BELARUSIAN STATE UNIVERSITY

Analytical model of a many-electron atom

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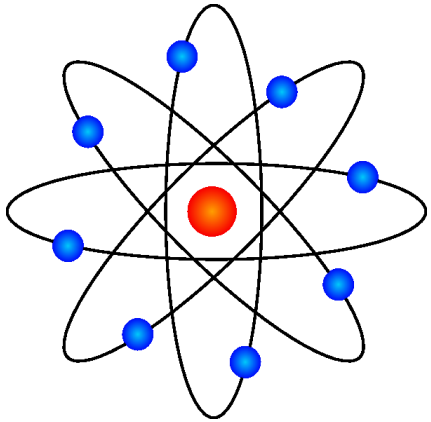
Accuracy vs Simplicity



Single-electron wave function (SEWF) is the key point of the initial approximation for both density functional theory and the solution of the Schrödinger equation.

High accuracy algorithms: HF, MCHF, post-HF and other.
Disadvantage: complexity of numerical simulations

There are many applications where there is no need for extremely high accuracy, but a simple algorithm of repeated calculations of atomic characteristics is required:

- computational plasma
- X-ray physics
- crystallography
- semiconductor physics
- strong laser-matter interactions

Models used: Thomas-Fermi, multi-parametric screening hydrogen, etc.

Can one introduce **something new** ?

Main features of our approach

Effective Charge Model (ECM) utilizes basis set of fully analytical SEWF – hydrogen-like wave functions with a **single free parameter** (identical for all SEWF).

⇒ complete and orthonormal basis is automatically provided !

- transition into secondary-quantized representation becomes possible
- various closed-form expressions can be implemented

Main goals of ECM:

1. sufficiently accurate analytical zeroth-order approximation
2. possibility to construct regular perturbation theory for higher order corrections

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Hamiltonian of the atomic system

Non-relativistic Hamiltonian of the atomic system (in atomic units)

$$\hat{H} = \sum_{i=1}^{N} \left(\frac{\vec{p}_i^{\,2}}{2} - \frac{Z}{r_i} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

can be re-written in the form as follows:

$$\hat{H} = \underbrace{\sum_{i=1}^{N} \left(\frac{\vec{p}_i^{\,2}}{2} - \frac{Z^*}{r_i} \right)}_{\hat{H}_0} + \underbrace{\sum_{i=1}^{N} \frac{-(Z - Z^*)}{r_i} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\hat{W}}$$

$\hat{H}_0$: describes a set of non-interacting electrons in a hydrogen-like atom with nucleus charge **Z*** and total number of electrons **N**

$\hat{W}$: can be considered as a "**perturbation**" operator

Hamiltonian of the atomic system

Transition to the **secondary-quantized representation**

$$\{\mathsf{a}_\nu, \mathsf{a}^\dagger_{\nu'}\} = \delta_{\nu\nu'}$$

$$\mathsf{H}_0 = \sum_\nu \langle\nu|\frac{\mathbf{p}^2}{2} - \frac{Z^*}{r}|\nu\rangle \mathsf{a}^\dagger_\nu \mathsf{a}_\nu$$

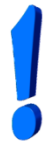
$$\mathsf{W} = \sum_{\nu\nu_1}\langle\nu|\frac{-(Z-Z^*)}{r}|\nu_1\rangle \mathsf{a}^\dagger_\nu \mathsf{a}_{\nu_1} + \frac{1}{2}\sum_{\nu\nu_1\mu\mu_1}\langle\nu|\langle\nu_1|\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}|\mu_1\rangle|\mu\rangle \mathsf{a}^\dagger_\nu \mathsf{a}^\dagger_{\nu_1}\mathsf{a}_\mu \mathsf{a}_{\mu_1}$$

Greek letters represent the collective quantum number: ν

- $nlmm_s$ (**discrete** states)
- $\boldsymbol{k}lmm_s$ (**continuous** spectrum)

Simple **hydrogen-like** wave-functions are used:

$$\varphi_{\binom{nlm}{klm}}(Z^*\boldsymbol{r})\chi_{m_s}(s)$$



Note: only **one** free **parameter** is used for **all SEWF** of the current atom (ion) !

How to calculate Z* ?

The **knowledge of the effective charge Z*** fully defines the Hamiltonian of the zeroth-order approximation $\mathbf{H}_0$.

