

QED corrections to the binding energy of the eka-radon ($Z=118$) negative ion

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Quantum electrodynamic (QED) electron self-energy and vacuum polarization corrections to the binding energy of the $8s$ electron in the eka-radon ($Z=118$) negative ion are calculated. This ion was found recently to be stable in the Dirac-Coulomb-Breit Hamiltonian; an improved basis and correlating all 119 electrons give a binding energy of $-0.064(2)$ eV. The QED contribution is $0.0059(5)$ eV, amounting to a 9% reduction of the binding energy. This is the largest relative QED effect reported for neutral or weakly ionized atoms, and confirms the importance of QED corrections for superheavy elements.

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Quantum electrodynamic (QED) corrections, including electron self-energy (SE) and vacuum polarization (VP) effects, were calculated recently for heavy and superheavy atoms with ns valence electrons up to $n=8$ ($Z=119$) [1,2], using the partial wave renormalization (PWR) approach developed in Refs. [3,4] and modified in Ref. [5]. The adequacy of the PWR approach for the one-loop electron self-energy calculations was proved rigorously by Goidenko *et al.* [6]. The results for heavy atoms [1,2] were confirmed recently by employing another QED renormalization scheme [7]. Contributions amounting up to 0.5% of the ionization potential were found for the superheavy elements. The absolute value of the QED correction in element 119 is $\Delta E_{8s}^{QED} = 0.0173$ eV. An accurate relativistic coupled cluster (CC) calculation in the framework of the Dirac-Coulomb-Breit (DCB) Hamiltonian [8] showed the existence of a negative ion of eka-radon ($Z=118$, E118) with a binding energy of $\Delta E_{8s}^b = -0.056(10)$ eV for an electron in the $8s$ orbital. As the QED correction calculated for E119 is not far in magnitude from the calculated electron affinity of eka-radon, the QED effect on the latter quantity may be significant. It is therefore calculated in the present paper.

The one-electron Dirac-Hartree-Fock approximation does not lead to an $8s$ electron bound to E118; only the highly correlated CC wave function gives the binding-energy cited above [8]. On the other hand, the rigorous QED approach employed for the evaluation of QED corrections in Ref. [2] is based essentially on the one-particle picture. This is due to the necessity of introducing intermediate states of the electron between the emission and absorption of the virtual photon in the expression for the self-energy operator. The description of the intermediate states with a correlated wave function is beyond the scope of this approach.

One possible solution to this dilemma is to reformulate the results of the CC calculation in terms of one-electron wave functions. The plausibility of such reformulation follows from density-functional theory, where the Dirac-Kohn-Sham (DKS) one-electron wave functions are widely used for the description of electron correlation effects. In particular, the DKS approach was applied to the evaluation of ionization potentials in heavy and superheavy atoms [9,10].

However, the use of the DKS equation with the exchange-correlation potential derived from electron-gas theory does not seem adequate for the very loosely bound $8s$ electron in E118⁻. We choose therefore another way for the one-electron reformulation of CC results. The normalized $8s$ orbital (four-spinor) of the eka-radon anion is extracted by taking the overlap of the Fock-space CC functions of the anion and neutral species,

$$\phi_{8s}(r) = \frac{\langle \Psi_{118}^{CC} | \Psi_{118^-}^{CC} \rangle}{(\langle \Psi_{118}^{CC} | \Psi_{118}^{CC} \rangle \langle \Psi_{118^-}^{CC} | \Psi_{118^-}^{CC} \rangle)^{1/2}}. \quad (1)$$

Note that the numerator of Eq. (1) is a configuration-space integral involving the product of Ψ_{118}^{*} , a 118-electron function, with the 119-electron function Ψ_{118^-} ; the integration is carried out over the coordinates of 118 electrons. It may be written explicitly as $\int \Psi_{118}^{CC*}(1, \dots, 118) \Psi_{118^-}^{CC}(1, \dots, 119) d1 \dots d118$, with the result being a one-electron function. The normalization integrals in the denominator involve integration over all electrons, 118 for the first integral and 119 for the second. The ϕ_{8s} orbital of eka-francium is obtained in similar fashion from the overlap

$$\langle \Psi_{119+}^{CC} | \Psi_{119}^{CC} \rangle / (\langle \Psi_{119+}^{CC} | \Psi_{119+}^{CC} \rangle \langle \Psi_{119}^{CC} | \Psi_{119}^{CC} \rangle)^{1/2}.$$

The radial Dirac equations with effective local potential $U(r)$ that we introduce for the $8s$ electron are (in atomic units):

$$c \left(f' + \frac{\kappa}{r} f \right) - [E + mc^2 - U(r)] g(r) = 0, \quad (2)$$

$$c \left(g' - \frac{\kappa}{r} g \right) - [E - mc^2 - U(r)] f(r) = 0, \quad (3)$$

where κ is the Dirac angular quantum number ($\kappa = -1$ for s electrons). The potential $U(r)$ is obtained by

$$U(r) = \frac{c \left(g' + \frac{g}{r} \right) + \varepsilon f}{f}, \quad (4)$$

where f and g are the large and small components, respectively, of ϕ_{8s} of Eq. (1), and $\varepsilon = E - mc^2$. The numerical value of ε is the coupled cluster electron affinity of the E118 atom.

