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Quantum electrodynamic corrections for the valence shell in heavy many-electron atoms

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We present quantum electrodynamic (QED) calculations within the picture of bound-state QED for the frequency-dependent Breit interaction between electrons, the vacuum polarization, and the electron self-energy correction starting from the Dirac-Coulomb Hamiltonian for the ionization potentials of the group 1, 2, 11, 12, 13, and 18 elements of the periodic table, and down to the superheavy elements up to nuclear charge $Z = 120$. The results for the s-block elements are in very good agreement with earlier studies by Labzowsky *et al.* [Phys. Rev. A **59**, 2707 (1999)]. We discuss the influence of the variational versus perturbative treatment of the Breit interaction for valence-space ionization potentials. We argue that the lowest-order QED contributions become as important as the Breit interaction for ionization potentials out of the valence s shell.

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I. INTRODUCTION

Considerable progress has been made in the past decade in accurately describing few-electron systems in strong Coulomb fields [1,2]. For example, calculations for Li-like uranium using relativistic many-body perturbation theory gives 322.33 eV for the $^2S_{1/2}$,$^2P_{1/2}$ level splitting [3], which corrects to 280.56 eV on inclusion of lowest-order vacuum polarization and electron self-energy [4,5]. This is already in excellent agreement with the experimental value of 280.59(9) eV of Schweppe *et al.* [6]. Higher-order quantum electrodynamic (QED) corrections including mass polarization and recoil contributions from the nucleus are not negligible but approximately cancel out [1]. Even more impressive is that QED effects regarding the electronic g factor are now that precise that hadronic contributions need to be considered to achieve agreement with experiments [7–9].

The situation completely changes for multielectron systems [10,11] as accurate relativistic electronic structure calculations including QED effects become prohibitively more demanding in computer time with increasing number of electrons involved. Moreover, one has to change from the simple free-particle Feynman-Dyson picture to the bound-state picture (e.g., the Furry picture) which modifies the electron propagator involving the actual one-particle functions from the Dirac-Coulomb Hamiltonian. An accurate QED treatment is therefore restricted mostly to few-electron systems [1,2,12–15], which provide the ideal testing ground for high-precision experiments [16]. Here we mention recent work by Glazov *et al.*, who obtained screened QED corrections of first order in α and $1/Z$ for the g factor and the hyperfine splitting of lithium-like ions [17].

The accurate treatment of electron correlation for multielectron systems currently remains the bottleneck in all quantum theoretical many-electron calculations. Nevertheless, in the past decade great progress has been made in relativistic quantum calculations of heavy atoms or molecules with high nuclear charge up to the superheavy elements [10,18–22], in particular at the Dirac-Breit level applying Fock-space coupled-cluster theory for valence shells in atoms [23,24]. These calculations now reach accuracies of approximately 10^{-2} eV for ionization potentials and excitation energies. Hence, they are now in the region where one has to consider self-energy (SE) and vacuum polarization (VP) contributions to lowest order to correct for valence properties. Here we note that the efficient treatment of QED effects in molecules is still an open question, and it is highly desirable to construct effective QED Hamiltonians which can be used variationally in molecular calculations.

To lowest order, QED effects consist of the one-photon Breit interaction (BI) [25–27], the Uehling form of the vacuum polarization (VP) [28], and the one-loop self-energy (SE) contribution [29,30], with BI being the dominant term, followed by the electron SE. The VP is usually much smaller than the SE for electrons in a Coulomb potential and of opposite sign. While the BI and pure VP (including higher order in the fine structure constant α) are more easily implemented into atomic program codes, the evaluation of the SE term requires a complete set of one-particle Dirac states within the bound-state picture of QED, which becomes rather tedious, and even in the lowest order it cannot be expressed anymore in closed form as a simple local potential. It is therefore desirable to have an expression for the self-energy free of an implicit dependence on the one-particle functions but still accurate enough to treat this term to lowest order. Such an approach may later be extended to molecular systems.

In a recent article Labzowsky and coworkers presented estimates for the Lamb shift of the valence ns electron levels in the alkali (Li-Fr) and coinage metal atoms (Cu-Au) [31]. In a subsequent article they confirmed these estimates by using the local potential method of Salvat *et al.* [32] for SE calculations within a Dirac-Fock and Dirac-Slater approach [33]. In this article we use a Dirac-Hartree-Fock approach within the bound-state QED picture [34,35] to evaluate QED corrections to valence-shell ionization potentials for the groups 1, 2, 11, 12, 13, and 18 elements of the periodic table down to the heaviest atoms with nuclear charge $Z = 120$ and compare them with the results of Labzowsky and coworkers [33].

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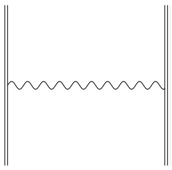

FIG. 1. Feynman diagram of the lowest-order Breit interaction.

II. COMPUTATIONAL DETAILS

Dirac-Hartree-Fock (DHF) calculations are carried out using the Dirac-Coulomb (DC) Hamiltonian (in relativistic units),

$$H_0 = \sum_i (\vec{\alpha}_i \vec{p}_i + m\beta_i + V_{\mathrm{nuc}}) + \sum_{i<j} \frac{1}{r_{ij}}, \tag{1}$$

where $\vec{\alpha}$ and β are the Dirac matrices in the standard Dirac representation. The equations are solved numerically using a modified code of the program system GRASP [36,37]. For the heavy elements the 1s-shell radius becomes very small ($\langle r \rangle_{1s} \approx 520$ fm for Cn), and as a consequence the influence of the finite nuclear size becomes an important contribution to the total energy. The electrostatic potential of the nucleus V_{nuc} was therefore modeled by a two-parameter Fermi-type charge distribution [38,39]

$$\varrho(r) = \frac{\varrho_0}{1 + \exp[(r - R_0)/t]}, \tag{2}$$

where the nuclear radius R_0 and the diffuseness parameter t are obtained from the nuclear mass (for details see Refs. [38,39]. Here we note that our results are not sensitive to the nuclear model chosen, and a Gaussian nuclear charge distribution leads virtually to the same results reported here.

