Relativistic calculations of the Lamb shift in highly charged molecules and atoms in the frame of the model operator approach

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in collaboration with

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Motivation

The accuracy of experimental and theoretical spectroscopic data has increased so much that it has become urgent to take into account the QED corrections in calculations of the electronic structure of many-electron ions, neutral atoms and molecules.

Ab initio calculations of QED corrections are extremely complicate and time-consuming. To date, these calculations can be performed only for H-like and few-electron ions.

For many-electron system the QED corrections can be calculated *ab initio* only using the one-electron local screening potential obtained by Dirac-Fock-Slater (DFS) method or density functional theory (DFT) in the local density approximation (LDA).

A simple method to incorporate the QED corrections into the relativistic many-electron calculation is desired.

Effective Hamiltonian derived from QED

A good starting point for the relativistic atomic calculations is given by the Dirac-Coulomb-Breit (DCB) Hamiltonian

$$H = \Lambda^{(+)} \left[\sum_i h_i^{(\mathrm{D})} + \sum_{i<j} h_{ij}^{(\mathrm{int})} \right] \Lambda^{(+)},$$

where $\Lambda^{(+)}$ is the projector on the positive-energy states.

The first-order one-electron QED contribution to the Hamiltonian H:

$$\begin{aligned} h^{\mathrm{QED}} &= h^{\mathrm{SE}} + h^{\mathrm{VP}} \\ &= \sum_{k,m}^{(\varepsilon_k,\varepsilon_m>0)} |\psi_k\rangle \left\langle \psi_k \left| \left[\frac{1}{2} \left(\Sigma^{\mathrm{SE}}(\varepsilon_k) + \Sigma^{\mathrm{SE}}(\varepsilon_m) \right) + V^{\mathrm{VP}} \right] \right| \psi_m \right\rangle \langle \psi_m|, \end{aligned}$$

where $\Sigma^{\mathrm{SE}}(\varepsilon)$ and V^{VP} are the renormalized SE and VP operators.

Details of the derivation: V. M. Shabaev, JPB **26**, 4704 1993.

Self-energy potential

h^{SE} is represented as a sum of local and nonlocal parts:

$$h^{\mathrm{SE}} = V_{\mathrm{loc}}^{\mathrm{SE}} + \sum_{k,m=1}^{n} |\phi_k\rangle B_{km} \langle\phi_m|,$$

The local part

$$V_{\mathrm{loc}}^{\mathrm{SE}} = \sum_{\kappa} A_\kappa \exp\left(-r/\lambda_C\right) P_\kappa,$$

P_κ is the projector on the states with the given value of κ.
A_κ are chosen to reproduce the SE shift for the lowest κ-state.

The determination of nonlocal part

$$\sum_{k,m=1}^{n} \langle\psi_l|\phi_k\rangle B_{km} \langle\phi_m|\psi_j\rangle = \left\langle \psi_l \middle| \left[\frac{1}{2}\left(\Sigma^{\mathrm{SE}}(\varepsilon_l) + \Sigma^{\mathrm{SE}}(\varepsilon_j)\right) - V_{\mathrm{loc}}^{\mathrm{SE}}\right] \middle| \psi_j \right\rangle.$$

V. M. Shabaev, I. I. Tupitsyn, and V. A. Yerokhin,
Phys. Rev. A **88**, 012513 (2013); Comp. Phys. Comm. **189**, 175 (2015).

Alkali metal valence electron energies. QED corrections

$$V_{\mathrm{X}\alpha}(r) = V_{\mathrm{nuc}}(r) - \int_0^\infty dr' \frac{\rho(r')}{r_>} + x_\alpha \left[\frac{81}{32\pi^2} r\rho(r)\right]^{1/3}$$

Total QED corrections (in meV) to the alkali metal valence electron energies obtained using the different implementations of the Xα method

Atom	Method	$x_\alpha = 0$	$x_\alpha = 1/3$	$x_\alpha = 2/3$	$x_\alpha = 1$
Na $3s_{1/2}$	$\langle v\|V^{\mathrm{QED}}\|v\rangle$	0.292	0.289	0.316	0.386
	Exact+WK	0.292	0.289	0.313	0.386
Rb $5s_{1/2}$	$\langle v\|V^{\mathrm{QED}}\|v\rangle$	1.041	1.079	1.293	1.807
	Exact+WK	1.040	1.074	1.291	1.804
Fr $7s_{1/2}$	$\langle v\|V^{\mathrm{QED}}\|v\rangle$	3.026	3.338	4.357	6.655
	Exact+WK	3.012	3.323	4.334	6.614

"Exact" - J. Sapirstein and K. T. Cheng, Phys. Rev. A **66**, 042501 (2002).

