QED CORRECTIONS FOR THE VALENCE ELECTRON IN HEAVY AND SUPER-HEAVY ATOMS

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The radiative QED corrections for the valence electron of the neutral Rg ($Z = 111$) atom are estimated within the framework of the post-Dirac–Fock method. In this method the Koopmans' approximation is proposed for the electron propagator in the QED diagrams. Such calculation is done for the first time for this super-heavy atom. These results contribute to the discussion concerning the accuracy of the QED corrections in the super-heavy elements. They also provide the accuracy limit of the modern relativistic theoretical calculations for the super-heavy elements.

Keywords: relativistic and quantum electrodynamic effects in atoms and molecules

PACS: 31.30.Jv

1. Introduction

Recent experimental success in the super-heavy nuclei synthesis strongly indicate the existence of the so-called "Island of Stability" for neutron-rich nuclei with nuclear charge numbers in the region $Z \sim 112$. According to theoretical predictions, the half-life time for nuclei with proton number $Z = 112$ and neutron numbers $N \sim 184$ could be rather long. These pairs of proton and neutron numbers are supposed to correspond to the filled proton and neutron shells.

The element $E111$ (Roentgenium) from the 11th group of Mendeleev Periodic Table (MPT) or from the coinage metal atoms group is very close to the peak of the stability island. The element has received its actual name only in 2004 from the International Union of Pure and Applied Chemistry (IUPAC). Nevertheless, it looks like that this element is the best candidate for the exploration of the quantum electrodynamics (QED) effects in the super-heavy atoms. The QED effects within the Dirac–Fock (DF) method for valence electrons is the main topic of our consideration. The electrons of heavy atoms move in very strong Coulomb field and therefore the corresponding calculations should be preferably done in the complete relativistic framework. For the valence electron in the super-heavy heavy atoms relativistic effects become so important that the super-heavy element chemistry does not simply follow the regular periodic trend. According to the chemical prop-

erties obtained within the first theoretical studies, the element 112 (the neighbour of Rg in MPT) should belong to the noble gases group (see [1]), but recent calculations contradict this conclusion (see [2, 3]). This means that more accurate theoretical studies of such elements are very important.

The main objective of the present study is the computation of the electronic states of the super-heavy coinage metal Rg atom within the post-Dirac–Fock (PDF) approach. The algorithm of PDF is described in the following sections. The energy levels both for the inner and for the valence states have been obtained with the main QED self-energy correction (SE) as an intermediate step of the Dirac–Fock procedure. It is shown that the inner-electron self-consistent DF procedure is quite important for 7s electron QED correction in Rg. The other QED correction (the vacuum polarization (VP)) can be taken into account within the same PDF framework.

The numerical evaluation of the binding energy for the inner and, particularly, for the valence electrons in super-heavy atoms are of special attention for the last forty years. The reasonable values can be found, for example, in [4]. The modern theoretical evaluations, like a modification of configuration interaction (CI) method [2] or coupled cluster (CC) method [5], are more reliable for the practical using. But all such calculations do not take into account the SE corrections in the framework of contemporary QED. It may be quite difficult to

incorporate the SE effects in CI or CC methods. Nevertheless, the CI or CC computations can define the accuracy of all present relativistic calculations without QED.

Our estimates can stimulate a discussion concerning the accuracy of the QED corrections in the super-heavy elements itself. The main difficulties of similar estimates are considered in Ref. [6] for the valence electrons of atoms from the 11th group of MPT and earlier in Ref. [7] for the element from the first group of MPT. Both papers have shown that the pure QED corrections in so-called local-potential approach are not enough to achieve the necessary accuracy of these calculations.

The present paper is organized as follows. In Sec. 2 the Koopmans' approximation is introduced for the one-particle Green's function in quantum mechanics. The main consequence of this approximation is the algorithm for the self-consistent solution of the Dyson equation with truncated mass-operator. This algorithm is then transferred to QED and here it comprises the self-consistent DF algorithm with the inherited radiative corrections (PDF).