Because of the small size of the quantum electrodynamic (QED) corrections they are treated as a perturbation [40], although a fully self-consistent implementation of these effects within the GRASP code is currently in progress. The major correction to the nonrelativistic Coulomb term comes from the Breit operator, which can be rigorously derived from QED [41]. We treat the Breit interaction in the Coulomb gauge [25–27]

$$g_{\omega,C}(1,2) = -\frac{\vec{\alpha}_1\vec{\alpha}_2}{r_{12}} \exp(i\omega_{12} r_{12}) \tag{3}$$

$$-(\vec{\alpha}_1 \vec{\nabla}_1)(\vec{\alpha}_2 \vec{\nabla}_2) \frac{\exp(i\omega_{12} r_{12}) - 1}{\omega_{12}^2 r_{12}}, \tag{4}$$

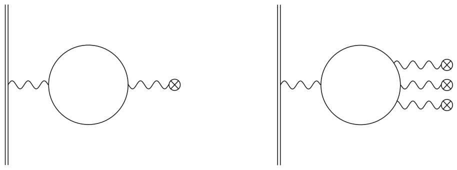

FIG. 2. Feynman diagrams for vacuum polarization of order $\alpha(Z\alpha)$ Uehling (left) and of order $\alpha(Z\alpha)^3$ Wichmann and Kroll (right).

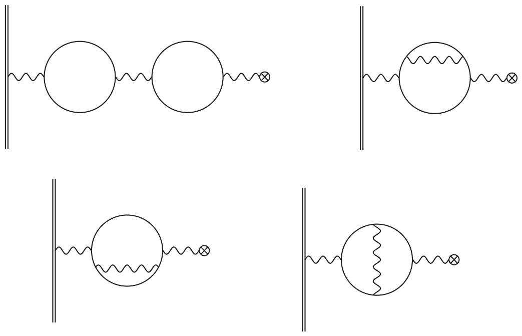

FIG. 3. Vacuum polarization of order $\alpha^2(Z\alpha)$ (Källen-Sabry).

where ω_{12} is the energy of the virtual (transversal) exchange photon. The first term is the retarded Gaunt term (GI) and the second term arises from the choice of the Coulomb gauge instead of the Feynman gauge, which we call the retarded gauge term. This correction to the electron-electron interaction accounts for magnetic interaction and retardation to the order α^2, and only includes the exchange of a single (left-right), virtual photon as shown in Fig. 1. In the following we adopt the low frequency limit for the Breit interaction, i.e., $\omega_{12} = 0$, if not otherwise stated. We mention that the frequency dependence of the Breit term has been explored in the past and refer to Gorceix and Indelicato for details [42].

The (other) radiative corrections are calculated by a nonlocal radiative potential, which is split into an self-energy and a vacuum polarization part and the energy shift can calculated perturbatively as an expectation value of a radiative one-electron potential using the eigenfunctions of the DHF operator. The vacuum polarization can be split into the following contributions:

$$\begin{aligned} \Delta E_{\mathrm{VP}} &= \langle \Psi | \Phi_{\mathrm{VP}}(r) | \Psi \rangle \\ &\simeq \langle \Psi | \Phi_{\mathrm{U}}(r) + \Phi_{\mathrm{WK}}(r) + \Phi_{\mathrm{KS}}(r) | \Psi \rangle, \end{aligned} \tag{5}$$

where Φ_{U} is the Uehling potential [28], Φ_{WK} the Wichmann-Kroll correction [43], and Φ_{KS} the Källen-Sabry term [44].

The radiative perturbation expansion is usually in the two parameters α and $Z\alpha$, where the powers of α describe the order of the QED corrections and $Z\alpha$ describes the order of relativistic corrections to the energy levels [40]. It is known that the latter expansion works quite well for lighter elements, but it is far from clear how well it works for elements with high nuclear charge such as the superheavy elements where $Z\alpha \lesssim 1$.

For the vacuum polarization the potential is well known. By utilizing perturbation theory for the polarization operator $\Pi(-p^2)$, the energy contribution of lowest-order $\alpha(Z\alpha)$ is

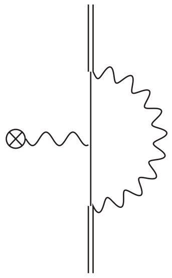

FIG. 4. Feynman diagram of the electron self-energy.

TABLE I. Adjusted coefficients $A_n(Z)$ for the electric interaction term in Eq. (13).

n	A_{n0}	A_{n1}	A_{n2}
1	0.7645	0.00230	112.930
2	0.7912	0.00629	101.636
3	0.7980	0.00738	101.611
4	0.8009	0.00779	101.047
5	0.8023	0.00799	100.632
6	0.8032	0.00813	100.607
7	0.8037	0.00824	100.591
∞	0.8061	0.00860	100.765

given by the Uehling potential [28], where the virtual electron-positron pair is allowed to propagate freely (Fig. 2),

$$\Phi_{\mathrm{U}}(r) = \frac{2\alpha}{3\pi}\phi(r)\int_1^\infty dt\,\frac{\sqrt{t^2-1}}{t^2}\left(1+\frac{1}{2t^2}\right)e^{-2trm}. \tag{6}$$

Here m is the electron mass and $\phi(r)$ is the nuclear Coulomb potential because in the short range of the interaction the difference to the DHF potential is negligible. The Uehling term gives typically more than 90% of the VP in hydrogen-like atoms. In presence of the nuclear Coulomb field the electron and positron wave functions become distorted. Wichmann and Kroll [43] have considered the vacuum polarization of order α in a strong Coulomb field (Fig. 2) and have shown that the polarization charge density is an analytic function of $Z\alpha$ for $|Z\alpha| \leqslant 1$,

$$\Phi_{\mathrm{WK}}(r) = \frac{\alpha(Z\alpha)^3}{\pi}\left[\left(-\frac{3}{2}\zeta(3)+\frac{\pi^2}{6}-\frac{7}{9}\right)\frac{1}{r}+2\pi\zeta(3) - \frac{\pi^3}{4}+\left(-6\zeta(3)+\frac{\pi^4}{16}-\frac{\pi^2}{6}\right)r+O(r^2)\right]. \tag{7}$$

The Källen-Sabry correction [44] cannot be written in such a short analytical form so we present just the crucial Feynman diagrams in Fig. 3. The VP terms presented here and the frequency-dependent Breit contribution in the Coulomb gauge are already available in GRASP [36,37].

