

**S-matrix calculations of energy levels of the lithium isoelectronic sequence**

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A QED approach to the calculation of the spectra of the lithium isoelectronic sequence is implemented. A modified Furry representation based on the Kohn-Sham potential is used to evaluate all one- and two-photon diagrams with the exception of the two-loop Lamb shift. Three-photon diagrams are estimated with Hamiltonian methods. After incorporating recent calculations of the two-loop Lamb shift and recoil corrections, a comprehensive tabulation of the  $2s$ ,  $2p_{1/2}$ , and  $2p_{3/2}$  energy levels as well as the  $2s-2p_{1/2}$  and  $2s-2p_{3/2}$  transition energies for  $Z = 10-100$  is presented.

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**I. INTRODUCTION**

The many-body problem in atoms and ions is most often treated in a Hamiltonian formalism. As a starting point the many-electron Schrödinger equation, or a relativistic extension of it, is treated with many-body perturbation theory (MBPT) [1], and QED corrections are then included as perturbations. An example of the first part of this approach is the MBPT treatment of the lithium-like [2] and sodium-like [3] isoelectronic sequences, where a Hartree-Fock potential is taken as a starting point of a perturbation expansion that includes Coulomb interactions through third order, instantaneous Breit interactions through second order, and the effect of retardation on the Breit interaction in lowest order. In these early works discrepancies with experiment were used to infer the QED corrections, but since then the direct calculation of the one-loop Lamb shift has been carried out [4], and the bulk of the discrepancy is removed when the one-loop Lamb shift is added to the MBPT results.

While this approach is successful in accounting for the spectra of the aforementioned sequences at the few tenths of an eV level, subtle effects relating to retardation and negative energy states begin to be important when levels under 0.1 eV are reached in modern experiments for high- $Z$  ions [5–7]. It is rather complicated to restore the effect of negative energy states, which are usually omitted from Hamiltonian treatments in order to avoid the continuum dissolution problem [8], and in addition the treatment of retardation is problematical [9]. These issues can be avoided altogether if the Hamiltonian formalism is simply abandoned and replaced with the Feynman-diagram-oriented approach offered by  $S$ -matrix theory [10], which is used here, or the essentially equivalent Green's function techniques used by the St. Petersburg group [11].

The application of either QED-based theory to highly charged ions is analogous to the QED treatment of the electron anomalous magnetic moment, where evaluation of a limited, unambiguous set of Feynman diagrams accounts

for all relevant physics up to a given precision governed by powers of the fine structure constant  $\alpha$ . For highly charged many-electron ions, the relevant expansion parameter is the number of virtual photons in the Feynman diagrams, with factors of  $\alpha$  or  $1/Z$  providing strong suppression of diagrams with three or more photons. For this reason, only the relatively few diagrams involving one or two photons need to be treated, although weak-field expansion in the parameter  $Z\alpha$ , which simplifies the treatment of light systems, is not suitable for high- $Z$  ions and bound-state electron propagators have to be used. Residual contributions from the large number of three-photon graphs have not yet been calculated with QED methods. They are dominated by correlation diagrams involving photon exchanges between different electrons, and, as is discussed in what follows, can be approximated by using the Hamiltonian method described in the first paragraph. This QED approach has been implemented for highly charged lithium-like ions in Refs. [11] and [12]. The latter paper concentrated on a single transition energy, the  $2s-2p_{3/2}$  splitting for lithium-like bismuth, and used basis-set techniques to evaluate two-photon exchange diagrams. In this paper, we replace the basis-set techniques with differential equation methods and give a complete treatment of the  $2s$ ,  $2p_{1/2}$ , and  $2p_{3/2}$  energy levels, as well as the  $2s-2p_{1/2}$  and  $2s-2p_{3/2}$  transition energies along the isoelectronic sequence.

Three additional theoretical issues enter when high precision is required. The first has to do with the finite mass of the nucleus, which leads to recoil corrections. While suppressed by a factor of  $m/M$ , where  $m$  is the electron mass and  $M$  the mass of the nucleus, these corrections, which are highly nontrivial to calculate, must be included. The second issue is higher-order contributions to the Lamb shift, specifically the two-loop Lamb shift. This effect is sufficiently large at high  $Z$  that its value was inferred in Ref. [12] for lithium-like bismuth, but, as with the one-loop Lamb shift, it can now be calculated directly [13,14]. Finally, the polarizability of some nuclei is large enough that a small but non-negligible effect results. These nuclear polarization corrections have been studied for the  $n = 2$  states of heavy lithium-like ions [15] and will be included in the present ionization and transition energies.

In our previous work [12] we showed that essentially identical results were obtained regardless of the

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model potential used to define the QED representation. Here we specialize to the Kohn-Sham potential [16], a self-consistent local potential similar to the Dirac-Fock potential. In the next section, the  $S$ -matrix formalism is described, and the Kohn-Sham potential defined. In Sec. III, one-photon diagrams are treated. In Sec. IV, two-photon diagrams, with the exception of the two-loop Lamb shift, are evaluated. In Sec. V, the smaller corrections from three-photon diagrams, nuclear recoil, two-loop Lamb shift, and nuclear polarization are discussed. The main result of this paper, Table I, is a comprehensive tabulation of the ionization potentials of the  $2s$ ,  $2p_{1/2}$ , and  $2p_{3/2}$  states for  $Z = 10$ – $100$ , along with the  $2s$ – $2p_{1/2}$  and  $2s$ – $2p_{3/2}$  transition energies. For the sake of brevity, only the complete theoretical result is presented for the isoelectronic series, but to illustrate the importance of the various corrections, the breakdown of contributions for a few ions along the isoelectronic sequence will be given in Table II. A discussion of the comparison of the present theory with experiment and other calculations, along with directions for future progress, is given in the concluding section.

## II. S-MATRIX FORMULATION

$S$ -matrix calculations [10] of atomic structure use the fact that energy levels of an atom can be related to matrix elements of an operator that evolves the atom from  $t = -\infty$  to  $t = \infty$ ,

$$S_{\epsilon,\lambda} = T(e^{-i\lambda \int dt e^{-\epsilon|t|} H_I(t)}), \quad (1)$$

through  $E = E_0 + \Delta E$ , where

$$\Delta E = \lim_{\epsilon \rightarrow 0} \frac{i\epsilon}{2} \lim_{\lambda \rightarrow 1} \frac{\partial}{\partial \lambda} \ln \langle \Phi_0 | S_{\epsilon,\lambda} | \Phi_0 \rangle. \quad (2)$$

Here  $E_0$  is the energy of the atom at times  $t = \pm\infty$ , where the interaction Hamiltonian, defined in what follows, is suppressed by the adiabatic damping factor  $\epsilon$ . For the isoelectronic sequence we will be treating here, the state  $|\Phi_0\rangle$  can be represented in a manner identical to that used in MBPT,

$$|\Phi_0\rangle = a_v^\dagger |0_c\rangle, \quad (3)$$

where  $v$  represents a valence electron and  $|0_c\rangle$  a filled helium-like core. The wave functions are defined by the interaction representation chosen to define  $H_I$  and obey the Dirac equation in a spherically symmetric potential  $U(r)$ ,

$$[\vec{\alpha} \cdot \vec{p} + \beta m + U(r)]\psi_n(\vec{x}) = \epsilon_n \psi_n(\vec{x}), \quad (4)$$

where  $r = |\vec{x}|$ . Natural units in which  $\hbar = c = 1$  are used in this work unless otherwise specified. The lowest-order energy  $E^{(0)}$  is given by

$$E^{(0)} = \epsilon_v + 2\epsilon_a, \quad (5)$$

where  $a$  represents the  $1s_{1/2}$  core state. The second term in the preceding formula for  $E^{(0)}$ , which does not contribute either to valence ionization or transition energies, will be suppressed in the following, and this convention will be followed for the higher-order corrections considered in this paper.

While there are sufficiently few electrons in lithium-like ions that reasonable results can be obtained starting from the Coulomb potential

$$U_C(r) = -\frac{Z_{\text{nuc}}(r)\alpha}{r}, \quad (6)$$

we instead choose to incorporate some screening by using the Kohn-Sham potential [16] defined by

$$U_{\text{KS}}(r) = U_C(r) + \alpha \int dr' \frac{1}{r_{>}} \rho_t(r') - \frac{2}{3} \left[ \frac{81}{32\pi^2} r \rho_t(r) \right]^{1/3} \frac{\alpha}{r}, \quad (7)$$

where

$$\rho_t(r) = g_v^2(r) + f_v^2(r) + 2[g_a^2(r) + f_a^2(r)]. \quad (8)$$

Here  $g(r)$  and  $f(r)$  are the upper and lower components of Dirac wave functions self-consistently determined,  $v$  is the  $2s$  valence electron, and  $Z_{\text{nuc}}(r)$  accounts for the finite size of the nucleus using a Fermi distribution with parameters taken from [17], except for thorium and uranium, where the  $c$  parameters are changed from 6.9264 and 6.9868 fm in [17] to 7.0598 and 7.13753 fm, as deduced from measurements [18,19]. A related potential that will arise in the treatment of screening of the Lamb shift is the core-Hartree (CH) potential defined by

$$U_{\text{CH}}(r) = U_C(r) + \alpha \int dr' \frac{1}{r_{>}} \rho_c(r'), \quad (9)$$

with

$$\rho_c(r) = 2[g_a^2(r) + f_a^2(r)]. \quad (10)$$

Neglecting core energies, the binding energies  $\epsilon_v$  associated with the Kohn-Sham potential are shown as  $E^{(0)}$  for a few lithium-like ions in Table II.

When dealing with free-electron processes, the most appropriate treatment of QED is the interaction representation, which is a unitary transformation that subtracts the free-electron Hamiltonian  $H_0$  from the full Hamiltonian. Early applications of QED to the bound-state problem were primarily concerned with hydrogen and employed a different kind of interaction representation known as the Furry representation [20] in which the interaction of the electron with the Coulomb field of the nucleus is also kept in  $H_0$ . Specifically, the transformation from a Schrödinger picture wave function  $|\Psi_S\rangle$  to a Furry picture wave function  $|\Psi_I\rangle$  is

$$|\Psi_I\rangle = e^{iH_0 t} |\Psi_S\rangle, \quad (11)$$

where

$$H_0 = \int d^3x \psi^\dagger(\vec{x}, t) [\vec{\alpha} \cdot \vec{p} + \beta m + U_C(r)] \psi(\vec{x}, t), \quad (12)$$

and the interaction Hamiltonian is defined as

$$H_I(t) = e \int d^3x \bar{\psi}(\vec{x}, t) \gamma_\mu A^\mu(\vec{x}, t) \psi(\vec{x}, t), \quad (13)$$

with normal ordering understood. This formalism applies equally well to the case when the Coulomb potential  $U_C(r)$  in Eq. (12) is replaced with a non-Coulomb local potential  $U(r)$ , chosen here to be  $U_{\text{KS}}(r)$ , providing that a *counterpotential* term is added to the interaction Hamiltonian,

$$\delta H_I(t) = \int d^3x \psi^\dagger(\vec{x}, t) [U_C(r) - U(r)] \psi(\vec{x}, t). \quad (14)$$

TABLE I. Ionization potentials (a.u.) and transition energies (eV) for the  $n = 2$  states of lithium-like ions.

