(3)		18226.100(20)[a]	18226.108(1)	[25]
				18226.11206(21)	[26]
4	26853.06(3)		26853.019(44)[a]	26853.0534(3)	[27]
				26853.1(0.2)	[42]
5	35377.37(3)	35377.409(30)	35377.336(86)[a]	35377.424(13)	[28]
6	43886.2	43886.2	43886.2	43886(1)	[29]
7	52429.0	52429.1	52429.2	52428.2(1.1)	[30]
				52429.0(0.6)	[43]
8	61037.3	61037.5	61037.7	61037.6(0.9)	[30]
9	69741.8	69742.1	69742.4	69739.9(3.4)	[31]
				69743.8(3.0)	[32]
10	78563.8	78564.2	78564.7	78565.7(1.8)	[30]
				78566.3(2.4)	[33]
12	96680	96681	96683	96682.8(5.6)	[31]

[a] The values for Z=3, 4, and 5 have been updated [24].

the complete QED treatment of corrections of this order is already included in the QED values given by Drake [2], so these terms must be taken out. Their value is [18]

$$\Delta E_{\rm MB}[(Z\alpha)^3] = \left(\frac{19}{3} - \frac{\pi}{2}\right)\langle\delta^3(\mathbf{r}_{12})\rangle, \qquad (3.3)$$

where

$$\langle\delta^3(\mathbf{r}_{12})\rangle = c\,(Z\alpha)^3 \,. \qquad (3.4)$$

We note that since $\langle\delta^3(\mathbf{r}_{12})\rangle = 0$ for triplet states, contributions of order $(Z\alpha)^3$ are not present for these states. The values of the constant c are $1/(8\pi)$, $6/(243\,\pi)$, and $2/(243\,\pi)$ for the states $1\,^1S_0$, $2\,^1S_0$, and $2\,^1P_1$, respectively. In order to avoid counting the $\Delta E_{\rm MB}[(Z\alpha)^3]$ terms twice, we have subtracted them from Drake's QED values and listed the resulting difference in the sixth col-

TABLE V. $2\,^3P_2$–$2\,^3S_1$ transition energies (in cm^{-1}). The quoted errors for the AO energies do not include Drake's revised QED error estimate [24] for Z = 3, 4, and 5.

Z	AO	CI Ref. [4]	Drake Ref. [2]	MBPT Ref. [3]	MCDF Ref. [6]	Experiment	Ref.
3	18228.20(3)		18228.197(18)[a]			18228.198(1)	[25]
						18228.19935(25)	[26]
4	26867.90(3)		26867.938(36)[a]			26867.9484(3)	[27]
						26867.9(2)	[42]
5	35430.06(3)	35430.060(30)	35430.076(59)[a]			35430.084(9)	[28]
6	44022.0	44022.0	44021.9			44022(1)	[29]
7	52720.0	52720.1	52720.1			52720.2(7)	[30]
						52719.5(6)	[43]
8	61588.9	61589.1	61589.0			61589.7(5)	[30]
9	70699.6	70699.9	70699.8			70697.9(3.5)	[31]
						70700.4(3.0)	[32]
10	80121.8	80121.9	80121.6	80121.9	80110.2	80123.3(8)	[30]
						80121.5(6)	[33]
						80121.1(1.9)	[34]
12	100252	100253	100253	100252	100236	100263(6)	[31]
14	122743	122743	122743	122743	122723	122746(3)	[35]
16	148496	148497	148497	148496	148472	148494(4)	[36]
						148493(5)	[35]
18	178576	178578	178577	178576	178546	178584(10)	[38]
						178591(31)	[37]
20	214170	214174	214172	214170	214136	214225(45)	[44]
22	256683	256688	256685	256683	256642	256746(46)	[45]
26	368742	368752	368745	368742	368692	368976(125)	[39]
28	441908	441920	441910	441907	441854	441950(80)	[46]
36	900009	900044	900012	900008	899983	900010(240)	[40]

[a] The values for Z=3, 4, and 5 have been updated [24].

TABLE VI. $2\,^3P_0$–$2\,^3P_1$ transition energies (in cm^{-1} except for Z = 28, 47, and 64 which are in eV). The quoted errors for the AO energies do not include Drake's revised QED error estimate [24] for Z =4 and 5.