The calculation of the self-energy operator $\Sigma(r,r',E)$ shown in Fig. 4 is more complicated and rather tedious. The problem can be divided into two parts. In the first part the electron interacts with a high-frequency virtual photon where the nuclear Coulomb field needs to be included only in first order. The second part represents the interaction with a low-frequency photon. The calculations of the vertex correction necessary electric $f(p^2)$ and magnetic $g(p^2)$ form factors can be found in Ref. [35],

$$\Phi_{\mathrm{SE}}(p) = \left[\frac{g(-p^2)}{2m}\vec{\gamma}\vec{p}+f(-p^2)-1\right]\phi(p). \tag{8}$$

TABLE II. Adjusted coefficients c_i for the coefficients A_{ni} in Eq. (14).

i	c_{i0}	c_{i1}	c_{i2}
0	0.80608	−0.0516	1.489
1	0.00860	−0.7329	1.465
2	100.76488	0.1207	3.473

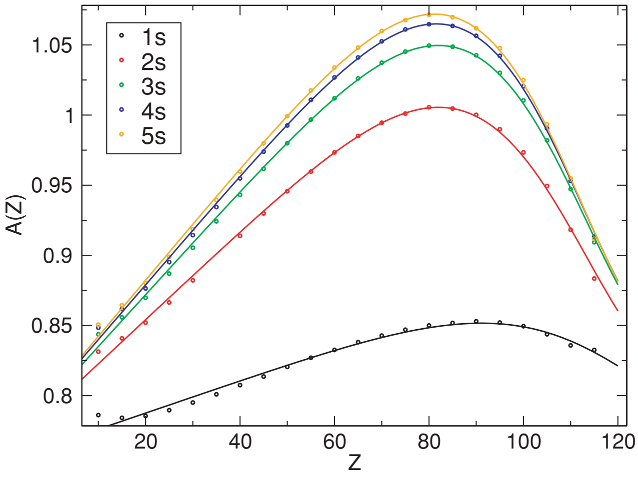

FIG. 5. (Color online) Adjusted coefficients $A_n(Z)$ for different ns orbitals for the electric interaction term in Eq. (13).

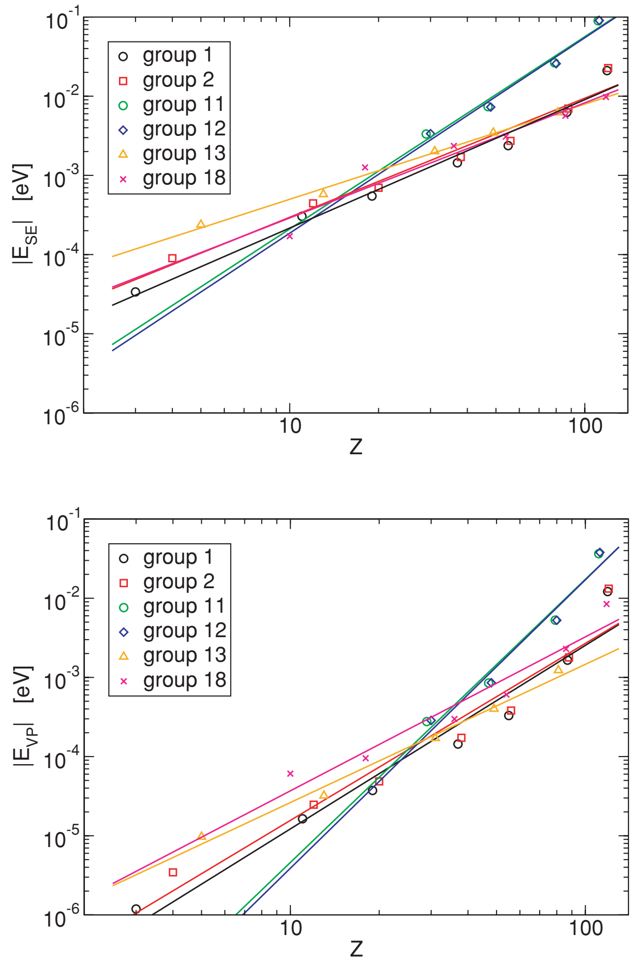

FIG. 6. (Color online) Self-energy and vacuum polarization contributions to the ionization potential for different atoms.

TABLE III. The self-energy (SE), vacuum polarization (VP), and frequency-dependent Breit contributions (BI) (in eV) and sum over all QED contributions to the ionization potential $E \to E^+$ of each element E at the DHF level of theory. Notation: SC, self-consistent treatment; PT, perturbative treatment; GI, gaunt term only; $\omega = 0$, low-frequency limit.