| Z  | 2s        | 2p <sub>1/2</sub> | 2p <sub>3/2</sub> | 2s-2p <sub>1/2</sub> | 2s-2p <sub>3/2</sub> | Z   | 2s        | 2p <sub>1/2</sub> | 2p <sub>3/2</sub> | 2s-2p <sub>1/2</sub> | 2s-2p <sub>3/2</sub> |
|----|-----------|-------------------|-------------------|----------------------|----------------------|-----|-----------|-------------------|-------------------|----------------------|----------------------|
| 10 | -8.786573 | -8.202716         | -8.195174         | 15.8876              | 16.0928              | 56  | -390.1477 | -385.5147         | -369.4820         | 126.069              | 562.342              |
| 11 | -11.01975 | -10.36338         | -10.35140         | 17.8606              | 18.1867              | 57  | -405.4716 | -400.7209         | -383.4008         | 129.272              | 600.577              |
| 12 | -13.50530 | -12.77626         | -12.75813         | 19.8382              | 20.3315              | 58  | -421.1434 | -416.2728         | -397.5850         | 132.534              | 641.057              |
| 13 | -16.24373 | -15.44179         | -15.41539         | 21.8219              | 22.5403              | 59  | -437.1677 | -432.1748         | -412.0351         | 135.863              | 683.892              |
| 14 | -19.23555 | -18.36047         | -18.32322         | 23.8123              | 24.8258              | 60  | -453.5492 | -448.4315         | -426.7520         | 139.261              | 729.189              |
| 15 | -22.48144 | -21.53287         | -21.48176         | 25.8118              | 27.2026              | 61  | -470.2924 | -465.0478         | -441.7361         | 142.713              | 777.058              |
| 16 | -25.98197 | -24.95961         | -24.89107         | 27.8198              | 29.6850              | 62  | -487.4023 | -482.0293         | -456.9878         | 146.206              | 827.621              |
| 17 | -29.73794 | -28.64142         | -28.55128         | 29.8380              | 32.2907              | 63  | -504.8851 | -499.3811         | -472.5078         | 149.772              | 881.033              |
| 18 | -33.75011 | -32.57898         | -32.46252         | 31.8681              | 35.0371              | 64  | -522.7451 | -517.1085         | -488.2968         | 153.379              | 937.386              |
| 19 | -38.01921 | -36.77309         | -36.62490         | 33.9086              | 37.9411              | 65  | -540.9890 | -535.2170         | -504.3554         | 157.063              | 996.849              |
| 20 | -42.54621 | -41.22462         | -41.03860         | 35.9623              | 41.0242              | 66  | -559.6227 | -553.7123         | -520.6846         | 160.830              | 1059.56              |
| 21 | -47.33211 | -45.93451         | -45.70381         | 38.0308              | 44.3084              | 67  | -578.6484 | -572.6002         | -537.2850         | 164.579              | 1125.56              |
| 22 | -52.37781 | -50.90371         | -50.62065         | 40.1124              | 47.8148              | 68  | -598.0810 | -591.8871         | -554.1573         | 168.545              | 1195.23              |
| 23 | -57.68441 | -56.13326         | -55.78933         | 42.2089              | 51.5677              | 69  | -617.9178 | -611.5790         | -571.3025         | 172.486              | 1268.47              |
| 24 | -63.25298 | -61.62422         | -61.21002         | 44.3209              | 55.5918              | 70  | -638.1702 | -631.6827         | -588.7214         | 176.535              | 1345.57              |
| 25 | -69.08477 | -67.37775         | -66.88297         | 46.4505              | 59.9142              | 71  | -658.8459 | -652.2056         | -606.4146         | 180.693              | 1426.73              |
| 26 | -75.18098 | -73.39500         | -72.80837         | 48.5989              | 64.5620              | 72  | -679.9497 | -673.1556         | -624.3826         | 184.876              | 1512.06              |
| 27 | -81.54295 | -79.67733         | -78.98646         | 50.7662              | 69.5656              | 73  | -701.4919 | -694.5404         | -642.6262         | 189.159              | 1601.82              |
| 28 | -88.17198 | -86.22608         | -85.41744         | 52.9507              | 74.9548              | 74  | -723.4766 | -716.3678         | -661.1463         | 193.441              | 1696.10              |
| 29 | -95.06961 | -93.04267         | -92.10162         | 55.1558              | 80.7632              | 75  | -745.9182 | -738.6462         | -679.9436         | 197.881              | 1795.26              |
| 30 | -102.2373 | -100.1285         | -99.03921         | 57.3821              | 87.0231              | 76  | -768.8199 | -761.3839         | -699.0192         | 202.345              | 1899.37              |
| 31 | -109.6765 | -107.4851         | -106.2305         | 59.6316              | 93.7714              | 77  | -792.1926 | -784.5898         | -718.3739         | 206.882              | 2008.71              |
| 32 | -117.3890 | -115.1141         | -113.6758         | 61.9035              | 101.044              | 78  | -816.0463 | -808.2734         | -738.0087         | 211.510              | 2123.51              |
| 33 | -125.3765 | -123.0172         | -121.3753         | 64.1994              | 108.879              | 79  | -840.3900 | -832.4441         | -757.9245         | 216.218              | 2244.00              |
| 34 | -133.6408 | -131.1962         | -129.3294         | 66.5196              | 117.317              | 80  | -865.2323 | -857.1120         | -778.1223         | 220.966              | 2370.38              |
| 35 | -142.1836 | -139.6528         | -137.5384         | 68.8659              | 126.401              | 81  | -890.5884 | -882.2884         | -798.6029         | 225.855              | 2503.05              |
| 36 | -151.0070 | -148.3890         | -146.0027         | 71.2399              | 136.174              | 82  | -916.4651 | -907.9848         | -819.3671         | 230.760              | 2642.17              |
| 37 | -160.1129 | -157.4066         | -154.7224         | 73.6423              | 146.682              | 83  | -942.8748 | -934.2122         | -840.4160         | 235.721              | 2788.04              |
| 38 | -169.5035 | -166.7079         | -163.6981         | 76.0731              | 157.974              | 84  | -969.8326 | -960.9831         | -861.7507         | 240.806              | 2941.06              |
| 39 | -179.1809 | -176.2949         | -172.9300         | 78.5335              | 170.097              | 85  | -997.3441 | -988.3106         | -883.3720         | 245.814              | 3101.34              |
| 40 | -189.1475 | -186.1698         | -182.4185         | 81.0253              | 183.104              | 86  | -1025.424 | -1016.208         | -905.2811         | 250.776              | 3269.26              |
| 41 | -199.4054 | -196.3351         | -192.1641         | 83.5488              | 197.047              | 87  | -1054.097 | -1044.691         | -927.4787         | 255.954              | 3445.45              |
| 42 | -209.9572 | -206.7929         | -202.1670         | 86.1041              | 211.982              | 88  | -1083.366 | -1073.772         | -949.9662         | 261.083              | 3630.00              |
| 43 | -220.8055 | -217.5459         | -212.4277         | 88.6964              | 227.969              | 89  | -1113.254 | -1103.467         | -972.7445         | 266.311              | 3823.46              |
| 44 | -231.9527 | -228.5967         | -222.9467         | 91.3199              | 245.066              | 90  | -1143.741 | -1133.791         | -995.8155         | 270.743              | 4025.25              |
| 45 | -243.4017 | -239.9480         | -233.7242         | 93.9791              | 263.338              | 91  | -1174.936 | -1164.768         | -1019.179         | 276.669              | 4238.37              |
| 46 | -255.1554 | -251.6026         | -244.7608         | 96.6765              | 282.849              | 92  | -1206.719 | -1196.406         | -1042.837         | 280.652              | 4459.46              |
| 47 | -267.2166 | -263.5631         | -256.0570         | 99.4141              | 303.667              | 93  | -1239.273 | -1228.736         | -1066.790         | 286.708              | 4693.50              |
| 48 | -279.5882 | -275.8327         | -267.6132         | 102.192              | 325.858              | 94  | -1272.477 | -1261.769         | -1091.040         | 291.376              | 4937.14              |
| 49 | -292.2738 | -288.4144         | -279.4299         | 105.020              | 349.502              | 95  | -1306.418 | -1295.529         | -1115.588         | 296.308              | 5192.76              |
| 50 | -305.2764 | -301.3113         | -291.5076         | 107.897              | 374.668              | 96  | -1341.095 | -1330.038         | -1140.435         | 300.890              | 5460.25              |
| 51 | -318.5993 | -314.5269         | -303.8468         | 110.816              | 401.436              | 97  | -1376.544 | -1365.321         | -1165.582         | 305.400              | 5740.56              |
| 52 | -332.2459 | -328.0650         | -316.4479         | 113.769              | 429.885              | 98  | -1412.778 | -1401.403         | -1191.031         | 309.526              | 6034.05              |
| 53 | -346.2207 | -341.9290         | -329.3114         | 116.781              | 460.124              | 99  | -1449.814 | -1438.309         | -1216.782         | 313.055              | 6341.12              |
| 54 | -360.5261 | -356.1228         | -342.4379         | 119.821              | 492.206              | 100 | -1487.696 | -1476.073         | -1242.837         | 316.288              | 6662.94              |
| 55 | -375.1674 | -370.6500         | -355.8279         | 122.923              | 526.255              |     |           |                   |                   |                      |                      |

When the field operators in the preceding equation are replaced with specific wave functions, we encounter the frequently occurring matrix element

$$\tilde{U}_{ij} \equiv \int d^3x \psi_i^\dagger(\vec{x}) \tilde{U}(r) \psi_j(\vec{x}), \quad (15)$$

where  $\tilde{U}(r) \equiv U_C(r) - U(r) = U_C(r) - U_{KS}(r)$  here. In this paper we are concerned with terms up to fourth order in  $H_I(t)$  and second order in  $\delta H_I(t)$ , which correspond to Feynman diagrams with up to two virtual photons.

### III. ONE-PHOTON PHYSICS

The diagrams involving one photon are shown in Fig. 1. If we define the matrix element

$$g_{ijkl}(E) = \alpha \int d^3x d^3y \frac{e^{iE|\vec{x}-\vec{y}|}}{|\vec{x}-\vec{y}|} \bar{\psi}_i(\vec{x}) \gamma^\mu \psi_k(\vec{x}) \bar{\psi}_j(\vec{y}) \gamma_\mu \psi_l(\vec{y}), \quad (16)$$

the one-photon exchange term of Fig. 1(a) and the counterpotential term of Fig. 1(b) give the energy shift

$$E^{(1)} = \sum_a [g_{avav}(0) - g_{avva}(E_{va})] - \tilde{U}_{vv}, \quad (17)$$

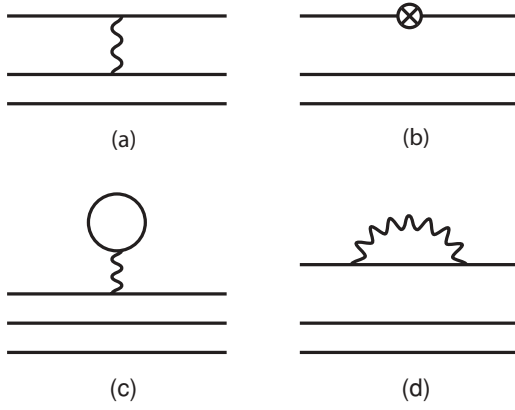


FIG. 1. One-photon correlation and radiative diagrams. A cross inside a circle represents a counterpotential.

where  $E_{va} = \epsilon_v - \epsilon_a$ . This part of one-photon physics we refer to as *structure*-related, as we do with any diagram that has, as a limit, an expression from MBPT. Specifically, while we work in the Feynman gauge, were we to work in the Coulomb gauge, the Coulomb photon part of  $E^{(1)}$  would exactly reproduce first-order MBPT results when only Coulomb interactions are included. We note here that because we use a local potential, gauge invariance ensures that a complete Coulomb gauge calculation, including retarded transverse-photon exchange, would reproduce the results of the present Feynman gauge calculation. The contributions of  $E^{(1)}$  are given in Table II. We present only its real part, but note that an imaginary part, related to the decay rate of the ion, is also in general present. While this plays no role in one-photon exchange, it plays a role in the two-photon calculations described below.

More difficult to evaluate are the radiative diagrams of Figs. 1(c) and 1(d) for the one-loop vacuum-polarization and self-energy, respectively. The vacuum polarization term in the Uehling approximation is given by

$$E_{\text{Uel}}^{\text{VP}} = \frac{\alpha^2}{4\pi^2} \int_0^1 dy \frac{y^2(1-y^2/3)}{1-y^2} \int d^3x \psi_v^\dagger(\vec{x}) \psi_v(\vec{x}) \times \int d^3r \frac{e^{-\frac{2m|\vec{x}-\vec{r}|}{\sqrt{1-y^2}}}}{|\vec{x}-\vec{r}|} \nabla_r^2 \left( \frac{Z_{\text{eff}}(r)}{r} \right), \quad (18)$$

where  $Z_{\text{eff}}(r) = -rU_{\text{KS}}(r)/\alpha$  is the effective charge for the Kohn-Sham potential. In addition, Wichmann-Kroll [21]

corrections  $E_{\text{WK}}^{\text{VP}}$ , must be added. We have developed techniques for the evaluation of both parts of the vacuum polarization calculation. The Wichmann-Kroll part of the calculation, in particular, is similar to the self-energy calculation and involves partial-wave expansions in configuration space using numerical bound-state Green's functions. Our method has been described in Ref. [22]. The present vacuum polarization results are shown as ‘‘Uehling’’ and ‘‘WK’’ in Table II.

The self-energy (SE) can be written as  $E_{1\gamma}^{\text{SE}} = \Sigma_{vv}(\epsilon_v)$ , where

$$\Sigma_{jl}(\epsilon) \equiv -ie^2 \int d^3x \int d^3y \int \frac{d^n k}{(2\pi)^n} \frac{e^{i\vec{k}\cdot(\vec{x}-\vec{y})}}{k^2 + i\delta} \times \bar{\psi}_j(\vec{x}) \gamma_\mu S_F(\vec{x}, \vec{y}; \epsilon - k_0) \gamma^\mu \psi_l(\vec{y}), \quad (19)$$

and the self-mass counterterm is understood to be included. In the preceding equation,  $n = 4 - \epsilon$  is used to regulate the integral over  $k$ , and after renormalization the limit  $\epsilon \rightarrow 0$  is taken. Here, self-energies are calculated nonperturbatively to all orders of  $Z\alpha$  with partial-wave expansions in configuration space using numerical bound-state Green's functions. Subtraction terms involving the free-electron propagator are evaluated in momentum space with Fourier-transformed wave functions. Details of these calculations, with references to earlier works, can be found in [23]. As mentioned earlier, we do not consider the self-energies of the core states, but note that they enter into the two-photon calculation. As with one-photon exchange, imaginary parts are generally present and play a role in the two-photon calculation. The real parts of the self-energies are presented as ‘‘SE’’ in Table II.