Section 3 presents the applications of this PDF method for the SE correction. The numerical results for the given correction are printed in Sec. 4. Some possible explanations for the obtained results are discussed in Sec. 4 as well.

The atomic unit system ($e = m_e = \hbar = 1$, where e is the electron charge, m_e is the electron mass, and $\hbar$ is the Planck's constant) is used throughout the paper.

2. Koopmans' approximation and one-particle Green's function

2.1. Energy of system and Koopmans' approximation

As follows from the Brillouin's conditions, in quantum mechanics of electrons the Koopmans' matrix $\tilde{K}$

$$K_{pq}^{(\text{Adv})} = \langle | \, [\hat{H}, a_p^\dagger] a_q \, | \rangle \qquad (1)$$

calculated with an optimal state function has to be Hermitean. The density matrix $\tilde{D}$ in atomic orbital (or molecular orbital) basis set is written as follows:

$$D_{pq} = (\rho_N)_{pq} = \langle | \, a_p^\dagger a_q \, | \rangle . \qquad (2)$$

Koopmans' hole (advanced) equations are

$$\sum_r K_{pr}^{(\text{Adv})} \psi_r^j = \varepsilon_j^{(\text{i.p.})} \sum_r D_{pr} \psi_r^j , \qquad (3)$$

where $-\varepsilon_j^{(\text{i.p.})} = I_j^{(\text{i.p.})}$ ($j = 1, \ldots$) are ionization potentials. From the Koopmans' equation the basis set for

simultaneous diagonal decompositions of $\{D_{pq}\}$ and $\{K_{pr}^{(\text{Adv})}\}$ are obtained:

$$D_{pq} = \sum_{jrs} \psi_r^j D_{pr} D_{sq} \psi_s^j , \qquad (4)$$

$$K_{pq}^{(\text{Adv})} = \sum_{jrs} \psi_r^j D_{pr} \varepsilon_j^{(\text{i.p.})} D_{sq} \psi_s^j . \qquad (5)$$

A similar equation is also valid for the retarded (particle) Koopmans' matrix

$$\sum_r K_{pr}^{(\text{Ret})} \phi_r^j = \sum_r \langle | \, [a_p, \hat{H}] a_r^\dagger \, | \rangle \phi_r^j$$

$$= \varepsilon_j^{(\text{e.a.})} \sum_r D_{pr}^{(\text{Ret})} \phi_r^j , \qquad (6)$$

where $\varepsilon_j^{(\text{e.a.})}$ ($j = 1, \ldots$) are the electron affinities.

The advanced one-particle Green's function in extended Koopmans' approximation is

$$G_{pq}^{(\text{Adv})}(\varepsilon) = \sum_{jrs} \psi_r^j D_{pr} \frac{1}{\varepsilon - \varepsilon_j^{(\text{i.p.})} - \text{i}0} D_{sq} \psi_s^j . \quad (7)$$

Similar to the electron density and the advanced Koppmans matrix the complement electron density and the retarded Koopmans' matrix are obtained as zero- and first-order momenta of advanced and retarded one-particle Green's function.

After this we can write the one-particle Green's function in Koopmans' approximation:

$$G_{pq}^{(\text{Koopm})}(\varepsilon) = \sum_j \Bigg(\Psi_p^j \frac{1}{\varepsilon - \varepsilon_j^{(\text{i.p.})} - \text{i}0} \Psi_q^j$$

$$+ \Phi_p^j \frac{1}{\varepsilon - \varepsilon_j^{(\text{e.a.})} + \text{i}0} \Phi_q^j \Bigg) . \qquad (8)$$