For this puprose we perform the **variational** calculation

$$E(Z^*) = \langle \lambda_1 \dots \lambda_N | \mathrm{H} | \lambda_1 \dots \lambda_N \rangle$$

with trial state vector $|\lambda_1 \dots \lambda_N\rangle$

depends on the set
of **occupation numbers**

All calculations can be done analytically, and finally we obtain:

$$E(Z^*) = -Z^*(2Z - Z^*)A + Z^*B$$

both values are analytically calculated
and **DO NOT** depend on **Z***

$$Z^* = Z - \frac{B}{2A}$$

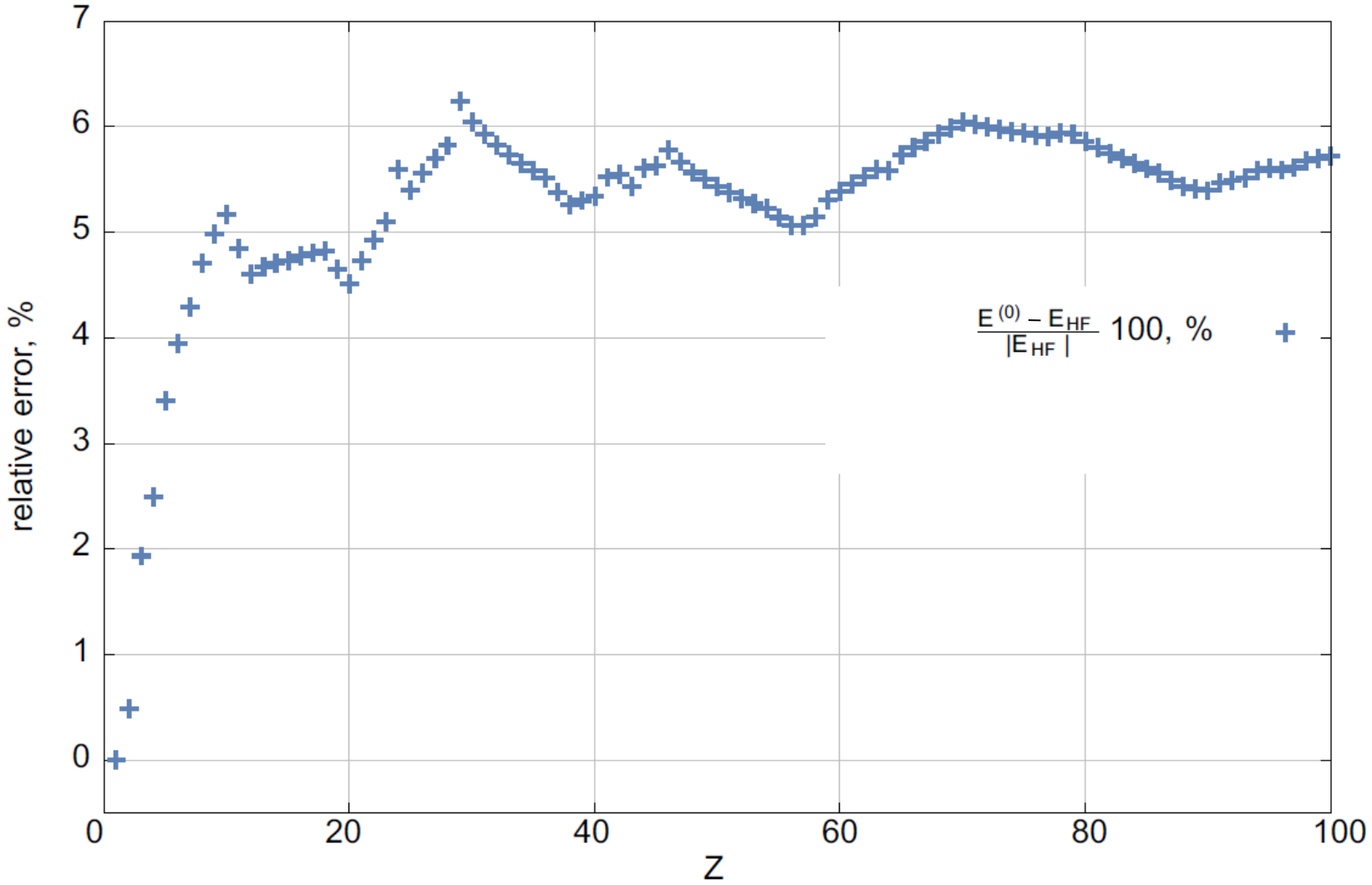
$$E^{(0)} = -AZ^{*2}$$

zeroth-order energies and SEWF are well-defined !