## IV. TWO-PHOTON PHYSICS

### A. Structure diagrams

We begin our discussion of two-photon physics with correlation diagrams in which there is only one electron propagator between two virtual photons that are exchanged among three different electrons [Fig. 2(a)], between a virtual photon and a counterpotential [Fig. 2(b)] and between two counterpotentials [Fig. 2(c)]. Since we omit diagrams in which the photons interact with only core electrons, there will always be one valence electron  $v$  and up to two core electrons  $a$  and  $b$ . Defining  $E_{ij} = \epsilon_i - \epsilon_j$ , we find

$$\begin{aligned} \Delta E_{2\gamma} = & \sum_{abi}^{i \neq v} \frac{[g_{bvbi}(0) - g_{vbvi}(E_{vb})][g_{iava}(0) - g_{iaav}(E_{va})]}{\epsilon_v - \epsilon_i} + \sum_{abi}^{i \neq a} \frac{[g_{vavi}(0) - g_{vavv}(-E_{va})][g_{ibab}(0) - g_{ibba}(E_{ab})]}{\epsilon_a - \epsilon_i} \\ & + \sum_{abi}^{i \neq a} \frac{[g_{viva}(0) - g_{vivv}(-E_{va})][g_{abib}(0) - g_{abbi}(E_{ab})]}{\epsilon_a - \epsilon_i} - \sum_{abi} \frac{[g_{avbi}(E_{ab}) - g_{avib}(E_{vb})][g_{ibva}(E_{ab}) - g_{ibav}(E_{vb})]}{\epsilon_a + \epsilon_v - \epsilon_i - \epsilon_b} \\ & + \sum_{abi} \frac{[g_{bavi}(-E_{vb}) - g_{abvi}(-E_{va})]g_{ivba}(-E_{av})}{\epsilon_a + \epsilon_b - \epsilon_v - \epsilon_i} - \sum_{ai}^{i \neq v} \frac{[g_{avai}(0) - g_{vaa}(E_{va})]\tilde{U}_{iv} + \tilde{U}_{vi}[g_{iaiv}(0) - g_{iaav}(E_{av})]}{\epsilon_v - \epsilon_i} \\ & - \sum_{ai}^{i \neq a} \frac{[g_{aviv}(0) - g_{vavv}(-E_{va})]\tilde{U}_{ia} + \tilde{U}_{ai}[g_{ivav}(0) - g_{ivva}(-E_{va})]}{\epsilon_a - \epsilon_i} + \sum_i^{i \neq v} \frac{\tilde{U}_{vi}\tilde{U}_{iv}}{\epsilon_v - \epsilon_i}. \end{aligned} \quad (20)$$

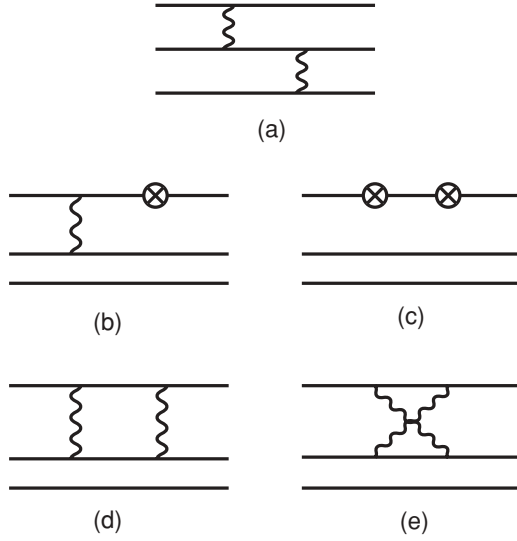


FIG. 2. Two-photon correlation diagrams. A cross inside a circle represents a counterpotential.

Note that the sign of  $E$  in  $g_{ijkl}(E)$  is significant. Furthermore, there is a second kind of contribution coming from these graphs known as derivative terms, which are sensitive to that sign. They are associated with the  $i = v$  and  $i = a$  terms excluded in the preceding equation and are given by

$$\begin{aligned} \Delta E'_{2\gamma} = & \sum_{ab} g'_{avvb}(E_{va})[g_{vbva}(0) - g_{vbav}(E_{va})] \\ & - \sum_{ab} g'_{vbaa}(-E_{va})[g_{vaba}(0) - g_{vaab}(0)] \\ & - \sum_{ab} g'_{vbbv}(E_{va})[g_{vava}(0) - g_{vaav}(E_{va})] \\ & + \tilde{U}_{vv} \sum_a g'_{vaav}(E_{va}) + \tilde{U}_{aa} \sum_a g'_{vaav}(-E_{va}). \quad (21) \end{aligned}$$

The second structure-related class of two-photon diagrams are shown in Figs. 2(d) and 2(e), which we refer to as the ladder (L) and crossed-ladder (X) diagrams, respectively. They give the energy shifts

$$\begin{aligned} \Delta E_L = & \frac{i}{2\pi} \sum_{aij} \int_{-\infty}^{\infty} dz \\ & \times \frac{g_{ijav}(z)[g_{avij}(z) - g_{avji}(z - E_{va})]}{[\epsilon_a + z - \epsilon_i(1 - i\delta)][\epsilon_v - z - \epsilon_j(1 - i\delta)]} \quad (22) \end{aligned}$$

and

$$\begin{aligned} \Delta E_X = & \frac{i}{2\pi} \sum_{aij} \int_{-\infty}^{\infty} dz \\ & \times \left\{ \frac{g_{ajiv}(z)g_{ivaj}(z)}{[\epsilon_a + z - \epsilon_i(1 - i\delta)][\epsilon_v + z - \epsilon_j(1 - i\delta)]} \right. \\ & \left. - \frac{g_{ajia}(z)g_{ivvj}(z - E_{va})}{[\epsilon_a + z - \epsilon_i(1 - i\delta)][\epsilon_a + z - \epsilon_j(1 - i\delta)]} \right\}. \quad (23) \end{aligned}$$

The analysis of these diagrams, which are structure-related inasmuch as they include contributions to the second-order MBPT result, is complicated, but parallels the treatment of the ladder and crossed ladder for excited states in helium [24], where more details can be found. The most computationally intensive part of the evaluation of these diagrams involves the  $z$  integration. A Wick rotation  $z \rightarrow i\omega$  leads to terms in which the contour surrounds poles or photon cuts plus the  $\omega$  integral, which is evaluated with Gaussian integration. If done with finite basis sets, considerable computational time is needed even when the partial-wave expansion of the propagators is relatively limited. To avoid this problem, we use differential equation techniques instead. When using this method, the relative magnitudes of the four position vectors involved must be considered, which leads to 24 regions for each diagram ( $x < y < z < w$ ,  $y < x < z < w$ , etc.). While this entails more coding than that required for finite basis sets, the resulting programs run far more quickly and allow us to extend the partial-wave expansion to  $l = 20$ . Use of this form of the propagator encounters one complication of note, which involves the fact that certain intermediate states must be excluded. As differential equation techniques implicitly include all intermediate states, they lead to linear divergences in two of the diagrams, the ladder direct and crossed-ladder direct. It can be shown, however, that the excluded states that cancel these divergences are equal and opposite in sign, so we simply combine these terms to obtain a finite answer. The result still includes certain finite terms coming from states that should be excluded, but these are simply evaluated independently and subtracted.

The sum of the two-photon structure diagrams is denoted  $E^{(2)}$  in Table II. It is notable that this rather involved set of calculations gives a result quite close to the MBPT procedure of Ref. [2], even though MBPT excludes contributions from the negative energy states and its treatment of retardation is less complete than the present approach. However, small differences that are important at the level of the most precise experiments do exist. An important example involves the  $2s-2p_{3/2}$  transition energy of lithium-like bismuth, where the inference of the two-loop Lamb shift requires a QED approach [12]. Specifically, the Hamiltonian method described in the Introduction contributes 0.174 eV in second order. While this calculation is part of the complete QED calculation, from Table II we see a very different  $E^{(2)}$  result of 0.052 eV. The difference of 0.122 eV is relatively small compared to most experimental uncertainties, but the high-precision electron-beam ion trap (EBIT) measurement [5] for lithium-like bismuth, which has achieved an accuracy of 0.039 eV, makes it important. In particular, since this difference is about the same size as the two-loop Lamb shift but of the opposite sign, were MBPT to be used and combined with an accurate screened Lamb-shift calculation, agreement with experiment would have been found, and the two-loop Lamb shift would have been inferred to be negligible. Use of the correct treatment of the structure term in Ref. [12], however, led to a discrepancy of 0.175 eV, which was identified as due mainly to the two-loop Lamb shift, a finding subsequently confirmed by the St. Petersburg group [13,14] with direct calculations.

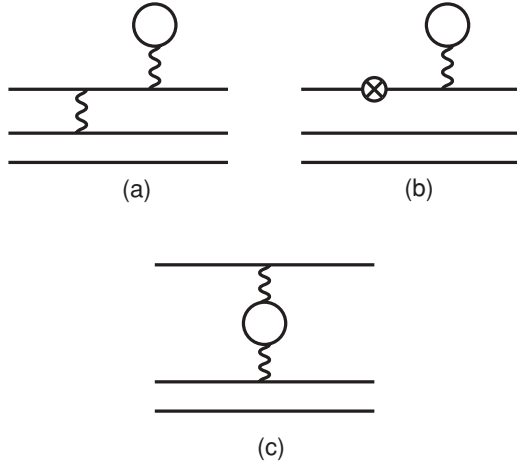


FIG. 3. Screened vacuum polarization diagrams. A cross inside a circle represents a counterpotential.

### B. Lamb-shift screening diagrams

Excluding two-loop Lamb shift, the two-photon diagrams that involve radiative corrections are shown in Figs. 3 and 4. We have in a previous paper [22] described the evaluation of screening corrections to vacuum polarization, depicted in Fig. 3, and refer details of these calculations to that work. The treatment of screening of the self-energy requires the evaluation of the graphs of Fig. 4. We begin with Figs. 4(a) and 4(b) in which a self-energy diagram is present with an exchanged photon or a counterpotential to one side. When the intermediate propagator is represented as a spectral decomposition and has no states degenerate with the core or valence states, the effect of these diagrams can be treated as self-energy diagrams with one state replaced with a perturbed orbital, and we have the contributions

$$\Sigma^{\text{PO}} = \Sigma_{v\bar{v}} + \Sigma_{\bar{v}v} + \sum_a (\Sigma_{a\bar{a}} + \Sigma_{\bar{a}a}), \quad (24)$$

where

$$\begin{aligned} \psi_{\bar{v}}(\vec{y}) \equiv & \alpha \sum_{m \neq v, a} \int \frac{d^3 z d^3 w}{|\vec{z} - \vec{w}|} \frac{\psi_m(\vec{y})}{\epsilon_v - \epsilon_m} \\ & \times [\bar{\psi}_m(\vec{z}) \gamma_\mu \psi_v(\vec{z}) \bar{\psi}_a(\vec{w}) \gamma^\mu \psi_a(\vec{w}) \\ & - e^{iE_{va}|\vec{z}-\vec{w}|} \bar{\psi}_m(\vec{z}) \gamma_\mu \psi_a(\vec{z}) \bar{\psi}_a(\vec{w}) \gamma^\mu \psi_v(\vec{w})] \\ & - \sum_{m \neq v} \int d^3 z \frac{\psi_m(\vec{y})}{\epsilon_v - \epsilon_m} \psi_m^\dagger(\vec{z}) \tilde{U}(z) \psi_v(\vec{z}) \end{aligned} \quad (25)$$

is a valence orbital perturbed either by the exchange of a photon with the core electrons or else by the counterpotential  $\tilde{U}(z)$ , and

$$\begin{aligned} \psi_{\bar{a}}(\vec{y}) \equiv & \alpha \sum_{m \neq a}^{\kappa_m = \kappa_a} \int \frac{d^3 z d^3 w}{|\vec{z} - \vec{w}|} \frac{\psi_m(\vec{y})}{\epsilon_a - \epsilon_m} \\ & \times [\bar{\psi}_m(\vec{z}) \gamma_\mu \psi_a(\vec{z}) \bar{\psi}_v(\vec{w}) \gamma^\mu \psi_v(\vec{w}) \\ & - e^{iE_{va}|\vec{z}-\vec{w}|} \bar{\psi}_m(\vec{z}) \gamma_\mu \psi_v(\vec{z}) \bar{\psi}_v(\vec{w}) \gamma^\mu \psi_a(\vec{w})] \end{aligned} \quad (26)$$

is a core orbital perturbed by the exchange of a photon with the valence electron.

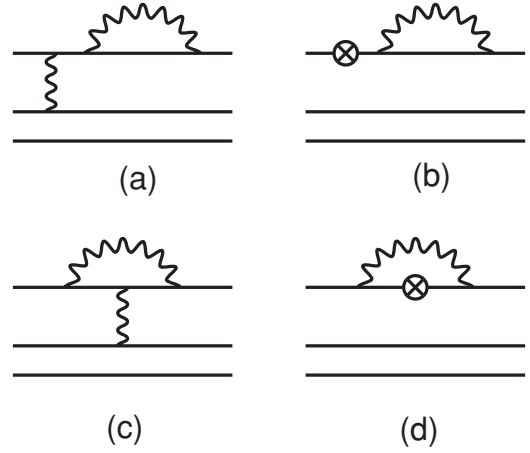


FIG. 4. Screened self-energy diagrams. A cross inside a circle represents a counterpotential.