System	PT-SE	PT-VP	SC-GI ($\omega = 0$)	SC-BI ($\omega = 0$)	PT-BI ($\omega = 0$)	PT-BI (ω)
Group 1 ($^2S_{1/2} \to {}^1S_0$)						
Li	-3.374×10^{-5}	1.189×10^{-6}	-1.418×10^{-4}	-1.279×10^{-4}	-1.279×10^{-4}	-1.279×10^{-4}
Na	-3.041×10^{-4}	1.637×10^{-5}	-2.735×10^{-4}	-2.799×10^{-4}	-2.800×10^{-4}	-2.807×10^{-4}
K	-5.478×10^{-4}	3.730×10^{-5}	-2.483×10^{-4}	-2.751×10^{-4}	-2.753×10^{-4}	-2.788×10^{-4}
Rb	-1.442×10^{-3}	1.439×10^{-4}	-2.631×10^{-4}	-3.570×10^{-4}	-3.575×10^{-4}	-3.852×10^{-4}
Cs	-2.377×10^{-3}	3.282×10^{-4}	-2.254×10^{-4}	-3.717×10^{-4}	-3.730×10^{-4}	-3.700×10^{-4}
Fr	-6.261×10^{-3}	1.586×10^{-3}	-4.729×10^{-4}	-7.401×10^{-4}	-7.400×10^{-4}	-1.255×10^{-3}
E119	-2.103×10^{-2}	1.207×10^{-2}	-4.136×10^{-3}	-4.547×10^{-3}	-4.580×10^{-3}	-7.640×10^{-3}
Group 2 ($^1S_0 \to {}^2S_{1/2}$)						
Be	-8.998×10^{-5}	3.450×10^{-6}	-3.763×10^{-4}	-3.460×10^{-4}	-3.460×10^{-4}	-3.460×10^{-4}
Mg	-4.436×10^{-4}	2.469×10^{-5}	-5.320×10^{-4}	-5.206×10^{-4}	-5.208×10^{-4}	-5.219×10^{-4}
Ca	-6.975×10^{-4}	4.860×10^{-5}	-4.603×10^{-4}	-4.692×10^{-4}	-4.693×10^{-4}	-4.738×10^{-4}
Sr	-1.705×10^{-4}	1.728×10^{-4}	-5.633×10^{-4}	-6.302×10^{-4}	-6.310×10^{-4}	-6.626×10^{-4}
Ba	-2.729×10^{-3}	3.817×10^{-4}	-5.669×10^{-4}	-6.792×10^{-4}	-6.800×10^{-4}	-7.770×10^{-4}
Ra	-6.980×10^{-3}	1.789×10^{-3}	-1.049×10^{-3}	-1.249×10^{-3}	-1.251×10^{-3}	-1.788×10^{-3}
E120	-2.264×10^{-2}	1.315×10^{-2}	-5.210×10^{-3}	-5.478×10^{-3}	-5.500×10^{-3}	-8.620×10^{-3}
Group 11 ($^2S_{1/2} \to {}^1S_0$)						
Cu	-3.328×10^{-3}	2.765×10^{-4}	-3.692×10^{-3}	-3.442×10^{-3}	-3.447×10^{-3}	-3.452×10^{-3}
Ag	-7.377×10^{-3}	8.930×10^{-4}	-5.441×10^{-3}	-5.196×10^{-3}	-5.207×10^{-3}	-5.253×10^{-3}
Au	-2.643×10^{-2}	5.284×10^{-3}	-1.274×10^{-2}	-1.225×10^{-2}	-1.228×10^{-2}	-1.275×10^{-2}
Rg	-8.925×10^{-2}	3.634×10^{-2}	-3.613×10^{-2}	-3.398×10^{-2}	-3.414×10^{-2}	-3.754×10^{-2}
Rg[a]	3.139×10^{-2}	-1.215×10^{-2}	2.820×10^{-2}	2.647×10^{-2}	2.660×10^{-2}	2.603×10^{-2}
Group 12 ($^1S_0 \to {}^2S_{1/2}$)						
Zn	-3.366×10^{-3}	2.864×10^{-4}	-3.418×10^{-3}	-3.221×10^{-3}	-3.225×10^{-3}	-3.236×10^{-3}
Cd	-7.286×10^{-3}	8.562×10^{-4}	-5.116×10^{-3}	-4.911×10^{-3}	-4.921×10^{-3}	-4.982×10^{-3}
Hg	-2.574×10^{-2}	5.261×10^{-3}	-1.207×10^{-2}	-1.162×10^{-2}	-1.165×10^{-2}	-1.217×10^{-2}
Cn	-9.051×10^{-2}	3.788×10^{-2}	-3.652×10^{-2}	-3.432×10^{-2}	-3.449×10^{-2}	-3.812×10^{-2}
Cn[b]	3.766×10^{-2}	-1.499×10^{-2}	3.070×10^{-2}	2.896×10^{-2}	2.985×10^{-2}	2.909×10^{-2}
Group 13 ($^2P_{1/2} \to {}^1S_0$)						
B	2.381×10^{-4}	-9.695×10^{-6}	-8.682×10^{-4}	-6.848×10^{-4}	-6.848×10^{-4}	-6.847×10^{-4}
Al	5.776×10^{-4}	-3.212×10^{-5}	-1.291×10^{-3}	-1.071×10^{-3}	-1.071×10^{-3}	-1.071×10^{-3}
Ga	2.018×10^{-3}	-1.707×10^{-4}	-4.163×10^{-3}	-3.486×10^{-3}	-3.491×10^{-3}	-3.483×10^{-3}
In	3.466×10^{-3}	-4.010×10^{-4}	-7.269×10^{-3}	-6.201×10^{-3}	-6.215×10^{-3}	-6.208×10^{-3}
Tl	6.223×10^{-3}	-1.226×10^{-3}	-1.681×10^{-2}	-1.496×10^{-2}	-1.502×10^{-2}	-1.524×10^{-2}
E113	-3.184×10^{-3}	2.860×10^{-3}	-4.896×10^{-2}	-4.634×10^{-2}	-4.668×10^{-2}	-4.988×10^{-2}
Group 18 ($^1S_0 \to {}^2P_{3/2}$)						
He	-1.781×10^{-4}	5.871×10^{-6}	-1.735×10^{-3}	-1.735×10^{-3}	-1.735×10^{-3}	-1.735×10^{-3}
Ne	1.075×10^{-3}	-6.326×10^{-5}	-2.152×10^{-3}	-1.473×10^{-3}	-1.682×10^{-3}	-1.668×10^{-3}
Ar	1.260×10^{-3}	-9.803×10^{-5}	-1.489×10^{-3}	-7.243×10^{-3}	-9.264×10^{-4}	-8.849×10^{-4}
Kr	2.354×10^{-3}	-3.042×10^{-4}	-3.060×10^{-3}	-1.675×10^{-3}	-2.055×10^{-3}	-1.751×10^{-3}
Xe	3.084×10^{-3}	-6.147×10^{-4}	-4.162×10^{-3}	-2.374×10^{-3}	-2.824×10^{-3}	-1.959×10^{-3}
Rn	5.663×10^{-3}	-2.338×10^{-3}	-4.886×10^{-3}	-2.365×10^{-3}	-2.993×10^{-3}	-2.960×10^{-3}
E118	9.769×10^{-3}	-9.154×10^{-3}	-1.779×10^{-3}	8.490×10^{-4}	3.200×10^{-4}	7.080×10^{-3}