Here we utilized the variable change

$$\tilde{\boldsymbol{r}} = Z^* \boldsymbol{r}$$

Zeroth-order results



Relative error of the total atomic energy as a function of nucleus' charge Z

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Perturbation theory over W-operator

Now it is possible to construct perturbation theory due to the operator **W** (eigenstates of the zeroth-order Hamiltonian $\mathbf{H}_0$ are utilized):

$$\mathsf{H}_0 = \sum_{\nu} \langle \nu | \frac{\mathbf{p}^2}{2} - \frac{Z^*}{r} | \nu \rangle \mathsf{a}^\dagger_\nu \mathsf{a}_\nu$$

$$\mathsf{W} = \sum_{\nu\nu_1} \langle \nu | \frac{-(Z - Z^*)}{r} | \nu_1 \rangle \mathsf{a}^\dagger_\nu \mathsf{a}_{\nu_1} + \frac{1}{2} \sum_{\nu\nu_1\mu\mu_1} \langle \nu | \langle \nu_1 | \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} | \mu_1 \rangle | \mu \rangle \mathsf{a}^\dagger_\nu \mathsf{a}^\dagger_{\nu_1} \mathsf{a}_\mu \mathsf{a}_{\mu_1}$$

1-st order correction: $\Delta E^{(1)} = \langle \lambda_1 \dots \lambda_N | \mathsf{W} | \lambda_1 \dots \lambda_N \rangle = -Z^*(Z - Z^*)2A + Z^* B$

$$Z^* = Z - \frac{B}{2A} \quad \Rightarrow \quad \Delta E^{(1)} = 0$$

1st order correction **vanishes** !

Calculating 2nd order corrections

2nd order perturbation theory due to the **W** operator:

$$\Delta E^{(2)} = -\frac{1}{2} \sum_{k<l} \sum_{\sigma_k \sigma_l}{}' \frac{|W_{\lambda_k \lambda_l, \sigma_k \sigma_l}|^2}{E_{\sigma_k} + E_{\sigma_l} - E_{\lambda_k} - E_{\lambda_l}}$$

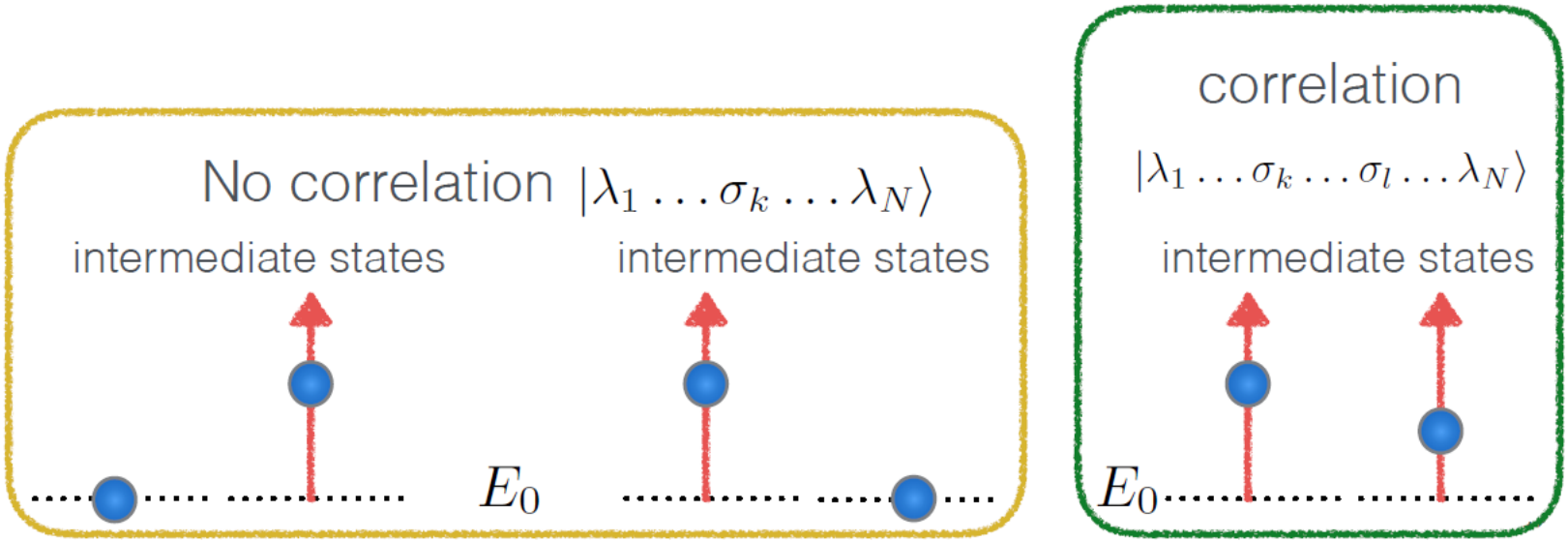
where $W_{\lambda_k \lambda_l, \sigma_k \sigma_l} = \langle \lambda_1 \dots \lambda_k \dots \lambda_l \dots \lambda_N | \mathrm{W} | \lambda_1 \dots \sigma_k \dots \sigma_l \dots \lambda_N \rangle$