When there is a degeneracy, derivative terms arise in which either the energy dependence of the self-energy function or the one-photon exchange part of the diagram gets differentiated. This leads to a single expression for the *valence* derivative term,

$$E_{der}(v) = E_v^{(1)} \Sigma'_{vv}(\epsilon_v) - \sum_a g'_{vavv}(E_{va}) \Sigma_{vv}(\epsilon_v), \quad (27)$$

and a set of *core* derivative terms,

$$\begin{aligned} E_{der}(a) = & \Sigma'_{aa} \sum_a [g_{vava}(0) - g_{avva}(-E_{va})] \\ & - \Sigma_{aa} \sum_a g'_{avva}(-E_{va}). \end{aligned} \quad (28)$$

These derivative terms have ultraviolet divergent parts that cancel with the vertex diagrams discussed in what follows. The ultraviolet divergent part comes from the part of the electron propagator when it is free, so this term is treated separately. The remaining term, where the full propagator has the free propagator subtracted to form an ultraviolet finite quantity, breaks into two terms upon the Wick rotation  $k_0 \rightarrow i\omega$ , one in which the  $\omega$  integration is carried out numerically and one in which double poles are encircled during the Wick rotation, which leads to a derivative term. The  $\omega$  integration has singularities at small  $\omega$  that we regulate through the device of taking  $\epsilon_v \rightarrow \epsilon_v(1 - \delta)$  and  $\epsilon_a \rightarrow \epsilon_a(1 - \delta)$ . The resulting integrals have a  $\ln(\delta)$  dependence that cancels similar behavior present in the vertex diagrams discussed in what follows.

We now treat the two vertex diagrams of Figs. 4(c) and 4(d), calling the contributions  $\Delta E_i$ ,  $i = 1 - 5$ , where

$$\begin{aligned} \Delta E_1 = & -4i\pi\alpha^2 \sum_a \int d^3 x d^3 y d^3 z d^3 w \frac{1}{|\vec{y} - \vec{w}|} \\ & \times \int \frac{d^n k}{(2\pi)^n} \frac{e^{i\vec{k}\cdot(\vec{x}-\vec{z})}}{k^2} \bar{\psi}_v(\vec{x}) \gamma_\mu S_F(\vec{x}, \vec{y}; \epsilon_v - k_0) \\ & \times \gamma_\nu S_F(\vec{y}, \vec{z}; \epsilon_v - k_0) \gamma^\mu \psi_v(\vec{z}) \bar{\psi}_a(\vec{w}) \gamma^\nu \psi_a(\vec{w}), \end{aligned} \quad (29)$$

$$\begin{aligned} \Delta E_2 &= 4i\pi\alpha^2 \sum_a \int d^3x d^3y d^3z d^3w \frac{e^{iE_{va}|\vec{y}-\vec{w}|}}{|\vec{y}-\vec{w}|} \\ &\times \int \frac{d^n k}{(2\pi)^n} \frac{e^{i\vec{k}\cdot(\vec{x}-\vec{z})}}{k^2} \bar{\psi}_v(\vec{x}) \gamma_\mu S_F(\vec{x}, \vec{y}; \epsilon_v - k_0) \gamma_\nu \\ &\times S_F(\vec{y}, \vec{z}; \epsilon_a - k_0) \gamma^\mu \psi_a(\vec{z}) \bar{\psi}_a(\vec{w}) \gamma^\nu \psi_v(\vec{w}), \end{aligned} \quad (30)$$

$$\begin{aligned} \Delta E_3 &= -4i\pi\alpha^2 \sum_a \int d^3x d^3y d^3z d^3w \frac{1}{|\vec{y}-\vec{w}|} \\ &\times \int \frac{d^n k}{(2\pi)^n} \frac{e^{i\vec{k}\cdot(\vec{x}-\vec{z})}}{k^2} \bar{\psi}_a(\vec{x}) \gamma_\mu S_F(\vec{x}, \vec{y}; \epsilon_a - k_0) \gamma_\nu \\ &\times S_F(\vec{y}, \vec{z}; \epsilon_a - k_0) \gamma^\mu \psi_a(\vec{z}) \bar{\psi}_v(\vec{w}) \gamma^\nu \psi_v(\vec{w}), \end{aligned} \quad (31)$$

$$\begin{aligned} \Delta E_4 &= 4i\pi\alpha^2 \sum_a \int d^3x d^3y d^3z d^3w \frac{e^{iE_{va}|\vec{y}-\vec{w}|}}{|\vec{y}-\vec{w}|} \\ &\times \int \frac{d^n k}{(2\pi)^n} \frac{e^{i\vec{k}\cdot(\vec{x}-\vec{z})}}{k^2} \bar{\psi}_a(\vec{x}) \gamma_\mu S_F(\vec{x}, \vec{y}; \epsilon_a - k_0) \gamma_\nu \\ &\times S_F(\vec{y}, \vec{z}; \epsilon_v - k_0) \gamma^\mu \psi_v(\vec{z}) \bar{\psi}_v(\vec{w}) \gamma^\nu \psi_a(\vec{w}), \end{aligned} \quad (32)$$

$$\begin{aligned} \Delta E_5 &= -4i\pi\alpha \int d^3x d^3y d^3z \\ &\times \int \frac{d^n k}{(2\pi)^n} \frac{e^{i\vec{k}\cdot(\vec{x}-\vec{z})}}{k^2} \bar{\psi}_v(\vec{x}) \gamma_\mu S_F(\vec{x}, \vec{y}; \epsilon_v - k_0) \gamma_0 \\ &\times \tilde{U}(y) S_F(\vec{y}, \vec{z}; \epsilon_v - k_0) \gamma^\mu \psi_v(\vec{z}). \end{aligned} \quad (33)$$

Here  $\Delta E_1$  and  $\Delta E_2$  are the direct and exchange vertex terms of Fig. 4(c) for the valence electron while  $\Delta E_3$  and  $\Delta E_4$  are those for the core electron. As for  $\Delta E_5$ , it is the counterpotential vertex term of Fig. 4(d). We can combine  $\Delta E_1$  and  $\Delta E_5$  because angular momentum and parity selection rules restrict the value of  $\nu$  to 0 in the former, which allows the  $d^3w$  integration and summation over  $a$  to be carried out, leading to the screening part of the core-Hartree potential,  $U_{\text{CH}}(y) - U_{\text{C}}(y) = \alpha \int dy' \frac{1}{y'} \rho_c(y')$ , defined in Eq. (9). Rather than evaluate  $\Delta E_1$  and  $\Delta E_5$  separately, we instead treat their sum,

$$\begin{aligned} \Delta E_{15} &= 4i\pi\alpha \int d^3x d^3y d^3z \int \frac{d^n k}{(2\pi)^n} \frac{e^{i\vec{k}\cdot(\vec{x}-\vec{z})}}{k^2} \bar{\psi}_v(\vec{x}) \gamma_\mu S_F \\ &\times (\vec{x}, \vec{y}; \epsilon_v - k_0) \gamma_0 \Delta U(y) S_F(\vec{y}, \vec{z}; \epsilon_v - k_0) \gamma^\mu \psi_v(\vec{z}), \end{aligned} \quad (34)$$

where  $\Delta U \equiv U - U_{\text{CH}} = U_{\text{KS}} - U_{\text{CH}}$  here. Note that had one used the core-Hartree potential, so that  $U = U_{\text{CH}}$ ,  $\Delta E_{15}$  would vanish. Similar cancelations also take place between the valence-direct *side* term and the counterpotential *side* term arising from the first and third terms in Eq. (25), as well as between the valence-direct and counterpotential terms in screened vacuum polarization calculations. The use of the core-Hartree potential thus simplifies the evaluation of screened Lamb shifts for alkali-like ions, a fact utilized by Blundell [25] in his QED calculations.

Besides combining  $\Delta E_1$  and  $\Delta E_5$  into  $\Delta E_{15}$ , a further simplification occurs for the core-direct term  $\Delta E_3$  which, like the valence-direct term  $\Delta E_1$ , can be shown to have only  $\nu = 0$ .

In this case the core electron can be thought of as being *screened* by the valence electron with the potential

$$Y_{vv}(r) = \alpha \int_{r'} \frac{1}{r'} [g_v(r')^2 + f_v(r')^2], \quad (35)$$

and we can write

$$\begin{aligned} \Delta E_3 &= -4i\pi\alpha \sum_a \int d^3x d^3y d^3z \int \frac{d^n k}{(2\pi)^n} \frac{e^{i\vec{k}\cdot(\vec{x}-\vec{z})}}{k^2} \bar{\psi}_a(\vec{x}) \gamma_\mu \\ &\times S_F(\vec{x}, \vec{y}; \epsilon_a - k_0) \gamma_0 Y_{vv}(y) S_F(\vec{y}, \vec{z}; \epsilon_a - k_0) \gamma^\mu \psi_a(\vec{z}). \end{aligned} \quad (36)$$

No simplifications are possible for the two exchange terms  $\Delta E_2$  and  $\Delta E_4$  outside of noting that they are equal to one another: Their evaluation is the most challenging part of the screening calculation.

All of the preceding expressions are ultraviolet divergent as  $n = 4 - \epsilon \rightarrow 4$ , but the divergences arise only from terms in which both electron propagators are treated as free propagators. For this reason we begin by evaluating  $\Delta E_i$  in this approximation, denoting such terms  $\Delta E_i(0,0)$ . It is possible to isolate the ultraviolet divergent part of these terms, which behave as  $1/\epsilon$  and can be shown to exactly cancel the divergences arising from the derivative terms mentioned earlier. There remains the ultraviolet finite part of  $\Delta E_i(0,0)$ , which involves certain difficulties associated with the treatment of angular momentum and the fact that there are imaginary parts in the integrals, which are treated as described in Ref. [12].

We next form the ultraviolet finite combination  $\Delta E_i - \Delta E_i(0,0)$  in coordinate space. As with the ladder and crossed-ladder diagrams, we first carry out a Wick rotation of the  $k_0$  integration,  $k_0 \rightarrow i\omega$ , which passes a set of poles. The remaining integration over  $\omega$  has the same singularities mentioned in connection with the derivative terms and are regulated in the same manner. The sums of all the correction terms give the screened self-energy contributions, which are shown as “SE-screen” in Table II, along with the screened vacuum polarization contributions which are shown as “VP-screen.”

## V. RESIDUAL CORRECTIONS

### A. Three-photon effects

A QED treatment of three-photon effects is a large-scale task that has not yet been carried out. However, as discussed earlier, second-order MBPT roughly reproduces the full QED calculation. For this reason, to approximate three-photon effects we simply use third-order MBPT (tabulated as  $E^{(3)}$  in Table II), including only the dominant Coulomb correction. An alternative approach would be to use configuration-interaction (CI) techniques which can give all-order results. To do this, one would have to carefully subtract out from the CI result the lowest-, first-, and second-order MBPT corrections using the same potential and would then have a more complete treatment of higher-order corrections. However, because of the  $1/Z$  expansion, these corrections are already quite small and this approach is not followed here.

**B. Nuclear recoil**

Recoil corrections arise from the small effect of the finite mass of the nucleus. For hydrogenic ions, while it suffices to simply use a reduced mass Rydberg constant as an overall scaling factor nonrelativistically, this is not valid when relativistic corrections are important. In the hydrogenic case, an exact treatment of terms first order in recoil leads to the formula [26]

$$E(n, j) = mf(n, j) + \frac{m^2(Z\alpha)^2}{2Mn^2} + \frac{m^2(Z\alpha)^4}{M} \left[ -\frac{1}{2n^4} + \frac{1}{2n^3(j+1/2)} \right] + \frac{m^2(Z\alpha)^5}{M} R(n, \kappa, Z\alpha), \quad (37)$$

where  $R(n, \kappa, Z\alpha)$  is given in Table III of Ref. [26] and

$$f(n, j) = \left\{ 1 + \frac{(Z\alpha)^2}{[n - (j + 1/2) + \sqrt{(j + 1/2)^2 - (Z\alpha)^2}]^2} \right\}^{-1/2} \quad (38)$$

is the Dirac-Coulomb energy in units of  $mc^2$ . While we are dealing with lithium-like ions, we make the approximation of using the recoil corrections in Eq. (37) for the  $n = 2$  states considered here. To gauge the accuracy of doing this, we note that at  $Z = 50$  the hydrogenic energy  $mf$  differs from the Kohn-Sham eigenvalues by only 5%. A comparable screening correction to the already small recoil term can definitely be ignored.