From the Eqs. (4), (5), and (7) it is seen that

$$(\tilde{D})_{pq} = D_{pq} = \frac{1}{2\pi\text{i}} \oint_{l_+} G_{pq}^{(\text{Koopm})}(\varepsilon) \, \mathrm{d}\varepsilon , \qquad (9)$$

$$(\tilde{K})_{pq} = K_{pq} = \frac{1}{2\pi\text{i}} \oint_{l_+} \varepsilon G_{pq}^{(\text{Koopm})}(\varepsilon) \, \mathrm{d}\varepsilon , \quad (10)$$

and the energy of the many-particle electron system can be written as

$$E = \frac{1}{2} \text{Tr} \left(\tilde{K} + h\tilde{D} \right) . \qquad (11)$$

2.2. Truncated irreducible mass-operators and perturbation corrections

Equations (8), (9), (10), and (11) of the many-particle quantum mechanics (MPQM) can be used for self-consistent solutions of the Dyson equation for the one-particle Green's function

$$\tilde{G} = \tilde{G}_{\mathrm{o}} + \tilde{G}_{\mathrm{o}} \tilde{M}^{(\mathrm{irr})}(\tilde{G})\tilde{G}\,, \qquad (12)$$

where the irreducible mass operator $\tilde{M}^{(\mathrm{irr})}(\tilde{G})$ is expressed as a sum of all irreducible Feynman diagrams with the one-particle Green's function as the electron propagator. The Feynman diagram of the lth order is called here irreducible if it does not contain parts of the lower orders ($< l$). From Eq. (11) and from the Dyson equation for the one-particle Green's function (12) it follows that

$$E = \frac{1}{2}\mathrm{Tr}\oint_{l_+} (\varepsilon + \hat{h})\tilde{G}(\varepsilon)\,\mathrm{d}\varepsilon$$

$$= \frac{1}{2}\mathrm{Tr}\oint_{l_+} \left[\hat{M}^{(\mathrm{irr})}(\tilde{G}(\varepsilon)) + 2\hat{h}\right]\tilde{G}(\varepsilon)\,\mathrm{d}\varepsilon\,. \quad (13)$$

Iterative solution of the Dyson equation (12) with the complete irreducible mass-operator obviously results in the perturbation series in powers of interaction with the propagators of non-interacting electrons. In practice only truncated irreducible mass-operators $\tilde{\mathfrak{M}}^{(\mathrm{irr})}$ are used in (12) instead of $\tilde{M}^{(\mathrm{irr})}$, then the iterations of the Dyson equation (12) lead to an expansion of a partially dressed one-particle Green's function, therefore the solutions of the Dyson equations with the truncated mass-operator correspond to partial summations in the initial perturbation series for the Green's function $\tilde{G}$. We obtain self-consistent solutions $\tilde{G}^{\mathfrak{M}}$ of the Dyson equation with the truncated mass-operator $\tilde{\mathfrak{M}}^{(\mathrm{irr})}$ as the expansion (8) using Koopmans' SCF procedure [8, 9] and call it the Koopmans' approximation. In Koopmans' SCF iterations of the Dyson equation at each step the Koopmans' operator is taken from the previous step according to Eq. (10). The density matrix in this approximation is written as

$$\tilde{D} = \frac{1}{2}\oint_{l_+} \Big[(\tilde{G}_{\mathrm{o}}(\varepsilon)\tilde{\mathfrak{M}}^{(\mathrm{irr})}(\tilde{G}^{(\mathrm{Koopm})}(\varepsilon))\tilde{G}^{(\mathrm{Koopm})}(\varepsilon)$$

$$+ \tilde{G}^{(\mathrm{Koopm})}(\varepsilon)\tilde{\mathfrak{M}}^{(\mathrm{irr})}(\tilde{G}^{(\mathrm{Koopm})}(\varepsilon))\tilde{G}_{\mathrm{o}}(\varepsilon)\Big]\,\mathrm{d}\varepsilon\,. \quad (14)$$