Z	AO	CI Ref. [4]	Drake Ref. [2]	MCDF	Experiment	Ref.
4	11.54(3)		11.60(9)[a]		11.5586(5)	[27]
5	16.22(3)	16.200(30)	16.33(21)[a]		16.203(18)	[28]
6	12.5	12.5	12.7		13.0(1.4)	[29]
7	-8.7	-8.7	-8.2		-8.2(1.6)	[30]
8	-58.8	-58.8	-58.0		-59.2(1)	[30]
9	-151.3	-151.2	-150.0		-149.0(4.8)	[31]
10	-300.7	-300.8	-298.8		-300.7(2.2)	[30]
12	-833.1	-833.8	-829.1		-832.2(9.2)	[31]
28	-2.323 eV	-2.325 eV	-2.309 eV		-2.33(0.15) eV	[47]
47	0.801	0.788	0.933	0.753	0.79(0.04)	[15]
64	18.571	18.548	19.082	18.530	18.57(0.19)	[48]

[a] The values for Z=4 and 5 have been updated [24].

umn of Table I. Total energies are given in the final column. In Table II, the total energies for all ions with Z = 3–24 are listed. We do not list values for $2\,^1P_1$ states for ions with Z = 3–6, since the iteration scheme described above did not converge for these states. For ions with Z = 26–100, only even-Z ions are considered with the exception of Z = 47, for which experimental data are available [15].

In Tables III–VIII, we give transition energies for which experimental results are available. Tables III–V give energies for the transitions $2\,^3P_n$–$2\,^3S_1$ for n=0,1,2, respectively. Table VI gives values for the fine structure splitting $2\,^3P_0$–$2\,^3P_1$. Tables VII and VIII give the results for the $1\,^1S_0$–$2\,^1P_1$ and $1\,^1S_0$–$2\,^3P_1$ transitions for which K_α x-ray experiments have been performed. Comparison is made between the all-order calculations, recent CI calculations [4,19], the unified method of Drake [2], MBPT calculations [3], MCDF calculations [6], and experiment.

We see that there is close agreement between the all-order and MBPT calculations throughout. Since the only corrections accounted for in the present method that are not included in the MBPT calculations [3] are relativistic corrections of fourth and higher order, we expect close agreement. Likewise, there is very good agreement with the CI calculations throughout the isoelectronic sequence. The differences between the CI and all-order values are due to two corrections included in the CI calculations that have not been considered here. The first of these differences is for two or more Breit interactions. The all-order values include only the second-order correction for two Breit interactions, while there are third- and higher-order corrections included in the CI calculations. The second source of difference is from higher-order corrections to the frequency-dependent Breit energy. We include frequency dependence only to first order while the CI calculations include it to higher order.

For the triplet states, agreement with the results of Drake are in general good for the transitions $2\,^3P_1$–$2\,^3S_1$ and $2\,^3P_2$–$2\,^3S_1$, but are not as good for $2\,^3P_0$–$2\,^3S_1$ and the fine structure $2\,^3P_0$–$2\,^3P_1$. The disagreement comes in particular from $(Z\alpha)^4$ corrections missing from Drake's values for the $2\,^3P_0$ state. This issue has already been carefully addressed in Refs. [3,4,20] and will not be further discussed here. For the singlet states, agreement between the present calculation and Drake is also fairly good, though both fall outside of the experimental errors

TABLE VII. $1\,^1S_0$–$2\,^1P_1$ transition energies (in eV).

Z	AO	CI Ref. [19]	Drake Ref. [2]	MCDF Ref. [6]	Experiment	Ref.
16	2460.630		2460.627		2460.649(0.09)	[49]
18	3139.582	3139.617	3139.577	3139.65	3139.553(0.038)	[50]
					3139.6(0.25)	[51]
19	3510.46		3510.46		3510.58(0.12)	[52]
21	4315.41		4315.40		4315.54(0.15)	[52]
22	4749.64	4749.71	4749.63		4749.74(0.17)	[52]
23	5205.16		5205.15		5205.27(0.21)	[52]
24	5682.06	5682.15	5682.05		5682.32(0.40)	[52]
26	6700.43	6700.54	6700.40	6700.60	6700.73(0.20)	[52]
					6700.90(0.25)	[53]
32	10280.19	10280.39	10280.14		10280.70(0.22)	[54]
36	13114.42	13114.70	13114.34	13114.80	13115.45(0.30)	[55]
54	30629.7	30630.6	30629.3	30630.8	30629.1(3.5)	[56]
92	100614	100616	100607		100626(35)	[57]

TABLE VIII. $1\,^1S_0$–$2\,^3P_1$ transition energies (in eV).