[a] The $^2D_{5/2}(6d^97s^2) \to {}^3F_4(6d^87s^2)$ transition is taken.

[b] The $^1S_0(6d^{10}7s^2) \to {}^2D_{5/2}(6d^97s^2)$ transition is taken.

After a lengthy but straightforward calculation [34,35] one obtains

$$\begin{aligned}\Phi_{\text{SE}}(r) &= \frac{1}{4\pi^2 r}\text{Im}\int \Phi_{\text{SE}}(p)e^{irp}pdp \\ &= \Phi_{\text{mag}}(r) + \Phi_{\text{el}}(r) + \Phi_{\text{low}}(r).\end{aligned} \tag{9}$$

The contribution from the magnetic form factor is given by

$$\Phi_{\text{mag}}(r) = \frac{\alpha}{4\pi m} i\vec{\gamma}\cdot\vec{\nabla}\left[\phi(r)\left(\int_1^\infty dt\frac{e^{2trm}}{t^2\sqrt{t^2-1}} - 1\right)\right] \tag{10}$$

where $\phi(r)$ is the electric potential of the nucleus. The last two terms are contributions from the electric form factor split into a high and a low-frequency part

$$\begin{aligned}\Phi_{\text{el}}(r) = A(Z)\frac{\alpha}{\pi}\phi(r)\int_1^\infty dt\frac{e^{-2trm}}{\sqrt{t^2-1}}\left[\left(1-\frac{1}{2t^2}\right)\right. \\ \times\left.\left(\ln(t^2-1)+4\ln\left(\frac{1}{Z\alpha}+\frac{1}{2}\right)\right)-\frac{3}{2}+\frac{1}{t^2}\right]\end{aligned} \tag{11}$$

where the function $A(Z)$ is obtained by fitting the total self-energy values to precise data of Mohr for one-electron systems. The (long-range) low-frequency contribution is given by

$$\Phi_{\text{low}}(r) = -B(Z)Z^4\alpha^5 m e^{-Zr/a_{\text{B}}}, \tag{12}$$

where $B(Z) = 0.074 + 0.35Z\alpha$ is a coefficient adjusted to reproduce the radiative shifts for the high Coulomb p levels [34] and a_B is the Bohr radius.

We choose the function $A(Z)$ to be dependent on the principal quantum number n, and $A_n(Z)$ in the electric interaction term (11) is obtained by adjusting our values to accurate calculations of self-energy contributions in hydrogen-like atoms for ns electrons by Mohr [45–48]. Mohr's SE corrections lead to excellent results for the K- and L-shell ionization potentials for the neutral elements up to high nuclear charge [49]. A suitable choice for $A_n(Z)$ is

$$A_n(Z) = A_{n0} + A_{n1}\frac{Z}{1+\exp[(Z/A_{n2})^5]}. \tag{13}$$

The adjusted coefficients A_{ni} for the different main quantum numbers are given in Table I and depicted in Fig. 5.

For higher principal quantum numbers n the coefficients A_{ni} can be derived from a least-squares fit to the data in Table I,

$$A_{ni} = c_{i0}(1 + c_{i1}n^{c_{i2}}) \tag{14}$$

with the coefficients as listed in Table II.

Due to the poles and the indefinite integration the calculation of the expectation values of Eqs. (6), (10), and (11) exhibit some numerical difficulties. The domain of integration is divided into three parts, the singularity around $t = 1$, the middle part, and the integration to infinity. The singularity part then integrated analytically by a series expansion of the potential. The middle part can then be integrated without any complications. For the integration to infinity we use the substitution $u = (1 + t)^{1/2}$ to reduce the integration domain to a finite interval which can again be integrated by a Runge-Kutta scheme.

TABLE IV. Adjusted parameters a and b from a linear fit of the loglog plot in Eq. (15).

Group	C_{SE} (eV)	γ_{SE}	C_{VP} (eV)	γ_{VP}
1	5.169×10^{-6}	1.621	5.867×10^{-8}	2.311
2	9.249×10^{-6}	1.504	9.073×10^{-8}	2.236
11	7.881×10^{-7}	2.427	1.216×10^{-9}	3.575
12	6.339×10^{-7}	2.468	8.843×10^{-10}	3.647
13	3.137×10^{-5}	1.202	4.723×10^{-7}	1.745
18	1.021×10^{-5}	1.453	4.187×10^{-7}	1.942

III. RESULTS AND DISCUSSION

The calculated contributions from the VP, the SE, and the BI to the ionization potential for groups 1, 2, 11, 12, 13, and 18 elements of the periodic table are given in Table III. For ionizations out of a valence s shell, the SE contribution is approximately an order of magnitude larger than the VP for the lighter elements and in general has the opposite sign as one expects. Moreover, the SE is as important in size as the Breit interaction, and for the ionization out of the valence s shell has same sign compared to the Breit contribution. However, the total VP contribution increases over several orders of magnitude for the heavier elements and becomes closer to the SE term with increasing nuclear charge Z. This originates from the strong Coulomb field the inner tail of the valence electrons experience with increasing nuclear charge, which is most important for the short-range Uehling potential. In fact, the VP and SE contributions for the valence-shell ionization potentials approximately fit a simple power law,

$$E(Z) = CZ^\gamma, \tag{15}$$

as shown in Fig. 6. The coefficients C and γ are obtained from a linear regression and given in Table IV. It is worth mentioning that the exponent γ of the vacuum polarization is roughly 40 to 50% larger than the one of the self-energy. Further, the γ values in Eq. (15) show strong Z scaling for

TABLE V. A comparison between our calculated SE contributions with those of Labzowsky *et al.* [33] for the ionization energies ($^2S_{1/2} \rightarrow {}^1S_0$) of the alkali and coinage metal atoms (in eV).