For many-electron systems such as the lithium-like ions, there is an additional recoil term given by the expectation values of the operator

$$H_{MP} = \frac{1}{2M} \sum_{i \neq j} \{ \vec{p}_i \cdot \vec{p}_j + U(r_i)[\vec{\alpha}_i + (\vec{\alpha}_i \cdot \hat{r}_i)\hat{r}_i] \cdot \vec{p}_j \}. \quad (39)$$

The first term in Eq. (39) is the mass polarization term and the second term is the leading relativistic correction [27]. The latter has been shown in Ref. [28] to arise from the exchange of one transverse photon in a QED formalism. The same work also showed that higher-order contributions from the exchange of two transverse photons, though extremely small at low  $Z$ , increase very rapidly along the isoelectronic sequence and are no longer negligible at high  $Z$ . Indeed, for the  $2p_{1/2}$  state of hydrogenic uranium, contributions from the two terms in Eq. (39) give  $-0.085$  and  $0.068$  eV for a sum of  $-0.017$  eV, while the higher-order correction is comparable in size at  $-0.013$  eV. Evaluations of these higher-order corrections with QED are nontrivial, but we find that they can be well approximated by the expectation values of the operator  $\frac{1}{2M} \sum_{i \neq j} \vec{q}_i \cdot \vec{q}_j$ , where

$$\vec{q}_i = \frac{1}{2} U(r_i)[\vec{\alpha}_i + (\vec{\alpha}_i \cdot \hat{r}_i)\hat{r}_i]. \quad (40)$$

Indeed, hydrogenic results thus obtained consistently agree with the QED results of [28] to within a few percent over a

change of five orders of magnitude from  $Z = 10$  to  $Z = 100$ . We thus use the operator

$$H_{MP}^{rel} = \frac{1}{2M} \sum_{i \neq j} [\vec{p}_i \cdot \vec{p}_j + 2\vec{q}_i \cdot \vec{p}_j + \vec{q}_i \cdot \vec{q}_j] \quad (41)$$

to evaluate the relativistic mass polarization corrections for lithium-like ions with Kohn-Sham wave functions. Total recoil corrections as given by the sums of the hydrogenic mass correction factor and the expectation values of  $H_{MP}^{rel}$  are tabulated as ‘‘Recoil’’ in Table II.

**C. Two-loop Lamb shift**

One of the major advances in QED bound-state theory of recent years has been in the treatment of the two-loop Lamb shift. For hydrogen, this effect must be understood precisely before the proton size can be determined, and considerable effort had to be put into the  $Z\alpha$  expansion of the effect before this could be done. As mentioned earlier, at high  $Z$  the effect, which in this case has to be calculated exactly without making the  $Z\alpha$  expansion, is large enough that it could be clearly seen when comparing theory and experiment for lithium-like bismuth [12]. In terms of a function  $G(Z\alpha)$ , the two-loop Lamb shift can be parameterized as

$$\Delta E_{2-loop} = \frac{m\alpha^2}{\pi^2 n^3} (Z\alpha)^4 G(Z\alpha). \quad (42)$$

The exact calculation of  $G(Z\alpha)$  is quite complicated, but enough  $Z$  values have been evaluated [13,14] that an interpolation can be made, and the results are tabulated as ‘‘2-loop’’ in Table II.

**D. Nuclear polarization**

By far the largest uncertainty associated with the properties of the nucleus in a lithium-like ion is the root-mean-square charge radius. We discuss in the next section how the use of different values of this parameter lead to significant changes in the  $2s$  energy. However, a smaller effect is beginning to become important as higher precisions are reached, which is the effect of the polarizability of the nucleus. This is a large effect in muonic atoms [29] and, while smaller, needs to be included for highly charged heavy ions. The graphs involved are of the same form as the ladder and crossed-ladder diagrams of Figs. 2(d) and 2(e), with the bottom electron replaced with a nucleus that is understood to be in an excited state. This nuclear polarization effect from the collective nuclear excitations, including vibrations, rotations, and giant dipole resonances, has been studied by Plenum and Soff [15] for even isotopes of actinide nuclei. Results from that work are included in our ionization and transition energies for some of the high- $Z$  ions and are listed as ‘‘NucPol’’ in Table II.

**VI. DISCUSSION AND CONCLUSION**

As we have mentioned in the Introduction, most works on high-precision calculations of the energy levels of lithium-like ions are based on the Hamiltonian approach for structure calculations, with QED corrections calculated separately. Examples



TABLE II. Breakdown of contributions to the ionization potentials (a.u.) for the  $n = 2$  states of selected lithium-like ions. See text for term notations.

| State      | Terms     | $Z = 20$   | $Z = 40$  | $Z = 60$  | $Z = 74$  | $Z = 83$  | $Z = 92$  |
|------------|-----------|------------|-----------|-----------|-----------|-----------|-----------|
| $2s_{1/2}$ | $E^{(0)}$ | -41.078 21 | -186.1698 | -449.2213 | -718.3888 | -937.4309 | -1201.067 |
|            | $E^{(1)}$ | -1.471 73  | -3.0515   | -4.6537   | -5.8045   | -6.5674   | -7.360    |
|            | $E^{(2)}$ | -0.003 44  | -0.0057   | -0.0098   | -0.0141   | -0.0178   | -0.023    |
|            | $E^{(3)}$ | -0.000 02  | 0.0000    | 0.0000    | 0.0000    | 0.0000    | 0.000     |
|            | Recoil    | 0.000 69   | 0.0013    | 0.0020    | 0.0027    | 0.0035    | 0.005     |
|            | Uehling   | -0.000 52  | -0.0094   | -0.0579   | -0.1656   | -0.3123   | -0.582    |
|            | WK        | 0.000 00   | 0.0001    | 0.0015    | 0.0060    | 0.0136    | 0.029     |
|            | SE        | 0.007 29   | 0.0896    | 0.3967    | 0.9017    | 1.4586    | 2.314     |
|            | VP-screen | 0.000 03   | 0.0003    | 0.0013    | 0.0033    | 0.0060    | 0.011     |
|            | SE-screen | -0.000 30  | -0.0020   | -0.0070   | -0.0147   | -0.0233   | -0.037    |
|            | 2-loop    | -0.000 01  | -0.0002   | -0.0009   | -0.0026   | -0.0046   | -0.008    |
|            | NucPol    |            |           |           |           |           |           |
| Sum        |           | -42.546 21 | -189.1475 | -453.5492 | -723.4766 | -942.8748 | -1206.719 |
| $2p_{1/2}$ | $E^{(0)}$ | -39.785 90 | -183.3083 | -444.4356 | -711.9216 | -929.7361 | -1192.233 |
|            | $E^{(1)}$ | -1.431 20  | -2.8467   | -3.9741   | -4.4418   | -4.5141   | -4.305    |
|            | $E^{(2)}$ | -0.007 43  | -0.0122   | -0.0226   | -0.0364   | -0.0502   | -0.070    |
|            | $E^{(3)}$ | 0.000 07   | 0.0000    | 0.0001    | 0.0001    | 0.0001    | 0.000     |
|            | Recoil    | 0.000 33   | 0.0006    | 0.0009    | 0.0012    | 0.0016    | 0.002     |
|            | Uehling   | 0.000 00   | -0.0002   | -0.0033   | -0.0157   | -0.0399   | -0.098    |
|            | WK        | 0.000 00   | 0.0000    | 0.0001    | 0.0008    | 0.0025    | 0.007     |
|            | SE        | -0.000 22  | -0.0014   | 0.0086    | 0.0570    | 0.1422    | 0.321     |
|            | VP-screen | 0.000 03   | 0.0003    | 0.0012    | 0.0032    | 0.0060    | 0.012     |
|            | SE-screen | -0.000 30  | -0.0020   | -0.0067   | -0.0147   | -0.0243   | -0.041    |
|            | 2-loop    | 0.000 00   | 0.0000    | 0.0001    | 0.0001    | 0.0001    | 0.000     |
|            | NucPol    |            |           |           |           |           |           |
| Sum        |           | -41.224 62 | -186.1698 | -448.4315 | -716.3678 | -934.2122 | -1196.406 |
| $2p_{3/2}$ | $E^{(0)}$ | -39.582 48 | -179.3907 | -422.1043 | -655.2997 | -833.7473 | -1035.279 |
|            | $E^{(1)}$ | -1.449 44  | -3.0233   | -4.6710   | -5.9317   | -6.8275   | -7.830    |
|            | $E^{(2)}$ | -0.006 97  | -0.0093   | -0.0124   | -0.0146   | -0.0159   | -0.017    |
|            | $E^{(3)}$ | 0.000 06   | 0.0000    | 0.0000    | 0.0000    | 0.0000    | 0.000     |
|            | Recoil    | 0.000 33   | 0.0005    | 0.0008    | 0.0010    | 0.0011    | 0.001     |
|            | Uehling   | 0.000 00   | 0.0000    | -0.0003   | -0.0010   | -0.0021   | -0.004    |
|            | WK        | 0.000 00   | 0.0000    | 0.0000    | 0.0001    | 0.0003    | 0.001     |
|            | SE        | 0.000 20   | 0.0059    | 0.0395    | 0.1070    | 0.1852    | 0.303     |
|            | VP-screen | 0.000 03   | 0.0002    | 0.0008    | 0.0016    | 0.0025    | 0.004     |
|            | SE-screen | -0.000 33  | -0.0019   | -0.0052   | -0.0089   | -0.0120   | -0.016    |
|            | 2-loop    | 0.000 00   | 0.0000    | 0.0000    | -0.0001   | -0.0002   | -0.001    |
|            | NucPol    |            |           |           |           |           |           |
| Sum        |           | -41.038 60 | -182.4185 | -426.7520 | -661.1463 | -840.4160 | -1042.837 |

are the relativistic many-body perturbation theory (RMBPT) calculations of Blundell [25] and the relativistic configuration-interaction (RCI) calculations of Chen *et al.* [30]. The works of the St. Petersburg group [14,31–33], on the other hand, should be comparable to the present  $S$ -matrix calculations, as both use similar QED-based approaches which treat electron correlations and radiative corrections consistently and systematically according to the number of virtual photons exchanged between electrons. Comparing the present work with other calculations on different contributions to the ionization and transition energies can reveal QED effects on the structure energies not attainable in the Hamiltonian approach and show the importance of the rigorous treatments of screened QED corrections.

In Table III, the present structure and nuclear recoil energies for the  $2s-2p$  transitions are presented. At low  $Z$ , uncertainties in the structure energies are estimates based on the incomplete three- and more-photon correlation calculations. At mid- to high  $Z$ , they are due mainly to uncertainties in the nuclear radii which are discussed in the following. As for the recoil energies, error estimates come from the use of the hydrogenic formula Eq. (37) for the one-electron recoils and the use of the  $\vec{q}_i \cdot \vec{q}_j$  term in Eq. (41) for the two-electron recoils. Also shown in Table III are the RMBPT energies of Blundell [25], which include some recoil corrections, and the structure energies of RCI [30] and the St. Petersburg group (StPete) [32]. Structure energies relative to the present results are shown in Figs. 5 and 6 for the  $2s-2p_{1/2}$  and  $2s-2p_{3/2}$  transitions, respectively.

TABLE III. The present structure and recoil energies (eV) for the  $2s-2p$  transitions of lithium-like ions are compared with other theoretical results. Blundell’s RMBPT energies [25] already include recoil corrections. RCI [30] and St. Petersburg group’s results StPete [32] are structure energies only.