$$\Delta E^{(2)} = \Delta E^{(2)}_{\text{single}} + \Delta E^{(2)}_{\text{multi}}$$

only **one** electron goes into an intermediate state

two electrons undergo the transition into intermediates states

Calculating 2nd order corrections



$$\Delta E^{(2)} = \Delta E^{(2)}_{\text{single}} + \Delta E^{(2)}_{\text{multi}}$$

only **one** electron goes into an intermediate state

two electrons undergo the transition into intermediates states

Calculating 2nd order corrections

The largest **advantage** of **ECM –** using a hydrogen-like basis the required summations can be done in a closed form through the **single-particle Coulomb Green functions**.

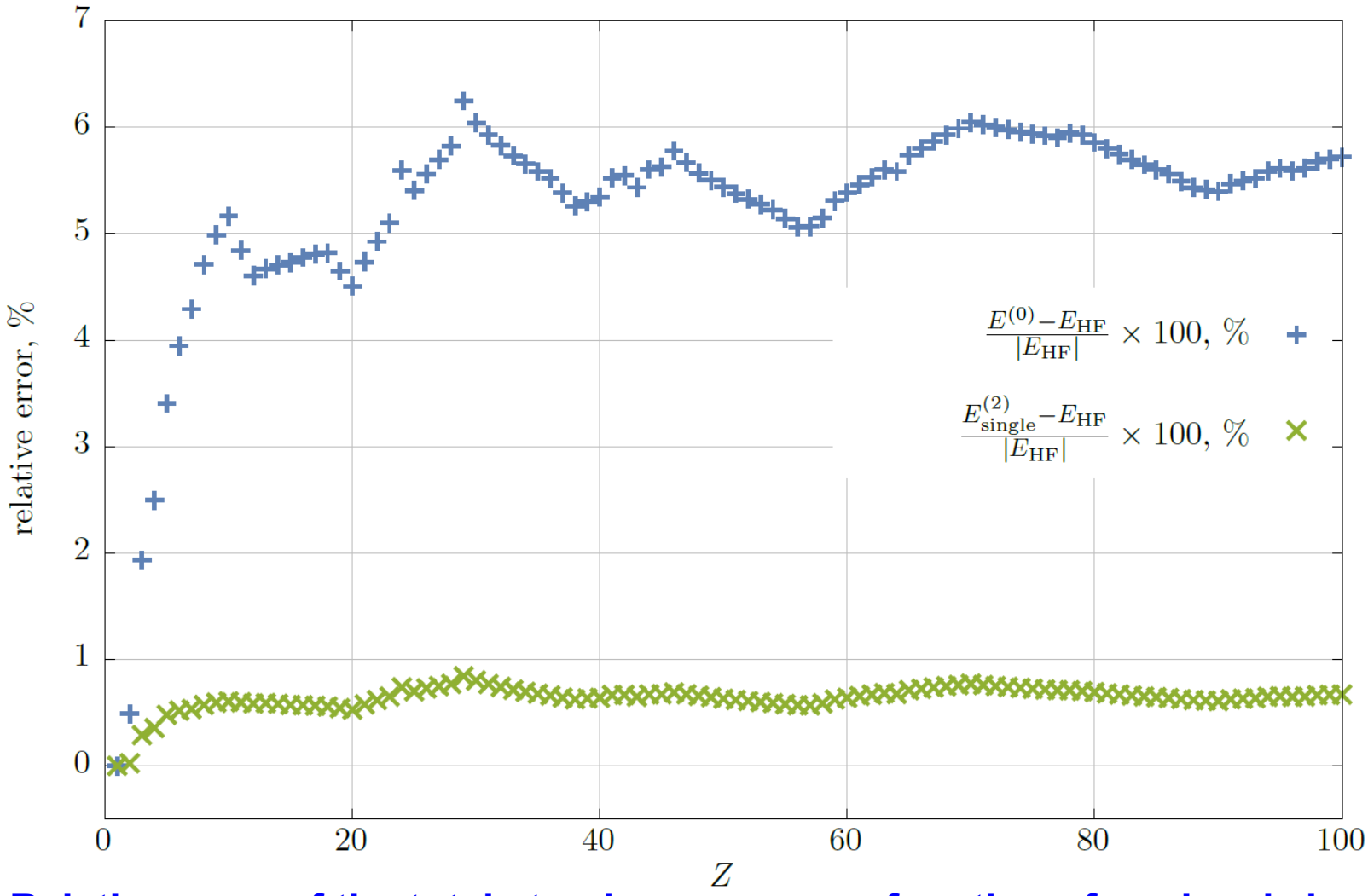
Taking into account the Pauli exclusion principle and that not all states are present, the **reduced Coulomb Green function** is utilized:

$$\tilde{G}^{\lambda_k}_{E_{\lambda_k}-\mathrm{i}\delta} = G_{E_{\lambda_k}-\mathrm{i}\delta} - \sum_l{}^{*} \frac{|\lambda_l\rangle\langle\lambda_l|}{E_{\lambda_l} - (E_{\lambda_k} - \mathrm{i}\delta)}$$

for mutli-electron excitations we need to obtain **a two-particle Coulomb Green function** that can be represented as a **convolution** of two **single** particle ones:

$$G_{E-\mathrm{i}\delta}(1,2) = -\int_{-\infty}^{\infty} \frac{dt}{2\pi\mathrm{i}} G_{t+\frac{E-\mathrm{i}\delta}{2}} \otimes G_{-t+\frac{E-\mathrm{i}\delta}{2}}$$

2nd order PT: single electron excitations



Relative error of the total atomic energy as a function of nucleus' charge Z

2nd order PT: single + multi electron excitations

	$E^{(2)}$	E_{var}	E_{MCHF}	E_{HF}
H^-	-0.532	-0.528	-0.528	-0.488
He	-2.907	-2.904	-2.903	-2.861
Li	-7.467	-7.478	-7.477	-7.433
He $2\,^3S$	-2.172	-2.175	-2.175	-2.174
He $2\,^1S$	-2.154	-2.146	-2.146	-2.143

$$E^{(2)} = E^{(0)} + \Delta E^{(2)}_{\mathrm{single}} + \Delta E^{(2)}_{\mathrm{multi}}$$