The same approach was used also for the $8s$ valence electron in neutral eka-francium (element 119), where the Lamb shift was calculated earlier in the Dirac-Hartree-Fock approximation [2]. For this case, the value of ε_{E119} in Eq. (4) is taken as -4.792 eV, the CC ionization potential of E119.

The potential $U(r)$ is all we need to apply a rigorous QED approach, based on partial wave renormalization of the SE operator [5] and used in Ref. [2] for the calculation of QED corrections in heavy and superheavy atoms with valence ns electrons. The solution of the Dirac equation with the potential $U(r)$ provides us with the full basis set necessary to construct the SE operator within our approach. One of the solutions represents the correlated $8s$ orbital of E118—.

Having found the potential, the Dirac equations (2) and (3) were solved to yield the full set of orbitals. This was achieved through the B -spline approach [11]. The number of grid points was $N = 140$ – 300 , the order of splines $k = 9$. $L = 16$ partial waves were used in the PWR expansion. The accuracy of the PWR approach with these characteristics is better than 2% [5].

The VP correction was obtained as the average value of the VP Uehling potential with ϕ_{8s} of Eq. (1). The Uehling potential usually gives a fairly good approximation to the exact VP correction. The ratio of the remainder (the Wichmann-Kroll term) to the Uehling term in a one-electron ion with $Z = 100$ is 1:20 [12]. The Wichmann-Kroll term represents higher-order contributions in powers of αZ , where α is the fine-structure constant, and its relative effect on the screened external electron of the E118 anion (with small effective Z) is therefore much smaller than for the single electron in the Coulomb field of $Z = 100$. The expected error of the Uehling approximation is therefore well below 5%. Another approximation involves the neglect of the indirect influence of QED corrections for the inner electrons on the energy of the valence electron, pointed out for Hartree-Fock functions by Desiderio and Johnson [13]. The relative corrections to the inner-shell electron energies are of order $\alpha(\alpha Z)^2$ and cannot exceed 1% [12], putting their effect well below the accuracy level sought here.

The calculations for E118 are complicated by the fact that the $8s$ orbital is not bound in the Dirac-Fock-Breit approximation, and may not be a good representation of the anionic orbital. In order to obtain a bound orbital, we put partial charges on some of the external electrons; this is compensated by adding an appropriate one-electron perturbation term, which is summed to infinite order in the CC method. Previous experience [8] has shown that the final electron affinity shows only weak dependence on the details of this approximation. Three one-electron schemes are used in the

TABLE I. Dirac-Coulomb-Breit electron affinity and QED corrections for E118 (eV).

Scheme	DCB EA	SE	VP	Total QED	Final EA
A	-0.0644	0.00911	-0.00355	0.00556	-0.0588
B	-0.0646	0.00904	-0.00336	0.00568	-0.0586
C	-0.0624	0.01016	-0.00369	0.00647	-0.0559

present calculations: scheme A puts charges of $0.8e$ on the four $7p_{3/2}$ electrons; scheme B puts charges of $0.9e$ on each of the six $7s$ and $7p_{3/2}$ electrons; and scheme C has $0.9e$ on the eight $7s$ and $7p$ electrons. This strategy was not necessary for E119.

The present coupled cluster calculations are better than the previous work [8] in two respects. The basis set, taken from the universal basis of Malli, Da Silva, and Ishikawa [14], was increased to $36s32p24d22f10g7h6i$ uncontracted Gaussian type orbitals, and all 119 electrons were correlated at the coupled cluster singles-and-doubles level. The electron affinities and QED effects calculated in the three schemes described above are shown in Table I. The differences between the three schemes result from the different sets of orbitals used. A full CI calculation would show no dependence on the orbitals; the relatively small differences obtained here attest to the robustness of our method. The average and standard deviation of the three DCB calculations give $-0.0638(12)$ eV. Trials with different basis sets indicate a remaining possible error of ~ 1 meV, yielding a DCB electron affinity (EA) of $-0.064(2)$ eV. The improved basis and correlation treatment yield somewhat stronger binding of the $8s$ electron than the $-0.056(10)$ eV reported before [8], but still within the error bounds of the previous calculation. The total QED correction (Lamb shift) is $0.0059(5)$ eV, giving a corrected electron affinity of $-0.058(3)$ eV.