| Z  | $2s-2p_{1/2}$ |           |          |        |        | $2s-2p_{3/2}$ |           |          |         |         |
|----|---------------|-----------|----------|--------|--------|---------------|-----------|----------|---------|---------|
|    | Structure     | Recoil    | Blundell | RCI    | StPete | Structure     | Recoil    | Blundell | RCI     | StPete  |
| 10 | 15.906(1)     | -0.004    | 15.903   | 15.907 | 15.906 | 16.110(1)     | -0.004    | 16.107   | 16.111  | 16.110  |
| 12 | 19.872(1)     | -0.005    | 19.867   |        | 19.872 | 20.364(1)     | -0.005    | 20.359   |         | 20.364  |
| 15 | 25.884(1)     | -0.006    | 25.878   | 25.886 | 25.885 | 27.272(1)     | -0.007    | 27.267   | 27.275  | 27.273  |
| 18 | 32.005(1)     | -0.008    | 31.998   |        | 32.006 | 35.167(1)     | -0.008    | 35.161   |         | 35.169  |
| 20 | 36.162(1)     | -0.010(1) | 36.154   | 36.167 | 36.163 | 41.213(1)     | -0.010(1) | 41.206   | 41.218  | 41.215  |
| 21 | 38.267(1)     | -0.009(1) |          |        | 38.268 | 44.532(1)     | -0.010(1) |          |         | 44.534  |
| 26 | 49.101(1)     | -0.012(1) |          | 49.106 | 49.103 | 65.030(1)     | -0.012(1) |          | 65.037  | 65.033  |
| 28 | 53.603(1)     | -0.014(1) |          |        | 53.603 | 75.560(1)     | -0.014(1) |          |         | 75.563  |
| 30 | 58.211(1)     | -0.014(1) | 58.199   |        | 58.213 | 87.789(1)     | -0.015(1) | 87.777   |         | 87.793  |
| 32 | 62.940        | -0.014(1) | 62.928   | 62.948 | 62.942 | 102.00        | -0.015(1) | 101.98   | 102.01  | 102.00  |
| 36 | 72.798        | -0.016(1) |          |        | 72.801 | 137.60        | -0.017(1) |          |         | 137.60  |
| 40 | 83.267        | -0.019(1) | 83.250   |        | 83.270 | 185.14        | -0.020(1) | 185.12   |         | 185.15  |
| 42 | 88.755        | -0.019(1) | 88.740   | 88.774 | 88.759 | 214.39        | -0.021(1) | 214.37   | 214.41  | 214.39  |
| 47 | 103.33        | -0.023(1) |          |        | 103.34 | 307.20        | -0.024(1) |          |         | 307.20  |
| 50 | 112.74        | -0.023(1) | 112.73   |        | 112.74 | 379.03        | -0.025(2) | 379.00   |         | 379.03  |
| 52 | 119.31        | -0.024(1) |          |        | 119.31 | 434.87        | -0.026(2) |          |         | 434.88  |
| 54 | 126.14        | -0.025(2) | 126.13   | 126.17 | 126.14 | 497.88        | -0.028(2) | 497.84   | 497.93  | 497.89  |
| 60 | 148.37        | -0.030(2) | 148.37   |        | 148.38 | 737.35        | -0.033(2) | 737.31   |         | 737.36  |
| 64 | 164.79(1)     | -0.032(2) |          | 164.81 | 164.74 | 947.61(1)     | -0.036(2) |          | 947.69  | 947.59  |
| 66 | 173.54(1)     | -0.033(2) |          |        | 173.47 | 1070.96(1)    | -0.038(2) |          |         | 1070.88 |
| 70 | 192.16(1)     | -0.036(2) | 192.17   |        | 192.10 | 1359.62(1)    | -0.042(3) | 1359.55  |         | 1359.56 |
| 74 | 212.46(2)     | -0.040(2) |          | 212.43 | 212.41 | 1713.27(2)    | -0.048(3) |          | 1713.40 | 1713.28 |
| 79 | 240.24(2)     | -0.046(3) |          |        | 240.26 | 2265.85(2)    | -0.056(3) |          |         | 2265.86 |
| 80 | 246.09(3)     | -0.047(3) | 246.11   |        | 246.13 | 2393.28(3)    | -0.057(3) | 2393.15  |         | 2393.32 |
| 82 | 258.20(3)     | -0.050(3) |          | 258.25 | 258.23 | 2667.29(3)    | -0.061(4) |          | 2667.43 | 2667.31 |
| 83 | 264.38(4)     | -0.052(3) |          |        | 264.43 | 2814.35(4)    | -0.064(4) |          |         | 2814.39 |
| 90 | 309.13(5)     | -0.065(4) | 309.17   | 309.21 | 309.78 | 4061.21(5)    | -0.084(5) | 4060.98  | 4061.42 | 4061.91 |
| 92 | 322.23(6)     | -0.071(4) | 322.33   | 322.29 | 322.33 | 4498.69(6)    | -0.092(5) |          | 4498.93 | 4498.79 |

While all calculations agree at low  $Z$ , it can be seen that RMBPT and RCI energies deviate more and more from the present results as  $Z$  increases, demonstrating the importance of rigorous QED treatments in calculating correlation energies beyond the no-pair approximation.

It is notable that the structure energies of the St. Petersburg group appear to scatter around our results at mid- to high  $Z$  and deviations can be as large as 0.7 eV at  $Z = 90$ . Apparently, these discrepancies are due mainly to the finite nuclear size effect from the use of different root-mean-square nuclear radii in the two calculations which affects the  $2s$  states considerably more than the  $2p_{1/2}$  and  $2p_{3/2}$  states; hence the similar scattered patterns in Figs. 5 and 6. While we use nuclear radius parameters from the tabulation of Johnson and Soff [17], except for thorium ( $Z = 90$ ) and uranium ( $Z = 92$ ), which are derived from measurements [18,19], recent works of the St. Petersburg group [14,32,33] use data from the tabulation of Angeli [34] except for  $Z = 43, 61, 85, 89,$  and  $91$ , where data are not available from [34] and have to be taken from Johnson and Soff [17]. Unfortunately, nuclear sizes are somewhat uncertain, and the fact that they can lead to large, irregular discrepancies such as those shown in Figs. 5 and 6 for high- $Z$  lithium-like ions can be seen in the  $2s-2p_{1/2}$  structure energy of thorium, which is listed in Table III as

309.78 eV from the St. Petersburg group’s 2007 paper [32], but is given as 309.19 eV in their earlier 2001 paper [31], which is much closer to the present value of 309.13 eV. At

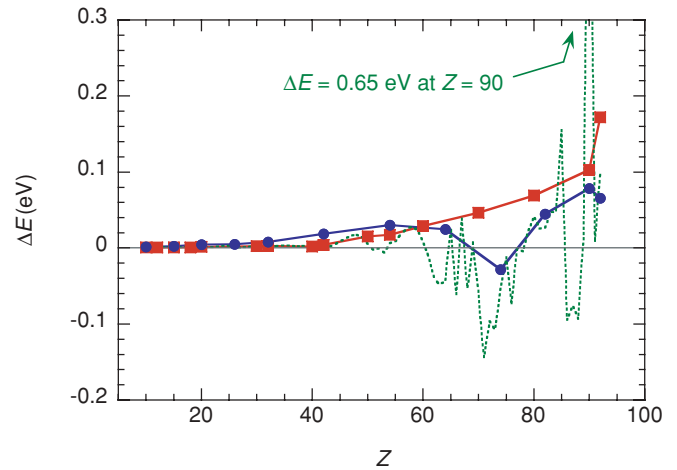


FIG. 5. (Color online) Structure energies (eV) of the  $2s-2p_{1/2}$  transition relative to the present results. Solid squares, Blundell [25]; solid circles, RCI [30]; dotted line, St. Petersburg group [32].

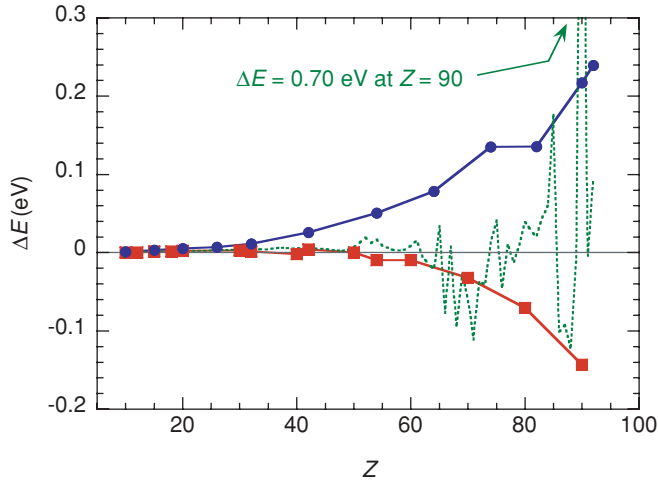


FIG. 6. (Color online) Structure energies (eV) of the  $2s-2p_{3/2}$  transition relative to the present results. Solid squares, Blundell [25]; solid circles, RCI [30]; dotted line, St. Petersburg group [32].

close to 0.7 eV, this is a very large change. Fortunately, errors from these nuclear uncertainties are small and only those in the lowest-order structure energies  $E^{(0)}$  matter at high  $Z$ . QED and other small corrections are hardly affected. Also, the works of Blundell [25] and RCI [30] both use the same nuclear parameters as the present work. Otherwise, it will be very difficult, if not impossible, to draw any useful conclusions from those comparisons.

As for the recoil energies, our results shown in Table III are in very good agreement with those of the St. Petersburg group [14,31,33]. Recoil energies in Blundell and RCI are obtained approximately from the reduced mass and mass polarization corrections and differ slightly from the present results at high  $Z$ . For simplicity, recoil energies from other calculations are not shown here.

In Table IV, the present screened one-loop QED energies are shown and are compared with results from other

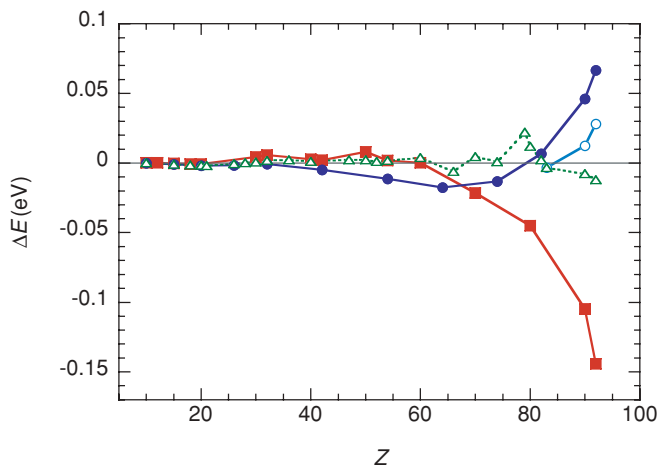


FIG. 7. (Color online) Screened QED energies (eV) of the  $2s-2p_{1/2}$  transition relative to the present results. Solid squares, Blundell; solid circles, RCI; open circles, RCI relaxed QED; open triangles, St. Petersburg group. See Table IV for references.

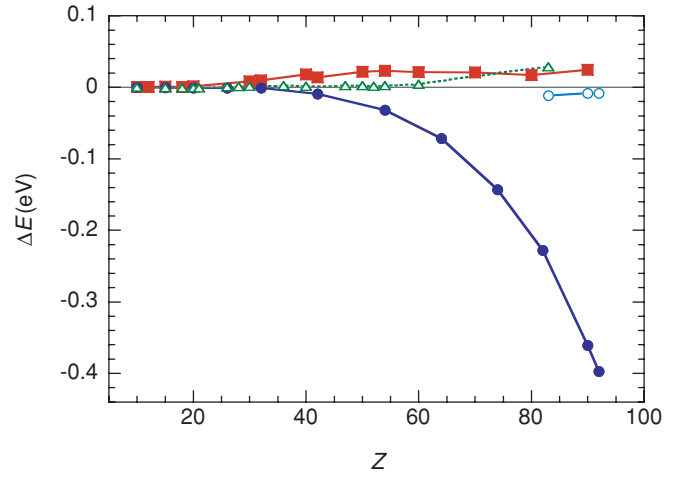


FIG. 8. (Color online) Screened QED energies (eV) of the  $2s-2p_{3/2}$  transition relative to the present results. Solid squares, Blundell; solid circles, RCI; open circles, RCI relaxed QED; open triangles, St. Petersburg group. See Table IV for references.

calculations. Also shown are the two-loop QED energies which are scaled from the available hydrogenic results of the St. Petersburg group [13,14], and error estimates are duly assigned. Here, Blundell's QED energies [25] already include estimates of two-loop Lamb-shift contributions, while those of RCI [30,35] and the St. Petersburg group [14,31,33] are screened one-loop results only. QED energies relative to the present results are shown in Figs. 7 and 8 for the  $2s-2p_{1/2}$  and  $2s-2p_{3/2}$  transitions, respectively. We note that QED calculations in RCI [30] are similar to this work and start from the Kohn-Sham potential, but only at the one-photon level as discussed in Sec. III, and lack two-photon screening corrections as discussed in Sec. IV B. Blundell's QED calculations start from the core-Hartree potential and include some screening corrections, but the vertex-exchange terms  $\Delta E_2$  and  $\Delta E_4$  in Eqs. (30) and (32) are not calculated. Because of these approximations, QED energies of Blundell and RCI tend to deviate more and more from the present results as  $Z$  increases. By contrast, QED energies from the St. Petersburg group are in very good agreement with our results along the isoelectronic sequence, as the screened QED diagrams are calculated correctly in both works. It is interesting to note that the relaxed QED energies from the RCI calculations of Cheng *et al.* [35] are in very good agreement with the present results at high  $Z$ . This method is relatively simple in that relaxation corrections to the QED energies of the  $2s-2p$  transitions are obtained by using different Kohn-Sham potentials specific to the  $2s$ ,  $2p_{1/2}$ , and  $2p_{3/2}$  states to calculate the one-loop radiative corrections for the initial and final states. While it appears to give very good screened QED results, it is nevertheless an *ad hoc* method that may not be suitable for systematic, high-precision calculations.