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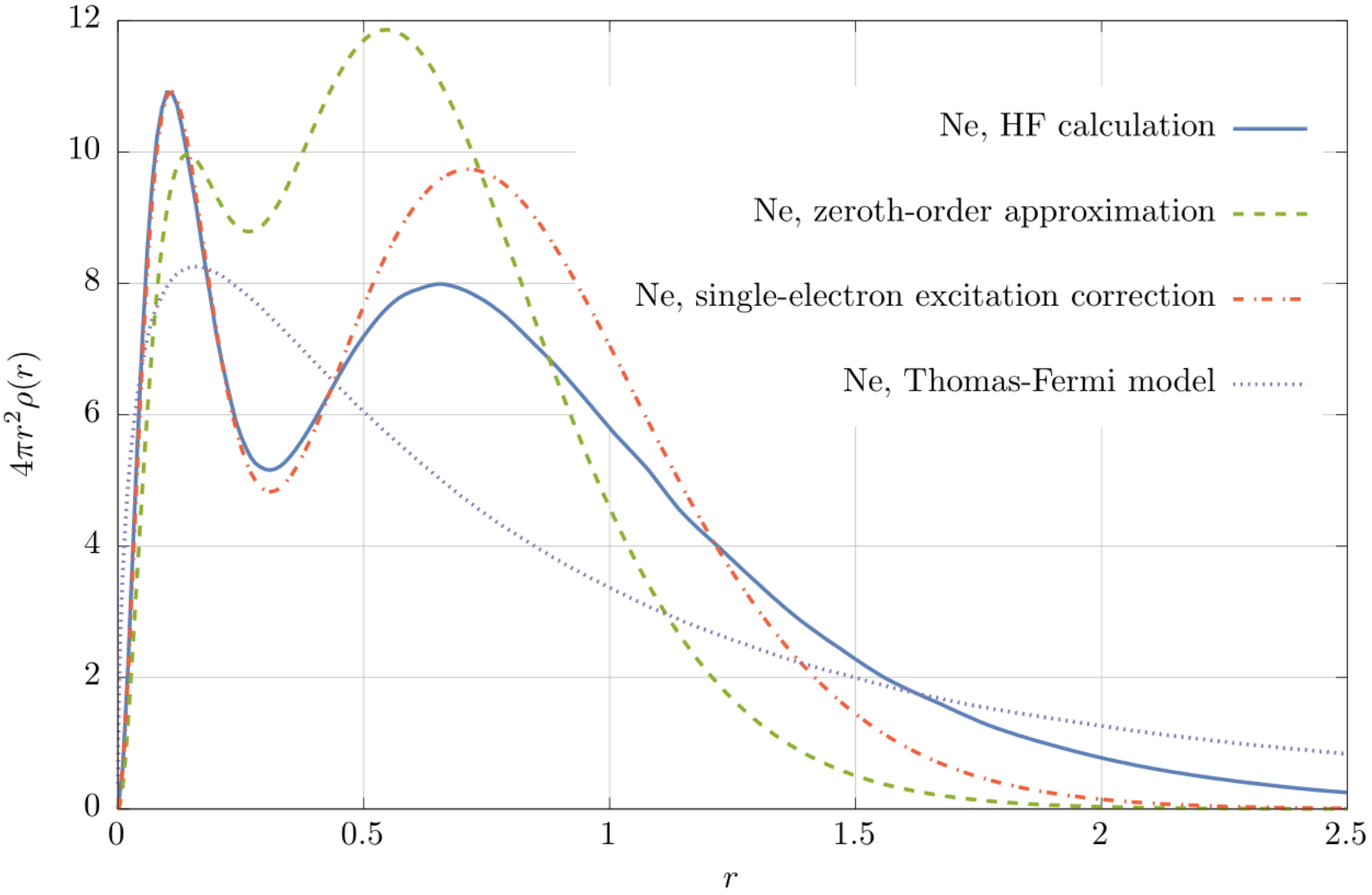