System	Our work	Ref. [33]
Li	-3.374×10^{-5}	-3.84×10^{-5}
Na	-3.041×10^{-4}	-2.83×10^{-4}
K	-5.478×10^{-4}	-4.93×10^{-4}
Rb	-1.442×10^{-3}	-1.23×10^{-3}
Cs	-2.377×10^{-3}	-2.15×10^{-3}
Fr	-6.261×10^{-3}	-6.03×10^{-3}
E119	-2.103×10^{-2}	-2.74×10^{-2}
Cu	-3.328×10^{-3}	-2.66×10^{-3}
Ag	-7.377×10^{-3}	-6.14×10^{-3}
Au	-2.643×10^{-2}	-2.21×10^{-2}
Rg	-8.925×10^{-2}	-8.66×10^{-2}

TABLE VI. A comparison between our calculated SE and VP contributions with those of Blundell [57] for the ${}^2S_{1/2} \rightarrow {}^2P_{1/2},{}^2P_{3/2}$ transitions for Li-like ($N = 3$), Na-like ($N = 11$), and Cu-like ($N = 29$) ions (in eV). Z is the nuclear charge, N the number of electrons, SE+VP is the total QED contribution, and SE+VP+FOSCR includes first-order screening effects (for the corresponding Feynman diagrams; see Fig. 2 in Blundell's work [57].

Z	N	Transition	SE	VP	SE + VP	SE [57]	VP [57]	SE + VP [57]	SE + VP + FOSCR [57]
Li-like ($2s^1$)									
10	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.0150	0.0008	−0.0142	−0.0150	0.0007	−0.0143	−0.0141
10	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.0144	0.0008	−0.0136	−0.0145	0.0007	−0.0138	−0.0135
20	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.206	0.0146	−0.192	−0.205	0.014	−0.191	−0.191
20	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.194	0.0149	−0.179	−0.193	0.014	−0.179	−0.178
30	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.885	0.0761	−0.809	−0.884	0.075	−0.809	−0.810
30	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.817	0.0767	−0.740	−0.822	0.075	−0.747	−0.743
40	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−2.440	0.254	−2.186	−2.46	0.25	−2.21	−2.22
40	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−2.230	0.258	−1.972	−2.27	0.25	−2.02	−2.00
50	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−5.351	0.665	−4.687	−5.45	0.65	−4.80	−4.81
50	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−4.875	0.685	−4.190	−5.00	0.67	−4.33	−4.31
60	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−10.21	1.512	−8.720	−10.52	1.48	−9.04	−9.08
60	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−9.374	1.587	−7.787	−9.68	1.56	−8.12	−8.11
70	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−17.91	3.156	−14.75	−18.57	3.08	−15.49	−15.61
70	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−16.69	3.400	−13.29	−17.32	3.33	−13.99	−13.99
80	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−29.53	6.264	−23.26	−30.91	6.07	−24.84	−25.12
80	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−28.40	6.981	−21.42	−29.56	6.81	−22.75	−22.82
90	3	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−46.81	12.13	−34.67	−49.44	11.57	−37.99	−38.45
90	3	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−47.31	14.15	−33.15	−49.26	13.62	−35.64	−35.87
Na-like ($3s^1$)									
20	11	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.0292	0.0020	−0.0272	−0.0288	0.0019	−0.0269	−0.0279
20	11	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.0275	0.0020	−0.0255	−0.0275	0.0019	−0.0256	−0.0264
30	11	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.174	0.0146	−0.159	−0.167	0.014	−0.153	−0.157
30	11	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.161	0.0147	−0.146	−0.156	0.014	−0.142	−0.145
40	11	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.546	0.0553	−0.491	−0.538	0.054	−0.484	−0.491
40	11	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.502	0.0563	−0.445	−0.497	0.055	−0.442	−0.449
50	11	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−1.286	0.155	−1.131	−1.27	0.15	−1.12	−1.14
50	11	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−1.177	0.160	−1.017	−1.18	0.16	−1.02	−1.03
80	11	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−7.806	1.579	−6.227	−7.82	1.52	−6.30	−6.41
80	11	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−7.473	1.780	−5.693	−7.56	1.73	−5.83	−5.88
90	11	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−12.53	3.072	−9.462	−12.58	2.93	−9.65	−9.86
90	11	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−12.51	3.647	−8.859	−12.69	3.52	−9.17	−9.26
Cu-like ($4s^1$)									
40	29	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.0790	0.0080	−0.0711	−0.0776	0.0075	−0.0701	−0.0736
40	29	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.0732	0.0081	−0.0651	−0.0728	0.0077	−0.0651	−0.0682
50	29	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.266	0.0318	−0.234	−0.255	0.031	−0.224	−0.231
50	29	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.244	0.0327	−0.212	−0.237	0.032	−0.205	−0.210
60	29	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−0.633	0.0893	−0.543	−0.613	0.086	−0.527	−0.541
60	29	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−0.583	0.0938	−0.490	−0.571	0.091	−0.480	−0.489
70	29	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−1.263	0.211	−1.052	−1.24	0.20	−1.04	−1.06
70	29	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−1.178	0.228	−0.950	−1.17	0.22	−0.95	−0.96
90	29	${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	−3.802	0.918	−2.884	−3.76	0.88	−2.88	−2.98
90	29	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	−3.773	1.089	−2.683	−3.79	1.05	−2.74	−2.78

the valence-s states and low scaling for the valence-p states. Extrapolation to high Z shows that the VP and SE curves cross at $Z = 269$ for the group 11 and $Z = 659$ for the group 1 elements. These are much higher nuclear charges than for the inner shell estimates given by Soff *et al.* [50], where for the $1s$ electron a nuclear charge of $Z = 170$ was obtained for cancellation of the VP and SE contributions.