QED contributions to the alkali metal ionization potentials

Total QED contributions (in meV) to the alkali metal ionization potentials obtained by the Dirac-Fock (DF) and CI+MBPT methods

Atom	DF[a]	DF[b]	DF	CI+MBPT
Na $3s_{1/2}$	−0.268	−0.288	−0.280	−0.320
Rb $5s_{1/2}$	−1.10	−1.298	−1.264	−1.428
Fr $7s_{1/2}$	−4.60	−4.675	−4.689	−5.073

[a] L. Labzowsky, I. Goidenko, M. Tokman and P. Pyykko, PRA, **59**, 2707 (1999).

[b] C. Thierfelder and P. Schwerdtfeger, PRA **82**, 062503 (2010).

CI+MBPT: M. G. Kozlov, S. G. Porsev, M. S. Safronova, I. I. Tupitsyn, Comp. Phys. Commun. **195** (2015) 199.

Model QED operator approach to molecules. Preliminary

The QED operator is short-range operator.

The dominant part is localized close to the nucleus.

Therefore, we represent the model operator for the molecule as a sum of two atomic operators:

$$\Delta E^{\rm QED} = \langle\, \psi \,|\, V_A^{\rm QED} + V_B^{\rm QED} \,|\, \psi \,\rangle\,,$$

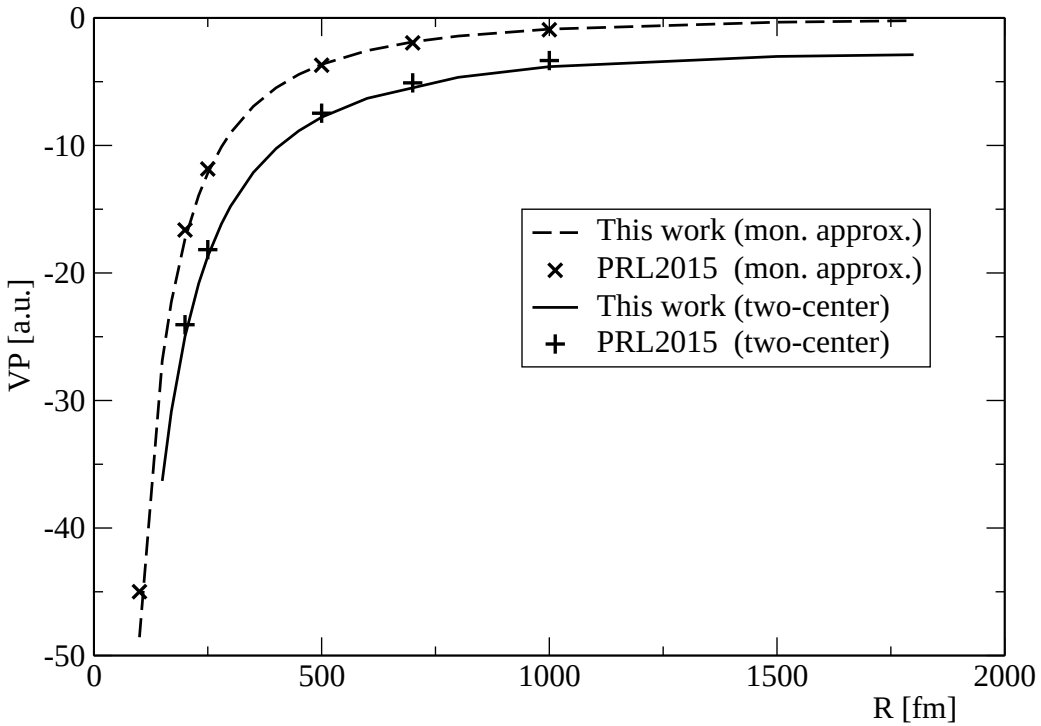
where ψ is a wave function obtained by the solution of the two-center Dirac equation.