In Table V, total transition energies are compared between theory and experiment. The present results are the sums of the structure, recoil, and one- and two-loop QED energies shown in Tables III and IV, with additional contributions from the nuclear polarization [15] at  $Z = 90$  and  $92$ . Our uncertainties are based on error estimates of these individual

TABLE IV. The present screened one-loop and two-loop QED energies (eV) for the  $2s-2p$  transitions of lithium-like ions are compared with other theoretical results. Blundell's energies are from [25], RCI and RCI-relax energies are from [30] and [35], respectively, and St. Petersburg group's results (StPete) are from [33] unless otherwise specified. While Blundell includes estimates of higher-order corrections, others are screened one-loop results only.

| Z  | $2s-2p_{1/2}$ |           |          |        |           | $2s-2p_{3/2}$       |        |           |          |        |           |                     |
|----|---------------|-----------|----------|--------|-----------|---------------------|--------|-----------|----------|--------|-----------|---------------------|
|    | 1-loop        | 2-loop    | Blundell | RCI    | RCI-relax | StPete              | 1-loop | 2-loop    | Blundell | RCI    | RCI-relax | StPete              |
| 10 | -0.014        | 0.000     | -0.014   | -0.014 |           | -0.014              | 0.000  | -0.014    | -0.014   |        |           | -0.014              |
| 12 | -0.029        | 0.000     | -0.028   |        |           |                     | -0.028 | 0.000     | -0.027   |        |           |                     |
| 15 | -0.066        | 0.000     | -0.066   | -0.067 |           | -0.067              | -0.063 | 0.000     | -0.062   | -0.063 |           | -0.064              |
| 18 | -0.129        | 0.000     | -0.130   |        |           | -0.131              | -0.123 | 0.000     | -0.122   |        |           | -0.124              |
| 20 | -0.190        | 0.000     | -0.191   | -0.192 |           | -0.192              | -0.180 | 0.000     | -0.178   | -0.181 |           | -0.181              |
| 21 | -0.228        | 0.000     |          |        |           | -0.229              | -0.214 | 0.000     |          |        |           | -0.215              |
| 26 | -0.491        | 0.001     |          | -0.493 |           | -0.492              | -0.457 | 0.001     |          | -0.458 |           | -0.457              |
| 28 | -0.639        | 0.001     |          |        |           | -0.639              | -0.592 | 0.001     |          |        |           | -0.591              |
| 30 | -0.816        | 0.002     | -0.810   |        |           | -0.815              | -0.753 | 0.002     | -0.743   |        |           | -0.751              |
| 32 | -1.024        | 0.002(1)  | -1.016   | -1.025 |           | -1.022 <sup>a</sup> | -0.941 | 0.002(1)  | -0.929   | -0.942 |           |                     |
| 36 | -1.545        | 0.004(1)  |          |        |           | -1.543              | -1.411 | 0.003(1)  |          |        |           | -1.409              |
| 40 | -2.228        | 0.005(1)  | -2.220   |        |           | -2.227              | -2.023 | 0.005(1)  | -2.000   |        |           | -2.022              |
| 42 | -2.638        | 0.007(2)  | -2.630   | -2.643 |           |                     | -2.390 | 0.006(2)  | -2.370   | -2.400 |           |                     |
| 47 | -3.899        | 0.010(3)  |          |        |           | -3.897              | -3.514 | 0.010(2)  |          |        |           | -3.512              |
| 50 | -4.831        | 0.013(3)  | -4.810   |        |           | -4.829              | -4.344 | 0.012(3)  | -4.310   |        |           | -4.342              |
| 52 | -5.534        | 0.015(4)  |          |        |           | -5.533              | -4.970 | 0.014(4)  |          |        |           | -4.968              |
| 54 | -6.309        | 0.018(4)  | -6.290   | -6.321 |           | -6.308              | -5.660 | 0.017(4)  | -5.620   | -5.692 |           | -5.658              |
| 60 | -9.107        | 0.027(7)  | -9.080   |        |           | -9.103              | -8.157 | 0.025(6)  | -8.110   |        |           | -8.152              |
| 64 | -11.41        | 0.037(9)  |          | -11.43 |           |                     | -10.22 | 0.034(8)  |          | -10.30 |           |                     |
| 66 | -12.71        | 0.042(11) |          |        |           | -12.72 <sup>a</sup> | -11.40 | 0.039(10) |          |        |           |                     |
| 70 | -15.64        | 0.056(14) | -15.61   |        |           | -15.64 <sup>a</sup> | -14.06 | 0.051(13) | -13.99   |        |           |                     |
| 74 | -19.05        | 0.073(18) |          | -19.06 |           | -19.05 <sup>a</sup> | -17.19 | 0.067(17) |          | -17.33 |           |                     |
| 79 | -24.07        | 0.101(25) |          |        |           | -24.05 <sup>a</sup> | -21.88 | 0.093(23) |          |        |           |                     |
| 80 | -25.18        | 0.107(27) | -25.12   |        |           | -25.17 <sup>a</sup> | -22.94 | 0.099(25) | -22.82   |        |           |                     |
| 82 | -27.51        | 0.121(30) |          | -27.51 |           | -27.51 <sup>a</sup> | -25.17 | 0.112(28) |          | -25.40 |           |                     |
| 83 | -28.74        | 0.129(32) |          |        | -28.74    | -28.74 <sup>a</sup> | -26.36 | 0.120(30) |          |        | -26.37    | -26.33 <sup>b</sup> |
| 90 | -38.54        | 0.197(49) | -38.45   | -38.50 | -38.53    | -38.55 <sup>a</sup> | -36.08 | 0.187(47) | -35.87   | -36.44 | -36.09    |                     |
| 92 | -41.76        | 0.222(56) | -41.68   | -41.69 | -41.73    | -41.77 <sup>b</sup> | -39.38 | 0.212(53) | -39.78   | -39.78 | -39.39    |                     |

<sup>a</sup>Reference [31].

<sup>b</sup>Reference [14].

terms. Uncertainties of other theories shown here are limited to the significant ones at high  $Z$  only. Energies relative to the present ones are shown in Figs. 9 and 10 for the  $2s-2p_{1/2}$  and  $2s-2p_{3/2}$  transitions, respectively. Empirical results at low to mid- $Z$  come from NIST's online database of atomic spectra [36], with beam-foil measurements at  $Z = 47, 50,$  and  $54$  [37–39]. At high  $Z$ , available experimental results are from EBIT measurements [5,41–44]. In general, our results are in very good agreement with experiment, while those of Blundell [25] and RCI [30] tend to deviate from our results and from experiment at high  $Z$ . For the  $2s-2p_{1/2}$  transition, St. Petersburg group's results differ from our results at high  $Z$  for two reasons. First of all, most of their total transition energies above  $Z = 60$  are from their 2001 paper [31] and do not include two-loop Lamb-shift corrections. This leads to the sudden jump in their results from  $Z = 90$  to  $92$ , as the latter is from their 2006 paper [14] and does include the two-loop correction. Second, as we have pointed out earlier, their structure energies are different from ours because of the choices of nuclear radii. Should they use our nuclear radius at  $Z = 92$ , their result would be lower by about 0.08 to 280.68 eV,

in much closer agreement with our result of 280.65 eV and with the measured value of 280.645(15) eV [43]. As for the  $2s-2p_{3/2}$  transition, total transition energies from the St. Petersburg group all include two-loop corrections. At  $Z = 83$ , their result is in very good agreement with experiment, with our energy lower by about 0.08 eV. In this case, if we use their nuclear radius, our result will go up by about 0.04 eV to 2788.08 eV, in closer agreement with their result of 2788.12 eV and with the measured value of 2788.139(39) eV [5]. Nevertheless, while we are not aware of any total  $2s-2p_{3/2}$  transition energy at  $Z = 90$  from the St. Petersburg group, their structure energy is higher than ours by 0.7 eV as we have shown in Table III and Fig. 6. That will surely make the transition energy much higher than experiment and no other corrections can come close to compensating for such a big difference.

It is interesting to note that in Fig. 10, the RCI-relax energies [35] are seen to be in very good agreement with experiment. This is due mainly to the changes in the QED energies after the relaxation corrections are included, but that is not the entire reason. As we have pointed out in Sec. IV A, for the  $2s-2p_{3/2}$  transition at high  $Z$ , QED corrections to the

TABLE V. The  $2s-2p$  transition energies (eV) of lithium-like ions. Blundell's results are from [25]. Unless otherwise specified, RCI results are from [30], St. Petersburg group's results (StPete) are from [33], and experimental results are from the NIST Atomic Spectra Database [36].

| Z  | $2s-2p_{1/2}$          |                         |        |                         |                          | $2s-2p_{3/2}$           |            |                      |                         |                            |
|----|------------------------|-------------------------|--------|-------------------------|--------------------------|-------------------------|------------|----------------------|-------------------------|----------------------------|
|    | Present                | Blundell                | RCI    | StPete                  | Expt.                    | Present                 | Blundell   | RCI                  | StPete                  | Expt.                      |
| 10 | 15.888(1)              | 15.889                  | 15.889 | 15.888                  | 15.88881                 | 16.093(1)               | 16.093     | 16.093               | 16.093                  | 16.09330                   |
| 12 | 19.838(1)              | 19.839                  |        |                         | 19.8393                  | 20.332(1)               | 20.332     |                      |                         | 20.3320                    |
| 15 | 25.812(1)              | 25.812                  | 25.813 | 25.811                  | 25.8140                  | 27.203(1)               | 27.205     | 27.205               | 27.203                  | 27.206                     |
| 18 | 31.868(1)              | 31.868                  |        | 31.867                  | 31.8672                  | 35.037(1)               | 35.039     |                      | 35.038                  | 35.0383                    |
| 20 | 35.962(1)              | 35.964                  | 35.963 | 35.961                  | 35.9625                  | 41.024(1)               | 41.028     | 41.028               | 41.025                  | 41.0286                    |
| 21 | 38.031(1)              |                         |        | 38.029                  | 38.03                    | 44.308(1)               |            |                      | 44.309                  | 44.31                      |
| 26 | 48.599(1)              |                         | 48.600 | 48.599                  | 48.5997                  | 64.562(1)               |            | 64.567               | 64.565                  | 64.5656                    |
| 28 | 52.951(1)              |                         |        | 52.950                  | 52.9503                  | 74.955(1)               |            |                      | 74.959                  | 74.9574                    |
| 30 | 57.382(1)              | 57.389                  |        | 57.385                  | 57.3843                  | 87.023(1)               | 87.033     |                      | 87.028                  | 87.0272                    |
| 32 | 61.904(1)              | 61.911                  | 61.907 | 61.906 <sup>a</sup>     | 61.9023                  | 101.04                  | 101.06     | 101.05               |                         | 101.043                    |
| 36 | 71.240(1)              |                         |        | 71.245                  | 71.2391                  | 136.17                  |            |                      | 136.18                  | 136.1711                   |
| 40 | 81.025(2)              | 81.04                   |        | 81.029                  |                          | 183.10                  | 183.12     |                      | 183.11                  |                            |
| 42 | 86.104(2)              | 86.12                   | 86.110 |                         | 86.1021                  | 211.98                  | 211.99     | 211.99               |                         | 211.9706                   |
| 47 | 99.414(3)              |                         |        | 99.432                  | 99.438(7) <sup>b</sup>   | 303.67                  |            |                      | 303.67                  | 303.67(3) <sup>b</sup>     |
| 50 | 107.90                 | 107.92                  |        | 107.90                  | 107.911(8) <sup>c</sup>  | 374.67                  | 374.68     |                      | 374.68                  |                            |
| 52 | 113.77                 |                         |        | 113.77                  |                          | 429.88                  |            |                      | 429.90                  |                            |
| 54 | 119.82                 | 119.84                  | 119.82 | 119.83                  | 119.820(8) <sup>c</sup>  | 492.21                  | 492.22     | 492.21               | 492.23                  | 492.34(62) <sup>d</sup>    |
| 60 | 139.26(1)              | 139.29                  |        | 139.28                  |                          | 729.19(1)               | 729.20     |                      | 729.20                  |                            |
| 64 | 153.38(1)              |                         | 153.35 |                         |                          | 937.39(1)               |            | 937.36               |                         |                            |
| 66 | 160.83(1)              |                         |        | 160.74 <sup>a</sup>     |                          | 1059.56(1)              |            |                      |                         |                            |
| 70 | 176.54(2)              | 176.56                  |        | 176.44 <sup>a</sup>     |                          | 1345.57(2)              | 1345.56    |                      |                         |                            |
| 74 | 193.44(3)              |                         | 193.33 | 193.33 <sup>a</sup>     |                          | 1696.10(3)              |            | 1696.03              |                         | 1697.34(1.03) <sup>e</sup> |
| 79 | 216.22(3)              |                         |        | 216.17 <sup>a</sup>     |                          | 2244.00(3)              |            |                      |                         |                            |
| 80 | 220.97(4)              | 220.99                  |        | 220.93 <sup>a</sup>     |                          | 2370.38(4)              | 2370.32    |                      |                         |                            |
| 82 | 230.76(4)              |                         | 230.70 | 230.68 <sup>a</sup>     |                          | 2642.17(4)              |            | 2641.98              |                         | 2642.26(10) <sup>f</sup>   |
| 83 | 235.72(5)              |                         |        | 235.62 <sup>a</sup>     |                          | 2788.04(5)              |            | 2788.10 <sup>g</sup> | 2788.12(7) <sup>h</sup> | 2788.139(39) <sup>i</sup>  |
| 90 | 270.74(7) <sup>j</sup> | 270.72(5)               | 270.67 | 270.60 <sup>a</sup>     |                          | 4025.25(7) <sup>j</sup> | 4025.10(4) | 4025.28 <sup>g</sup> |                         | 4025.23(14) <sup>k</sup>   |
| 92 | 280.65(8) <sup>j</sup> | 280.68(10) <sup>l</sup> | 280.55 | 280.76(14) <sup>h</sup> | 280.645(15) <sup>m</sup> | 4459.46(8) <sup>j</sup> |            | 4459.48 <sup>g</sup> |                         | 4459.37(21) <sup>n</sup>   |

<sup>a</sup>Reference [31].

<sup>b</sup>Beam-foil, Ref. [37].

<sup>c</sup>Beam-foil, Ref. [38].

<sup>d</sup>Beam-foil, Ref. [39].

<sup>e</sup>EBIT, Ref. [40].

<sup>f</sup>EBIT, Ref. [41].