A comparison of our SE results to the results obtained by Labzowsky *et al.* [33] for the groups 1 and 11 valence shell ionization potentials shows good agreement (Table V). Our results are also in good agreement with recent first-order QED corrections for valence electrons of heavy elements obtained by Goidenko [51]. We note that all three SE terms (10), (11), and (12) are important for the total SE contribution. For example, for the ${}^2S_{1/2} \rightarrow {}^1S_0$ ionization of gold the magnetic form factor contribution to the total SE is 20%, the one for the electric form factor is 58%, and the one from the (long-range) low-frequency contribution is 21%. Note that for Rg ($Z = 111$) and Cn ($Z = 112$) the relativistic $7s$ contraction is so large that ionization occurs out of the $6d_{5/2}$ shell instead of the $7s$ shell [52–55]. This is in contrast to the lighter groups 1 and 11 elements where ionization occurs out of the valence ns shell. This explains the changing trend in all QED contributions down the groups 11 and 12 in the periodic table. Labzowsky *et al.* [33] only considered removal of an electron out of the ns shell. If we consider the ${}^2D_{5/2}(6d^97s^2) \rightarrow {}^3D_3(6d^97s^1)$ for Rg, i.e., the removal of a $7s$ valence electron, we obtain SE and VP values of -8.088×10^{-2} and 3.298×10^{-2} eV, respectively, very close to the corresponding values for the ${}^2S_{1/2}(6d^{10}7s^1) \rightarrow {}^1S_0(6d^{10})$ transition. We also note a recent article by Indelicato *et al.* [10] on QED effects in superheavy elements. Their total SE term within the Welton model [56] at the DHF level of theory for Rg is 0.084 eV which again is in reasonable agreement with our value.

The accuracy of our implemented self-energy term can be assessed by comparison with more accurate treatment for multielectron systems. Here we compare to Blundell's results who also included direct and exchange SE and VP screening effects within a relativistic many-body perturbation theory treatment in ${}^2S_{1/2} \rightarrow {}^2P_{1/2},{}^2P_{3/2}$ transitions for Li-like, Na-like, and Cu-like ions [57]. The results are presented in Table VI. The VP and SE contributions are in very good agreement with Blundell's results for all ions. Somewhat larger deviations are only obtained for the SE contributions at low principal quantum number and high nuclear charges, which is to be expected. However, even for Li-like ions with Z up to 90 we get for the ${}^2S_{1/2} \rightarrow {}^2P_{1/2},{}^2P_{3/2}$ transitions deviations in the SE term of no more than 5.3%. For the correct order in the SE contributions to the ${}^2P_{1/2},{}^2P_{3/2}$ splitting one requires a rather more accurate treatment of the SE term. Further improvements could be made by choosing the coefficient $B(Z)$ in Eq. (12) to be n dependent as well similar to the $A_n(Z)$ coefficients.

We also list SE and VP contributions for the groups 13 and 18 elements of the periodic table for comparison. A self-consistent treatment of the QED effects to account for second-order effects originating from SE and VP core relaxation of the s electrons at the nucleus, which leads to shielding/deshielding of the nuclear charge, shows only minor deviations from the perturbative results. For a detailed discussion see Flambaum and Ginges [34] as well as Derevianko *et al.* [58]. Nevertheless, the results clearly show that even for the superheavy elements SE and VP contributions for the p shell rarely exceed 0.01 eV, and we expect even smaller effects for d and f shells. As the error in the electron correlation procedure in future high-precision atomic or molecular calculations in many-electron systems (as opposed to few electron systems) is expected to be much larger, QED effects coming from the $l > 0$ valence shells can perhaps be neglected or included only at the Dirac-Hartree-Fock level in lowest order.

Table III shows that, as expected, the frequency independent (instantaneous) Gaunt term is the dominant contribution to the total Breit interaction for all elements considered, as this was discussed earlier in great detail by Lindroth *et al.* [59]. We

TABLE VII. Dirac-Coulomb-Hartree-Fock (DHF) orbital energies and self-consistent (SC) as well as perturbative (PT) Breit (BI) contributions (eV) in the low-frequency limit to the corresponding orbital energies of the neutral mercury atom in comparison with Lindroth *et al.* [59]. In the usual angular-momentum notation * denotes $j = l - 1/2$, otherwise $j = l + 1/2$ is chosen.

Hg	DHF	PT-BI	PT-BI [59]	SC-BI	SC-BI [59]
$1s$	−83654.153	312.191	315.103	298.661	298.233
$2s$	−14973.120	41.981	41.714	33.486	33.470
$3s$	−3622.197	9.926	9.635	6.198	6.193
$4s$	−833.983	2.761	2.496	1.272	1.270
$5s$	−138.861	0.568	0.493	0.192	0.191
$6s$	−8.926	0.038	0.042	0.012	0.012
$2p^*$	−14336.449	66.549	65.470	56.259	56.245
$3p^*$	−3337.174	15.397	14.337	10.704	10.702
$4p^*$	−710.872	4.153	3.491	2.269	2.269
$5p^*$	−96.271	0.778	0.593	0.330	0.330
$2p$	−12385.444	45.457	43.918	35.505	35.510
$3p$	−2899.240	11.147	9.736	6.386	6.386
$4p$	−603.781	3.203	2.322	1.186	1.186
$5p$	−77.333	0.628	0.373	0.131	0.131
$3d^*$	−2433.699	9.369	8.304	4.648	4.648
$4d^*$	−402.639	2.405	1.349	0.625	0.625
$5d^*$	−17.689	0.273	0.119	0.007	0.007
$3d$	−2340.726	7.619	8.304	2.989	2.988
$4d$	−382.390	1.972	1.349	0.260	0.260
$5d$	−15.637	0.219	0.119	−0.030	−0.030
$4f^*$	−121.714	1.218	0.759	−0.158	−0.158
$4f$	−117.328	1.032	0.597	−0.313	−0.313

also confirm that the frequency-dependent contribution to the BI is negligible for the lighter elements but can become rather large for high nuclear charges. For high Z such contributions cannot be neglected anymore in the valence space in lowest order. Moreover, the gauge term (difference between the Breit term in the Coulomb gauge and the Gaunt term) leads to quite sizable contributions (difference between SC-GI and SC-BI in Table III) for the ionization potentials of the lighter and heavier elements.