If we use for $\tilde{G}^{\mathfrak{M}}(\varepsilon)$ the Koopmans' approximation $\tilde{G}^{(\mathrm{Koopm})}(\varepsilon)$, the energy $E^{\mathfrak{M}}$ is calculated as

$$E^{\mathfrak{M}} = \mathrm{Tr}\frac{1}{2}\oint_{l_+} (\varepsilon + \hat{h})\tilde{G}^{(\mathrm{Koopm})}(\varepsilon)\,\mathrm{d}\varepsilon$$

$$= \frac{1}{2}\mathrm{Tr}\oint_{l_+} \left[\tilde{\mathfrak{M}}^{(\mathrm{irr})}(\tilde{G}^{(\mathrm{Koopm})}(\varepsilon)) + 2\hat{h}\right]\tilde{G}^{(\mathrm{Koopm})}(\varepsilon)\,\mathrm{d}\varepsilon$$

$$= \frac{1}{2}\mathrm{Tr}\oint_{l_+} \left[\tilde{\mathfrak{M}}^{(\mathrm{irr})}(\tilde{G}^{(\mathrm{Koopm})}(\varepsilon)) + 2\hat{h}\right]\tilde{G}^{(\mathrm{Koopm})}(\varepsilon)\,\mathrm{d}\varepsilon\,.$$

$$(15)$$

The main pecularity of this application of Koopmans' SCF procedure is that the Koopmans' matrix calculated as Eq. (10) is non-Hermitean and therefore in Koopmans' SCF iterations the singular value decomposition is applied. When in MPQM the mass-operator is truncated to the irreducible terms of the first order, then the Koopmans' SCF solution of the Dyson equation corresponds to the Hartree–Fock approximation of the one-electron Green's function.

3. Post-Dirac–Fock estimates of radiative self-energy correction

The Koopmans' SCF algorithm to obtain a self-consistent solution of the Dyson equation for the one-particle Green's function in quantum mechanics can be extended to QED. In QED the truncated mass-operators have to be renormalized. The ultraviolet divergent terms are isolated by the expansion in powers of the external field potential. Then the divergent terms are combined with the corresponding counter-terms. The direct use of the external potential expansion for the mass-operator renormalization has become practical due to recent developments of the numerical methods (B-spline technique) and the space discretization. The infrared divergences cancel in the sum of zero- and one-potential terms. The Koopmans' SCF solution of the Dyson equation with renormalized mass-operator we call post-Dirac–Fock method (PDF).

In this section we use a simplified version of this algorithm for the Dyson equation in QED to calculate the lowest order radiative QED corrections for valence electron of the neutral Roentgenium (Rg). The lowest-order valence electron radiative corrections have been estimated in the paper [6]. As shown in [6], the conventional DF method is not enough for adequate estimates of the self-energy (SE) terms.

Here we use PDF Eq. (15) and the corresponding expression for the DF energy to calculate the radiative correction as the difference of the PDF and DF energies. The ε-plane singularities of the integrands originate from the singularities of the electron and photon propagators. The contour l_+ of the integrals in Eqs. (9)–(15) runs in the complex energy plane around the iso-
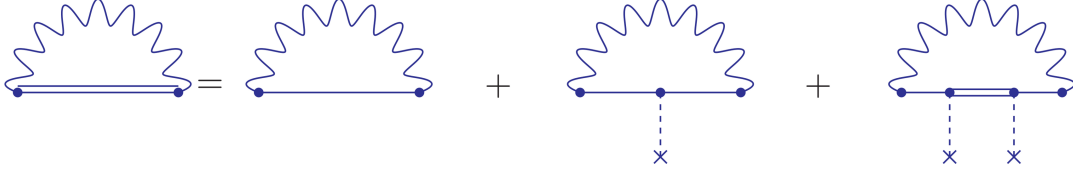
Fig. 1. Expansion of the electron mass-operator $\tilde{\mathfrak{M}}$ graph in powers of the effective interaction with the external field V_{eff}. The double solid line denotes the electron propagator in the external field, the ordinary solid line denotes the free electron propagator, and the wavy line denotes the photon propagator. The dashed line with the cross at the end denotes the interaction with the field V_{eff}.

lated poles of the integrands and around the poles of $\hat{\mathfrak{M}}^{(\text{irr})}(\tilde{G}^{(\text{Koopm})}(\varepsilon))$. This factor in the integrands has poles on the boundaries of the branch cuts. Practically, we will use the loop around the pole within energy level of the valence electron as it is following from the perturbation theory.