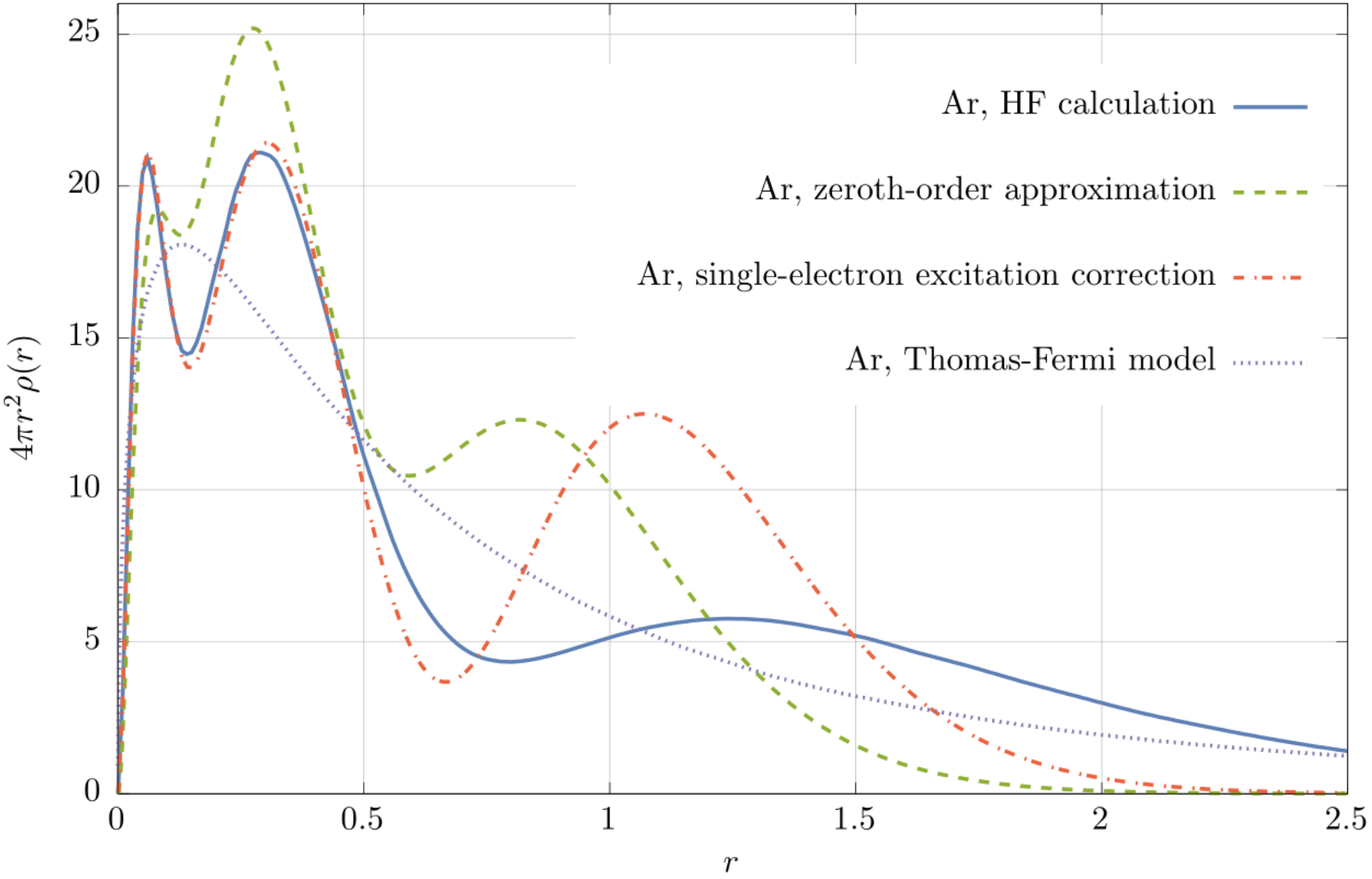
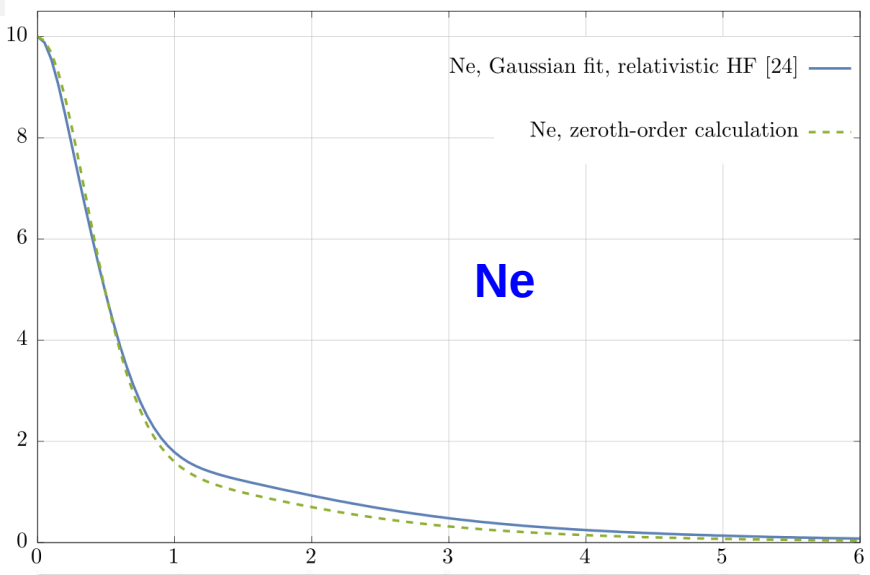
Radial densities: Ne