Z	AO	CI Ref. [19]	Drake Ref. [2]	MCDF Ref. [6]	Experiment	Ref.
18	3123.534	3123.574	3123.530	3123.59	3123.522(0.036)	[50]
					3123.6(0.24)	[51]
26	6667.57	6667.69	6667.55	6667.75	6667.50(0.25)	[53]
32	10220.76	10220.98	10220.73		10221.80(0.35)	[54]
36	13026.05	13026.36	13026.00	13026.50	13026.8(3)	[55]
54	30205.9	30206.9	30205.6	30206.5	30209.6(3.5)	[56]
92	96172	96178	96167		96171(52)	[57]

for $Z = 26$, 32, and 36 in the case of $2\,^1P_1 - 1\,^1S_0$ transitions. For both the $2\,^1P_1 - 1\,^1S_0$ and $2\,^3P_1 - 1\,^1S_0$ transitions, both CI and MCDF are in better agreement with experiment, though their values are uniformly larger for all Z than are the all-order and Drake calculations and are in worse agreement with experiment for $Z = 18$. We also note that while the discrepancies with Drake for $Z = 92$ are much smaller than the present experimental uncertainties, they still amount to 7 eV for the $2\,^1P_1 - 1\,^1S_0$ transition and 5 eV for the $2\,^3P_1 - 1\,^1S_0$ transition, and will be significant for the next generation of experiments.

IV. DIRECTIONS FOR FUTURE PROGRESS

One of the main drawbacks of MBPT and all-order calculations, and the main source of numerical error in the present work, is the fact that infinite partial wave summations must be dealt with. One possible approach to this problem is the use of asymptotic formulas. As an example, one frequently encounters radial integrals of the form

$$I_L \equiv \int dr \int dr' \frac{r_<^L}{r_>^{L+1}} f(r,r'). \tag{4.1}$$

When L is large this integral is dominated by the region $r' \approx r$, and one easily finds

$$I_L \approx \frac{2L+1}{L(L+1)} \int dr f(r,r). \tag{4.2}$$

In this way large L limits can be calculated, though we have not done this for the present calculation. If higher accuracy is desired, such calculations would allow the analytic summation of the leading $1/L$ dependence, which should lead to much more precise extrapolations. Alternatively, the basis set and numerical methods could be extended to higher angular momentum, although this would be extremely expensive in terms of computer time.

However, the errors of the present calculation are already substantially below experimental precision for a wide range of high-Z ions. It is, in a sense, unfortunate that agreement with experiment is as good as it is. This is because the $(Z\alpha)^4$ a.u. QED corrections referred to in the Introduction are (now that the "structure" part of the helium calculations has been understood) the most interesting theoretical problem left for the helium isoelectronic sequence. At present, the only calculations of such terms are the recent work of Drake *et al.* [21] in which contributions of order $\alpha^4 \ln \alpha$ a.u. are determined for $Z = 2$, and the work of Ref. [18], in which $(Z\alpha)^4$ a.u. contributions associated with two photon exchange are evaluated for the ground state of heliumlike ions. The next theoretical steps must be the extension of the latter calculation to excited states along with the evaluation of radiative corrections where a single photon is exchanged. We note that significant progress in this direction has been made for alkalilike ions [22,23]. The two-loop Lamb shift must also be evaluated at some point, but because loop expansions tend to involve extra powers of α/π, these latter corrections may be numerically small. Because no large discrepancies are presently seen between theory and experiment, the investigation of new QED effects in the helium isoelectronic sequence will require improving the experimental accuracies along with new calculations.