The *ab initio* evaluation:

A. N. Artemyev, A. Surzhykov, Phys. Rev. Lett. **114**, 243004 (2015).

U_2^{183+}: vacuum polarization (VP)

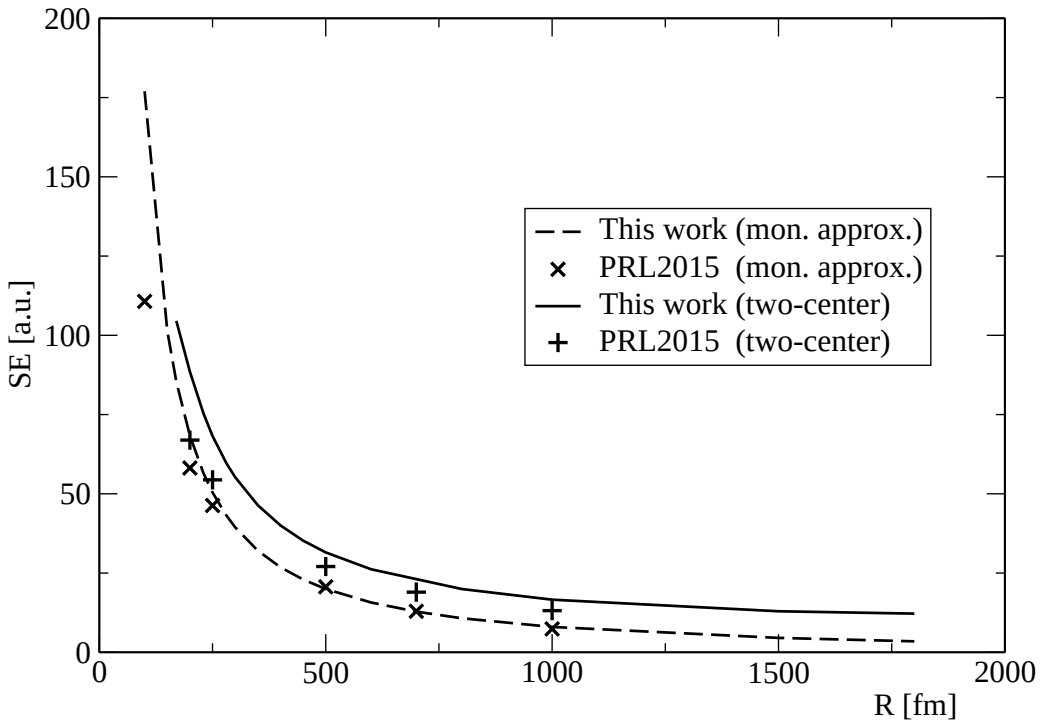
VP energy shift as a function of the internuclear distance R for $U2^{183+}$ one-electron quasi-molecule.



A. N. Artemyev, A. Surzhykov, Phys. Rev. Lett. **114**, 243004 (2015)

U_2^{183+}: self-energy (SE)

SE energy shift as a function of the internuclear distance R for $U2^{183+}$ one-electron quasi-molecule.



A. N. Artemyev, A. Surzhykov, Phys. Rev. Lett. **114**, 243004 (2015)

Conclusion

- The QED contribution can be approximated by a model operator, which provides a very simple and efficient tool for evaluation of the Lamb shifts in many-electron atoms, ions and molecular ions.
- The QED corrections to the alkali metal ionization energies were evaluated with the use of the model Lamb-shift operator.
- The first attempt to apply the model operator approach to the evaluation of the Lamb shift in molecular systems is undertaken.
- There are a significant difference at the very short internuclear distances (40-100 fm) between the results of QED model operator calculations and *ab initio* Artemyev's data. The work has to be continued.

Thank you for your attention!