The same method was used to calculate the ionization potential and QED correction of eka-francium (E119). Here it was not necessary to put fractional charges on the electrons. The DCB CC ionization potential is 4.792 eV. The self-energy and vacuum polarization corrections are, respectively, 0.0268 and -0.0092 eV, for a total Lamb shift of 0.0176 eV. This value is very close to the 0.0173 eV obtained from Dirac-Hartree-Fock wave functions [2].

Another approach to the calculation of Lamb shifts is to use the local potential proposed by Salvat *et al.* [15], fitting the Slater exchange parameter α_x to available data. We constructed this local potential using the closed-shell CC one-electron densities $\rho_{118}^{CC}(r)$ and $\rho_{119}^{CC}(r)$. From these densities, the moments

$$R_n = \frac{1}{(n+1)!Z} \int r^n \rho^{CC}(r) d^3r \quad (5)$$

were calculated for $-1 \leq n \leq 5$. The local potentials were presented in the five-parameter approximation (see details in Ref. [15]),

$$U(r) = -\frac{Z}{r} \sum_{i=1}^3 A_i e^{\alpha_i r} - \frac{3}{2} \alpha_x \left[\frac{3}{\pi} \rho^{CC}(r) \right]^{1/3}. \quad (6)$$

The Slater parameter α_x was adjusted to fix the binding energy of $8s$ valence electron at the CC values of -0.064 eV for E118⁻ and -4.792 eV for E119. The parameters A_i and α_i were determined using Eq. (5). With the parameters $\alpha_1 = 10.8320$, $\alpha_2 = 0.080$, $\alpha_3 = 0$, $A_1 = 0.5129$, $A_2 = 0.4871$, and $A_3 = 0$, we get for E118 in orbital scheme B a self-energy correction of 0.00901 eV, very close to the corresponding value in Table I.

The total QED correction for the electron affinity of E118 reduces the Dirac-Coulomb-Breit coupled cluster value by

9.2%. To our knowledge, this is the largest relative QED correction observed for neutral or weakly ionized atomic systems, and it confirms the importance of these corrections in superheavy atoms.

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- [1] P. Pyykkö, M. Tokman, and L. Labzowsky, *Phys. Rev. A* **57**, R689 (1998).
 [2] L. Labzowsky, I. Goidenko, M. Tokman, and P. Pyykkö, *Phys. Rev. A* **59**, 2707 (1999).
 [3] H. Persson, I. Lindgren, and S. Salomonson, *Phys. Scr.*, T **T46**, 125 (1993).
 [4] H.M. Quiney and I.P. Grant, *Phys. Scr.*, T **T46**, 132 (1993).
 [5] L. Labzowsky, I. Goidenko, and A. Nefiodov, *J. Phys. B* **31**, L477 (1998).
 [6] I. Goidenko, G. Plunien, S. Zschocke, L. Labzowsky, and G. Soff, *Phys. Rev. A* **65**, 042110 (2002).
 [7] J. Sapirstein and K.T. Cheng, *Phys. Rev. A* **66**, 042501 (2002).
 [8] E. Eliav, U. Kaldor, Y. Ishikawa, and P. Pyykkö, *Phys. Rev. Lett.* **77**, 5350 (1996).
 [9] S. Kotochigova, Z.H. Levine, E.L. Shirley, M.D. Stiles, and C.W. Clark, *Phys. Rev. A* **55**, 191 (1997).
 [10] X-M. Tong and S-I. Chu, *Phys. Rev. A* **57**, 855 (1998).
 [11] W.R. Johnson, S.A. Blundell, and J. Sapirstein, *Phys. Rev. A* **37**, 37 (1988).
 [12] L.N. Labzowsky, G.L. Klimchitskaya, and Yu.Yu. Dmitriev, *Relativistic Effects in the Spectra of Atomic Systems* (IOP Publishing Ltd., Bristol, 1993).
 [13] A.M. Desiderio and W.R. Johnson, *Phys. Rev. A* **3**, 1267 (1971).
 [14] G.L. Malli, A.B.F. Da Silva, and Y. Ishikawa, *Phys. Rev. A* **47**, 143 (1993).
 [15] F. Salvat, J.D. Martinez, R. Mayol, and J. Parellada, *Phys. Rev. A* **36**, 467 (1987).