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[1] H. Araki, Prog. Theor. Phys. **17**, 619 (1957); J. Sucher, Phys. Rev. **109**, 1010 (1958).
[2] G. W. F. Drake, Can. J. Phys. **66**, 586 (1988).
[3] W. R. Johnson and J. Sapirstein, Phys. Rev. A **46**, 2197 (1992).
[4] M. H. Chen, K. T. Cheng, and W. R. Johnson, Phys. Rev. A **47**, 3692 (1993).
[5] J. Hata and I. P. Grant, J. Phys. B **16**, 523 (1983); **17**, 931 (1984).
[6] P. Indelicato, Nucl. Instrum. Methods B **31**, 14 (1988);

P. Indelicato, O. Gorceix, and J. P. Desclaux, J. Phys. B **20**, 651 (1987); P. Indelicato, F. Parente, and R. Marrus, Phys. Rev. A **40**, 3505 (1989).

[7] L. A. Vainshtein and U. I. Safronova, Phys. Scr. **31**, 519 (1985).

[8] J. Sucher, Phys. Rev. A **22**, 348 (1980).

[9] W. R. Johnson, S. A. Blundell, and J. Sapirstein, Phys. Rev. A **37**, 307 (1988).

[10] W. R. Johnson and G. Soff, At. Data Nucl. Data Tables **33**, 405 (1985).

[11] J. Sapirstein, Phys. Scr. **T46**, 52 (1993).

[12] W. R. Johnson, S. A. Blundell, and J. Sapirstein, Phys. Rev. A **37**, 2764 (1988).

[13] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed. (Springer-Verlag, Berlin, 1986), p. 189.

[14] C. Schwartz, Phys. Rev. **126**, 1015 (1962).

[15] B. B. Birkett, J. P. Briand, P. Charles, D. D. Dietrich, K. Finlayson, P. Indelicato, D. Liesen, R. Marrus, and A. Simionovici, Phys. Rev. A **47**, 2454 (1993); R. Marrus, A. Simionovici, P. Indelicato, D. D. Dietrich, P. Charles, J. P. Briand, K. Finlayson, F. Bosch, D. Liesen, and F. Parente, Phys. Rev. Lett. **63**, 502 (1989).

[16] J. B. Mann and W. R. Johnson, Phys. Rev. A **4**, 41 (1971).

[17] M. H. Mittleman, Phys. Rev. A **4**, 893 (1971); **5**, 2395 (1972); **24**, 1167 (1981).

[18] S. A. Blundell, P. J. Mohr, W. R. Johnson, and J. Sapirstein, Phys. Rev. A **48**, 2615 (1993).

[19] K. T. Cheng, M. H. Chen, and W. R. Johnson (unpublished).

[20] H. G. Berry, R. W. Dunford, and A. E. Livingston, Phys. Rev. A **47**, 698 (1993).

[21] G. W. F. Drake, I. B. Khriplovich, A. I. Milstein, and A. S. Yelkhovsky, Phys. Rev. A **48**, 15 (1993).

[22] P. Indelicato and P. J. Mohr, Theor. Chim. Acta **80**, 207 (1991).

[23] S. A. Blundell, Phys. Rev. A **47**, 1790 (1993).

[24] G. W. F. Drake, (private communication).

[25] R. A. Holt, S. D. Rosner, T. D. Gaily, and A. G. Adam, Phys. Rev. A **22**, 1563 (1980); R. A. Holt, S. D. Rosner, and T. D. Gaily, *ibid.* **29**, 1544 (1984).

[26] E. Riis, H. G. Berry, O. Poulsen, S. A. Lee, and S. Y. Tang, Phys. Rev. A **33**, 3023 (1986).

[27] T. J. Scholl, R. Cameron, S. D. Rosner, L. Zhang, R. A. Holt, Craig J. Sansonetti, and J. D. Gillaspy, Phys. Rev. Lett. **71**, 2188 (1993).

[28] T. P. Dinneen, N. Berrah-Mansour, H. G. Berry, L. Young, and R. C. Pardo, Phys. Rev. Lett. **66**, 2859 (1991).

[29] B. Edlén and B. Löfstrand, J. Phys. B **3**, 1380 (1970).

[30] M. F. Stamp, D. Phil. thesis, Oxford University, 1983 (unpublished); N. J. Peacock, M. F. Stamp, and J. D. Silver, Phys. Scr. **T8**, 10 (1984).