<sup>g</sup>RCI with relaxed QED corrections, Ref. [35].

<sup>h</sup>Reference [14].

<sup>i</sup>EBIT, Ref. [5].

<sup>j</sup>Include nuclear polarization corrections of 0.02 eV for  $Z = 90$  and 0.03 eV for  $Z = 92$ .

<sup>k</sup>EBIT, Ref. [42].

<sup>l</sup>With corrected nuclear polarization corrections of 0.03 instead of 0.18 eV.

<sup>m</sup>EBIT, Ref. [43].

<sup>n</sup>EBIT, Ref. [44].

structure energies from the correct treatment of the ladder and cross-ladder diagrams happen to be about the same size as the two-loop Lamb shifts but in opposite signs. Thus, the good agreement between RCI-relax and experiment is partly due to cancellation of errors, as neither corrections are included in those calculations.

There are other approaches that produce ionization and transition energies for the  $n = 2$  states of lithium-like ions. Complete tabulations along the isoelectronic sequences are available from Cheng *et al.* [45] and Kim *et al.* [46]. Both are multiconfiguration Dirac-Fock (MCDHF) calculations that are not particularly accurate, though the latter does include

correlation corrections as derived from RMBPT energies [2]. As for the QED corrections, the treatments in these early works are crude: Cheng *et al.* used estimated QED energies based on Mohr's Coulomb results [47], while Kim *et al.* employed the *ad hoc* Welton's method [48] for their calculations. Neither of these tabulations are at the same level of accuracy as the calculations mentioned here. A complete high-precision QED treatment of the series is given here.

We have shown that theory and experiment have reached a point where small corrections such as the two-loop Lamb shift and nuclear recoil can now be studied. On a more practical side, comparisons between theory and experiment on the transition

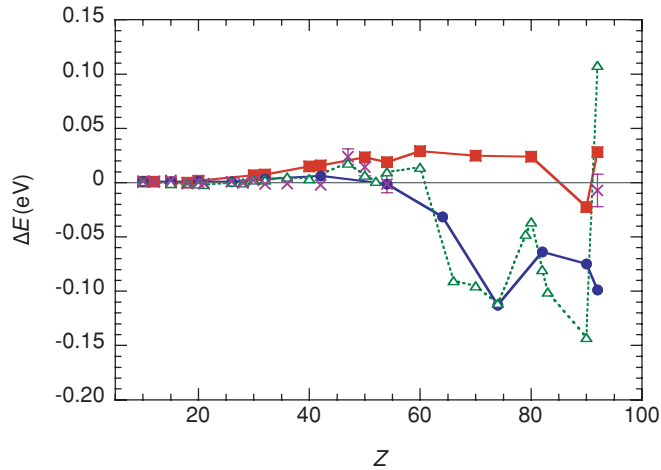


FIG. 9. (Color online) The  $2s-2p_{1/2}$  transition energies (eV) relative to the present results. Solid squares, Blundell; solid circles, RCI; open triangles, St. Petersburg group; crosses, experiment. See Table V for references.

energies of high- $Z$  lithium-like ions can also be used to check, or even deduce the radii of heavy nuclei with high precision. The next step for the lithium isoelectronic sequence will be quite challenging, both theoretically and experimentally. On the latter side, the achievement of sub-0.1 eV precision requires extraordinary care, and issues of fitting resonance curves and controlling systematics make getting another order of magnitude problematical. The very high precision achieved for copperlike tungsten [6], however, suggests that this problem may be overcome. If so, the challenge to theory is considerable. We have already shown that the treatment of recoil involves approximations that will require basic progress in bound-state quantum field theory to remove. In addition, our treatment of the third- and higher-order photon diagrams has been extremely crude, involving only MBPT with Coulomb photons. If a QED approach is to be implemented, the correlation diagrams that give this third-order contribution should, in principle, be replaced with QED exchange diagrams

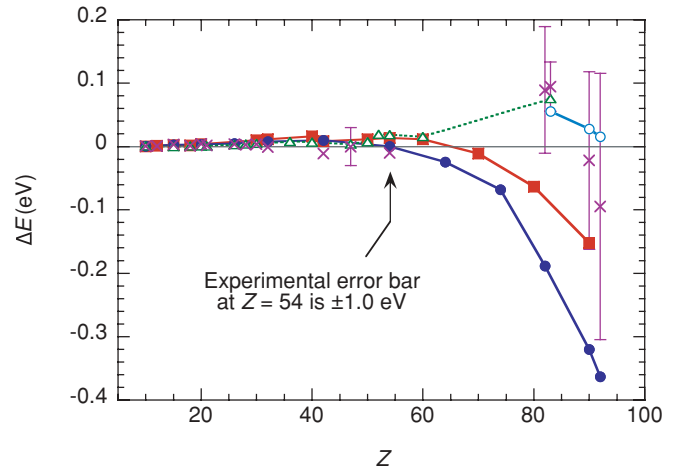


FIG. 10. (Color online) The  $2s-2p_{3/2}$  transition energies (eV) relative to the present results. Solid squares, Blundell; solid circles, RCI; open circles, RCI with relaxed QED; open triangles, St. Petersburg group; crosses, experiment. See Table V for references.

involving three photons. In addition, the three-loop Lamb shift would have to be treated, along with screening corrections to the two-loop Lamb shift and two-photon screening corrections to the one-loop Lamb shift. Finally, one must confront the fact that nuclear polarization effects will start to become important. As with many other situations in atomic physics, an interesting blend of advanced QED bound-state theory, advances in experimental technique, and nuclear structure theory will be involved as the lithium isoelectronic sequence is studied in the future.

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- [1] H. P. Kelly, *Phys. Rev.* **131**, 684 (1963).  
 [2] W. R. Johnson, S. A. Blundell, and J. Sapirstein, *Phys. Rev. A* **37**, 2764 (1988).  
 [3] W. R. Johnson, S. A. Blundell, and J. Sapirstein, *Phys. Rev. A* **38**, 2699 (1988).  
 [4] S. A. Blundell, *Phys. Rev. A* **46**, 3762 (1992); H. Persson, I. Lindgren, and S. Salomonson, *Phys. Scr. T* **46**, 125 (1993); K. T. Cheng, W. R. Johnson, and J. Sapirstein, *Phys. Rev. A* **47**, 1817 (1993).  
 [5] P. Beiersdorfer, A. L. Osterheld, J. H. Scofield, J. R. Crespo Lopez-Urrutia, and K. Widmann, *Phys. Rev. Lett.* **80**, 3022 (1998).  
 [6] E. Lindroth, H. Danared, P. Glans, Z. Pesic, M. Tokman, G. Viktor, and R. Schuch, *Phys. Rev. Lett.* **86**, 5027 (2001).  
 [7] J. D. Gillaspay, I. N. Draganic, Yu. Ralchenko, J. Reader, J. N. Tan, J. M. Pomeroy, and S. M. Brewer, *Phys. Rev. A* **80**, 010501(R) (2009).  
 [8] J. Sucher, *Int. J. Quantum Chem.* **25**, 3 (1984).  
 [9] M. Mittleman, *Phys. Rev. A* **4**, 893 (1971); **5**, 2395 (1972).  
 [10] J. Sucher, *Phys. Rev.* **107**, 1448 (1957).  
 [11] V. A. Yerokhin, A. N. Artemyev, T. Beier, G. Plunien, V. M. Shabaev, and G. Soff, *Phys. Rev. A* **60**, 3522 (1999).  
 [12] J. Sapirstein and K. T. Cheng, *Phys. Rev. A* **64**, 022502 (2001).  
 [13] V. A. Yerokhin, *Phys. Rev. A* **80**, 040501(R) (2009).  
 [14] V. A. Yerokhin, P. Indelicato, and V. M. Shabaev, *Phys. Rev. Lett.* **97**, 253004 (2006).

- [15] G. Plunien and G. Soff, *Phys. Rev. A* **51**, 1119 (1995). Due to a mistake in the formulas, results of this work are too large by a factor of  $2\pi$ , as pointed out in the erratum: G. Plunien and G. Soff, *Phys. Rev. A* **53**, 4614(E) (1996).
- [16] R. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981), Chap. 7, Sec. 7-11.
- [17] W. R. Johnson and G. Soff, *At. Data Nucl. Data Tables* **33**, 405 (1985).
- [18] J. D. Zumbro, R. A. Naumann, M. V. Hoehn, E. B. Shera, C. E. Bemis Jr., and Y. Tanaka, *Phys. Lett. B* **167**, 383 (1986).
- [19] J. D. Zumbro, E. B. Shera, Y. Tanaka, C. E. Bemis, Jr., R. A. Naumann, M. V. Hoehn, W. Reuter, and R. M. Steffen, *Phys. Rev. Lett.* **53**, 1888 (1984).
- [20] W. H. Furry, *Phys. Rev.* **81**, 115 (1951).
- [21] E. H. Wichmann and N. M. Kroll, *Phys. Rev.* **101**, 843 (1956).
- [22] J. Sapirstein and K. T. Cheng, *Phys. Rev. A* **68**, 042111 (2003).
- [23] J. Sapirstein and K. T. Cheng, *Phys. Rev. A* **73**, 012503 (2006).
- [24] P. J. Mohr and J. Sapirstein, *Phys. Rev. A* **62**, 052501 (2000).
- [25] S. A. Blundell, *Phys. Rev. A* **47**, 1790 (1993).
- [26] G. S. Adkins, S. Morrison, and J. Sapirstein, *Phys. Rev. A* **76**, 042508 (2007).
- [27] C. W. P. Palmer, *J. Phys. B* **20**, 5987 (1987); A. P. Stone, *Proc. Phys. Soc.* **77**, 786 (1961); **81**, 868 (1963).
- [28] A. N. Artemyev, V. M. Shabaev, and V. A. Yerokhin, *Phys. Rev. A* **52**, 1884 (1995).
- [29] E. Borie and G. A. Rinker, *Rev. Mod. Phys.* **54**, 67 (1982).
- [30] M. H. Chen, K. T. Cheng, W. R. Johnson, and J. Sapirstein, *Phys. Rev. A* **52**, 266 (1995).
- [31] V. A. Yerokhin, A. N. Artemyev, V. M. Shabaev, M. M. Sysak, O. M. Zherebtsov, and G. Soff, *Phys. Rev. A* **64**, 032109 (2001).
- [32] V. A. Yerokhin, A. N. Artemyev, and V. M. Shabaev, *Phys. Rev. A* **75**, 062501 (2007).
- [33] Y. S. Kozhedub, A. V. Volotka, A. N. Artemyev, D. A. Glazov, G. Plunien, V. M. Shabaev, I. I. Tupitsyn, and Th. Stöhlker, *Phys. Rev. A* **81**, 042513 (2010).
- [34] I. Angeli, *At. Data Nucl. Data Tables* **87**, 185 (2004).
- [35] K. T. Cheng, M. H. Chen, and J. Sapirstein, *Phys. Rev. A* **62**, 054501 (2000).
- [36] NIST Atomic Spectra Database [<http://physics.nist.gov/PhysRefData/ASD>].
- [37] Ph. Bosselmann, U. Staude, D. Horn, K.-H. Schartner, F. Folkmann, A. E. Livingston, and P. H. Mokler, *Phys. Rev. A* **59**, 1874 (1999).
- [38] D. Feili, Ph. Bosselmann, K.-H. Schartner, F. Folkmann, A. E. Livingston, E. Träbert, X. Ma, and P. H. Mokler, *Phys. Rev. A* **62**, 022501 (2000).
- [39] R. Büttner, B. Kraus, K.-H. Schartner, F. Folkmann, P. H. Mokler, and G. Möller, *Z. Phys. D* **22**, 693 (1992).
- [40] Y. Podpaly, J. Clementson, P. Beiersdorfer, J. Williamson, G. V. Brown, and M. F. Gu, *Phys. Rev. A* **80**, 052504 (2009).
- [41] X. Zhang, N. Nakamura, C. Chen, M. Andersson, Y. Liu, and S. Ohtani, *Phys. Rev. A* **78**, 032504 (2008).
- [42] P. Beiersdorfer, A. Osterheld, S. R. Elliott, M. H. Chen, D. Knapp, and K. Reed, *Phys. Rev. A* **52**, 2693 (1995).
- [43] P. Beiersdorfer, H. Chen, D. B. Thorn, and E. Träbert, *Phys. Rev. Lett.* **95**, 233003 (2005).
- [44] P. Beiersdorfer, D. Knapp, R. E. Marrs, S. R. Elliott, and M. H. Chen, *Phys. Rev. Lett.* **71**, 3939 (1993); P. Beiersdorfer, *Nucl. Instrum. Methods Phys. Res. B* **99**, 114 (1995).
- [45] K. T. Cheng, Y.-K. Kim, and J. P. Desclaux, *At. Data Nucl. Data Tables* **24**, 111 (1979).
- [46] Y.-K. Kim, D. H. Baik, P. Indelicato, and J. P. Desclaux, *Phys. Rev. A* **44**, 148 (1991).
- [47] P. Mohr, *Ann. Phys. (NY)* **88**, 26 (1974); **88**, 52 (1974).
- [48] T. A. Welton, *Phys. Rev.* **74**, 1157 (1948).