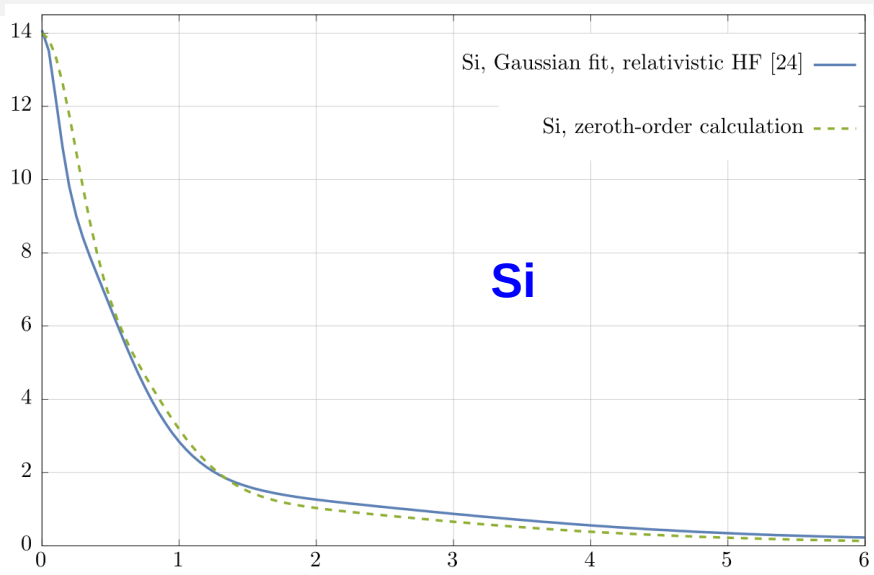


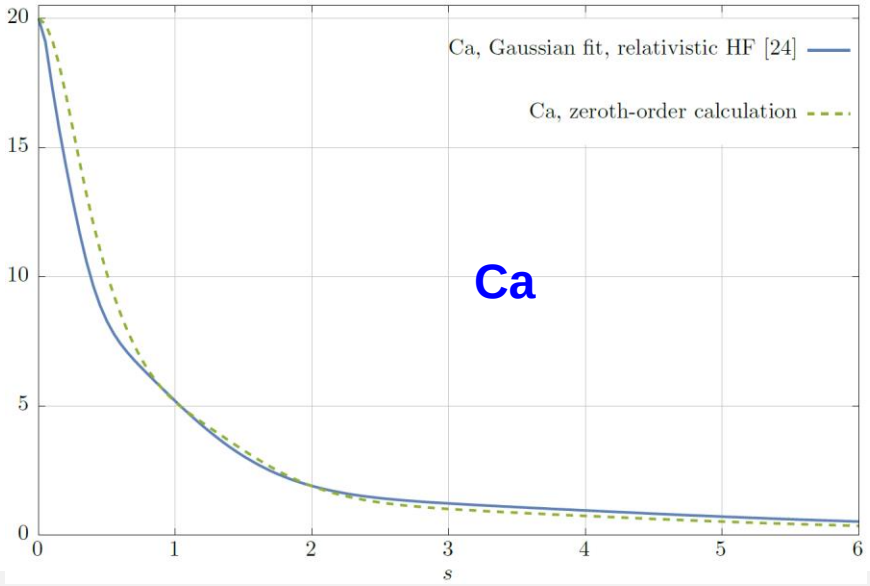
Radial densities: Ar

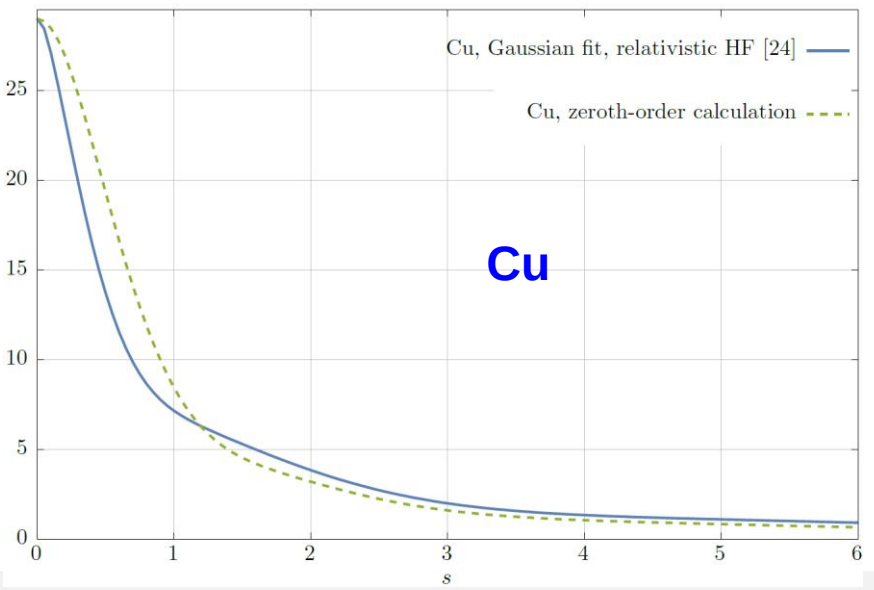


Atomic scattering factors









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Conclusions

- A fully analytical approximation for the observable characteristics of many-electron atoms and ions is developed

- Both qualitative and quantitative estimations can be done

- Straightforward calculation of subsequent corrections and direct generalization for the relativistic calculations is possible

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Analytic model of a multi-electron atom

O D Skoromnik[1], **I D Feranchuk**[2,3,4,5], **A U Leonau**[4] **and C H Keitel**[1]

SOFTWARE AVAILABLE: https://github.com/tupos/effz

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