We start the calculation of the PDF energy with the renormalization, which is done via the potential expansion of the mass-operator. The Feynman graphs representing the expansion of $\tilde{\mathfrak{M}}$ in the vicinity of the bound electron energy in the state a are shown in Fig. 1. The ultraviolet divergences appear respectively in the first two terms, called "zero-potential" (z), $\tilde{\mathfrak{M}}_a^{(z)}$, and "one-potential" (o), $\tilde{\mathfrak{M}}_a^{(o)}$, terms. The third term, so-called "many-potential" (m) term $\tilde{\mathfrak{M}}_a^{(m)}$, is finite but it is most complicated one for numerical evaluations. The evaluation of this term together with renormalization may be achieved according to the scheme presented in [10]. The renormalized radiative energy shift (SE) of the one-electron energy level a in the energy (15) appears as

$$\Delta E_a^{\text{SE(ren)}} = \Delta E_a^{\text{ren(z)}} + \Delta E_a^{\text{ren(o)}} + \Delta E_a^{\text{ren(m)}}, \quad (16)$$

where this quantity includes the occupation number of this one-electron level.

In order to calculate the potential expansion in our simplified PDF procedure we use the local effective potential V_{eff} calculated via the DF wave functions:

$$V_{\text{eff}}(r) = \frac{\left(\dfrac{\mathrm{d}}{\mathrm{d}r} - \dfrac{\kappa}{r}\right) F^{\text{DF}}(r) + \varepsilon G^{\text{DF}}(r)}{G^{\text{DF}}(r)}, \quad (17)$$

where G^{DF} and F^{DF} are the large and the small radial components of Dirac wave function, $\varepsilon = E_{n\kappa} - c^2$. At each step of conventional DF procedure the $V_{\text{eff},i}(r)$ is calculated for every orbital χ_i state function as done in [6].

$$\tilde{\chi}_i = \chi_i + \delta\chi_i$$

with

$$\delta\chi_i = \sum_{n \neq i} \frac{\langle \chi_n | \Delta\tilde{\mathfrak{M}}^{\text{SE(ren)}} | \chi_i \rangle}{\epsilon_i - \epsilon_n} \chi_n, \quad (18)$$
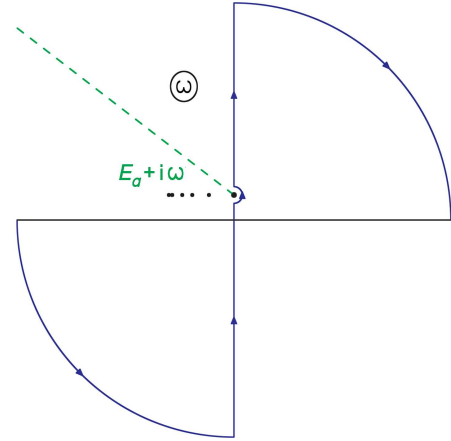

Fig. 2. The integration over the frequency of the virtual photon ω in many-potential term. The contour of integration is a solid line.

where $\mathfrak{M}^{\text{SE(ren)}} \equiv \Delta E_a^{\text{SE(ren)}}$ only and the summation is done over all one-electron orbitals of atom. To some extent it is a redefinition of the Fock operator

$$\tilde{f} = \tilde{h} + \sum_j \left[\tilde{\mathcal{J}}_j - \tilde{\mathcal{K}}_j \right]$$

in PDF: at each step of DF procedure for each electron the new term $\Delta\tilde{\mathfrak{M}}^{\text{SE(ren)}}$ is added. However, this is a simplification of PDF method, where fractional occupation numbers appear and this feature of PDF is seen from the one-electron density (14).

In comparison with of the conventional DF method, Eq. (15) reveals additional pole terms in $\Delta\hat{\mathfrak{M}}^{\text{SE(ren)}} \times (\tilde{G}^{(\text{Koopm})}(\varepsilon))$. It follows from the definition of Green's function and from Eq. (15). During the calculation of the so-called "many-potential term" by the method from Ref. [10], the contour of integration over the virtual photon frequency ω will run around the "pole" $E_a - \omega$, as shown in Fig. 2.