[31] H. A. Klein, F. Moscatelli, E. G. Myers, E. H. Pinnington, J. D. Silver, and E. Träbert, J. Phys. B **18**, 1483 (1985).

[32] W. Engelhardt and J. Sommer, Astrophys. J. **167**, 201 (1971).

[33] W. A. Hallett, D. D. Dietrich, and J. D. Silver, Phys. Rev. A **47**, 1130 (1993).

[34] H. G. Berry and J. E. Hardis, Phys. Rev. A **33**, 2778 (1986).

[35] R. DeSerio, H. G. Berry, R. L. Brooks, J. Hardis, A. E. Livingston, and S. J. Hinterlong, Phys. Rev. A **24**, 1872 (1981).

[36] E. J. Galvez, Ph.D. thesis, University of Notre Dame, 1990 (unpublished).

[37] H. F. Beyer, F. Folkmann, and K. H. Schartner, Z. Phys. D **1**, 65 (1986).

[38] A. E. Livingston (private communication).

[39] J. P. Buchet, M. C. Buchet-Poulizac, A. Denis, J. Désesquelles, M. Druetta, J. P. Grandin, and X. Husson, Phys. Rev. A **23**, 3354 (1981).

[40] S. Martin, A. Denis, M. C. Buchet-Poulizac, J. P. Buchet, and J. Désesquelles, Phys. Rev. A **42**, 6570 (1990).

[41] C. T. Munger and H. Gould, Phys. Rev. Lett. **57**, 2927 (1986).

[42] B. Löfstrand, Phys. Scr. **8**, 57 (1973).

[43] S. C. Baker, J. Phys. B **6**, 709 (1973).

[44] S. J. Hinterlong and A. E. Livingston, Phys. Rev. A **33**, 4378 (1986).

[45] E. J. Galvez, A. E. Livingston, A. J. Mazure, H. G. Berry, L. Engström, J. E. Hardis, L. P. Somerville, and D. Zei, Phys. Rev. A **33**, 3667 (1986).

[46] A. S. Zacarias, A. E. Livingston, Y. N. Lu, R. F. Ward, H. G. Berry, and R. W. Dunford, Nucl. Instrum. Methods B **31**, 41 (1988); A. S. Zacarias, Ph.D. thesis, University of Notre Dame, 1990 (unpublished).

[47] R. W. Dunford, C. J. Liu, J. Last, N. Berrah-Mansour, R. Vondrasek, D. A. Church, and L. J. Curtis, Phys. Rev. A **44**, 764 (1991).

[48] P. Indelicato, B. B. Birkett, J. P. Briand, P. Charles, D. D. Dietrich, R. Marrus, and A. Simionovici, Phys. Rev. Lett. **68**, 1307 (1992).

[49] L. Schleinkofer, F. Bell, H.-D. Betz, G. Trollmann, and J. Rothermel, Phys. Scr. **25**, 917 (1982).

[50] R. D. Deslattes, H. F. Beyer, and F. Folkmann, J. Phys. B **17**, L689 (1984).

[51] J. P. Briand, J. P. Mossé, P. Indelicato, P. Chevallier, D. Girard-Vernhet, A. Chetioui, M. T. Ramos, and J. P. Desclaux, Phys. Rev. A **28**, 1413 (1983).

[52] P. Beiersdorfer, M. Bitter, S. von Goeler, and K. W. Hill, Phys. Rev. A **40**, 150 (1989).

[53] J. P. Briand, M. Tavernier, R. Marrus, and J. P. Desclaux, Phys. Rev. A **29**, 3143 (1984).

[54] S. MacLaren, P. Beiersdorfer, D. A. Vogel, D. Knapp, R. E. Marrs, K. Wong, and R. Zasadzinski, Phys. Rev. A **45**, 329 (1992).

[55] P. Indelicato, J. P. Briand, M. Tavernier, and D. Liesen, Z. Phys. D **2**, 249 (1986).

[56] J. P. Briand, P. Indelicato, A. Simionovici, V. San Vicente, D. Liesen, and D. Dietrich, Europhys. Lett. **9**, 225 (1989).

[57] J. P. Briand, P. Chevallier, P. Indelicato, K. P. Ziock, and D. D. Dietrich, Phys. Rev. Lett. **65**, 2761 (1990).