There has been intensive discussion in the past if the two-electron Breit term should be used perturbatively or variationally [60–62]. Grant pointed out that a variational procedure is clearly preferred in a subsequent treatment of electron correlation [63,64]. Moreover, it has been argued that a variational treatment of the Breit interaction is most important for valence properties in many-electron systems [59]. In order to analyze this in more detail, we compare the difference of a self-consistent with a perturbative treatment for the Breit interaction for a series of elements in the periodic table (for the self-consistent treatment we used the program of Indelicato [65]). From the results shown in Table III we see that the self-consistent total energy contribution to the ionization potential does not differ significantly from the perturbative treatment even for high Z atoms, except perhaps for the group 18 elements, where the Breit contribution for the ionization out of the $p_{3/2}$ shell is small anyway. This is in agreement with the results of Ishikawa *et al.*, who found similar small changes [66].

We also performed a detailed study of the Breit contributions to the orbital energies for the neutral mercury atom similar to the work by Lindroth *et al.* [59] (Table VII). For the self-consistent treatment we nicely reproduce the results of Lindroth and coworkers [59]. Also the perturbative treatment gives qualitatively the same values for the orbital energy contributions. Here we used the orbitals from a Dirac-Hartree-Fock calculation (without Breit or any other QED contributions) to calculate the change in orbital energies due to the frequency-independent Breit term (our procedure here differs slightly from Lindgren's perturbative treatment as the Fock matrix including Breit was diagonalized in the Dirac-Fock-Coulomb basis to obtain first-order Breit corrected orbital energies). It is evident that the largest contributions come from the inner shells. However, the difference in both treatments becomes rather large in the valence shell as observed earlier by Lindroth *et al.* [59].

Naturally, one relates orbital energies to ionization potentials through Koopmans theorem [67]. The data in Table VIII prove that Koopmans' theorem is still valid for the two-electron Breit contributions, as both changes in orbital energies and direct calculations of energy differences between the neutral and charged atoms give very similar results for all ionizations out of specific nlj levels in the mercury atom. A full variational treatment includes changes in Coulomb and exchange contributions of the Breit interaction due to orbital relaxation, which obviously cannot be neglected anymore for orbital energies. Moreover, the DHF orbitals are not eigenfunctions to the Fock operator including the Breit term. One should therefore not conclude from the original perturbative analysis for orbital energies [59] that the Breit interaction for valence energies cannot be treated perturbatively anymore for the valence shell. On the contrary, the results clearly demonstrate that, if high precision is not required, a perturbative treatment of the Breit interaction for the valence space is sufficient. However, to incorporate changes in atomic (or molecular) properties due to the Breit term (see for example Refs. [68,69] for recent molecular work), a variational treatment is preferred.

TABLE VIII. Comparison of the Breit contribution (eV) to the ionization energy ΔE of mercury atom compared to the Breit contribution to the orbital energy $\Delta\varepsilon$ obtained from a variational treatment of the Breit interaction in the low-frequency limit for the neutral mercury atom. Here the removal of an electron is calculated for each shell with quantum number nlj. In the usual angular-momentum notation * denotes $j = l - 1/2$, otherwise $j = l + 1/2$ is chosen.

nl	ΔE	$\Delta\varepsilon$
$1s$	302.439	298.661
$2s$	33.693	33.486
$3s$	6.186	6.198
$4s$	1.250	1.272
$5s$	0.184	0.192
$6s$	0.012	0.012
$2p^*$	56.452	56.259
$3p^*$	10.661	10.704
$4p^*$	2.232	2.269
$5p^*$	0.316	0.330
$2p$	35.741	35.505
$3p$	6.374	6.386
$4p$	1.165	1.186
$5p$	0.125	0.131
$3d^*$	4.651	4.648
$4d^*$	0.608	0.625
$5d^*$	0.004	0.007
$3d$	3.010	2.989
$4d$	0.251	0.260
$5d$	−0.029	−0.030
$4f^*$	−0.161	−0.158
$4f$	−0.308	−0.313

Finally we mention recent accurate Fock-space coupled-cluster calculations for the gold atom the Eliav *et al.* [70]. The calculated ionization potential of 9.197-eV changes to 9.176 eV when VP and SE is included, which now is in less good agreement with the experimental value of 9.225 eV [71]. Hence the total correlation error is estimated to be 0.049 eV in Eliav's calculation; that is, 96.9% of the total electron correlation contribution to the ionization potential ($\Delta E_{\mathrm{cor}} = \Delta E_{\mathrm{exp}} - \Delta E_{\mathrm{DC-HF}} - \Delta E_{\mathrm{Breit}} - \Delta E_{\mathrm{QED}} = 1.565$ eV) has been accounted for. This clearly demonstrates that the bottleneck in such calculations still remains within the electron correlation treatment. Our further development will be in the construction of effective Hamiltonians with one-particle semilocal SE and VP operators which, in a similar fashion to valence electron pseudopotentials [72], could be fitted to precise atomic QED contributions to inner- and outer-shell ionization potentials of neutral and charged atoms. Such effective (lower bound) Hamiltonians can then be used variationally in accurate all-electron molecular Dirac-Coulomb-Breit calculations treating QED and electron correlation on the same footing. Work in this direction is currently in progress.

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