Finally, taking into account poles of the "many-potential term", we can write their complete contribution to the radiation correction for one-electron energy as follows:

$$\lim_{\omega \to 0} \int \mathrm{d}x_1 \, \mathrm{d}x_2 \, \mathrm{d}x_3 \, \mathrm{d}x_4 \, \overline{\Psi}_a(x_1) \gamma^\mu G_{\text{o}}(x_1, x_2)$$

Table 1. The binding energy and radiative correction for the valence electron in Rg (in a. u.).

Rg (7s)		
$\delta\epsilon_{ns}^{(3)\mathrm{PT}}$	$3.26\cdot10^{-3}$	from [6]
$\delta\epsilon_{ns}^{(3)\mathrm{DF}}$	$3.75\cdot10^{-3}$	from [6]
$\epsilon_{ns}^{(1)}$	0.42852	
$\delta\epsilon_{ns}^{(3)\mathrm{PDF}}$	$0.03\cdot10^{-3}$	

$$\times\, V_{\mathrm{eff}}(x_2) \sum_n \frac{\overline{\Psi}_n(x_3)\,\Psi_n(x_2)}{E_A - \omega - E_n - \mathrm{i}0}\, G_{\mathrm{o}}(x_3, x_4)$$

$$\times\, V_{\mathrm{eff}}(x_3)\,\gamma_\nu\,\Psi_a(x_4)\,D_\mu^\nu(x_1 - x_4, \omega)\,, \qquad (19)$$

where $\Psi_n(x)$ denotes the Dirac state function n, $D(x_1 - x_4, \omega)$ is the photon propagator, and the sum

$$\sum_n \frac{\overline{\Psi}_n(x_3)\,\Psi_n(x_2)}{E_A - \omega - E_n - \mathrm{i}0}$$

is the Koopmans' expansion for the advanced one-electron propagator. This term should be added to the pure DF value of SE correction.

4. Numerical result and summary

In Table 1 we present the estimates of the radiative corrections for the valence electron of the neutral Rg. Some estimates are taken from [6] and they are complemented with the new data obtained within simplified approach to our PDF method. The first two values with the SE correction (16) are obtained within different modifications of the DF procedure. The values $\delta\epsilon_{ns}^{(3)\mathrm{PT}}$ were obtained first in [11], and later they were verified several times (see for example in [12]). The next line in Table 1 is the binding energy for the 7s valence electron in the DF approach with the Fermi nuclear charge distribution. This line was included in Table 1 to demonstrate that the QED effects are not at all negligible in the studies of the valence states in such systems. The result which presents an estimate of the Eq. (15) is shown on the last line.

The Green's function method provides a straightforward instrumentation for one-particle description of interacting particles (density matrix, self-energy, correlation interaction) within QED. The electrons of atoms or molecules in QED are in mixed state and therefore the pure states of the quantum mechanics have the statistical interpretation. In this work we have outlined an approach which relates to the variational approach to the MCSCF treatment of correlation and which is based on the extended Koopmans' theorem. We have shown that the Koopmans' approximation makes it possible to obtain the self-consistent approximations for one-particle Green's functions and to extend this algorithm to QED. In this way some basic properties of the MCSCF Green's function are preserved and it can be used in many applications.

Acknowledgement

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KVANTINĖS ELEKTRODINAMIKOS PATAISOS SUNKIŲ IR YPAČ SUNKIŲ ATOMŲ VALENTINIAM ELEKTRONUI

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Santrauka

Radiacinės kvantinės elektrodinamikos (KED) pataisos neutralaus Rg ($Z = 111$) atomo valentiniam elektronui įvertintos vėlesnio nei Dirako ir Foko metodo požiūriu. Šiame metode elektrono propagatorių KED diagramose pasiūlyta aproksimuoti pagal Koopmansą. Šiam ypač sunkiam atomui toks skaičiavimas atliktas pirmą kartą. Rezultatai papildo diskusiją apie KED pataisų ypač sunkiems atomams tikslumą. Jie taip pat rodo šiuolaikinių teorinių skaičiavimų ypač sunkiems atomams tikslumo ribą.