RADIAL DIRAC-FOCK SOLVER USING INTEGRAL EQUATION METHOD

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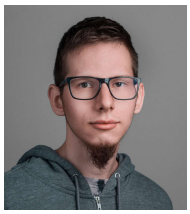


Motivation

We present a fully numerical relativistic generalized Kohn-Sham solver for spherically symmetric atoms. It solves the time-independent Dirac equation

$$\left(\beta c^2 - ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \hat{V}\right)\Psi = E\Psi,$$

where $\hat{V}$ contains a non-local contribution from (screened) Fock exchange.

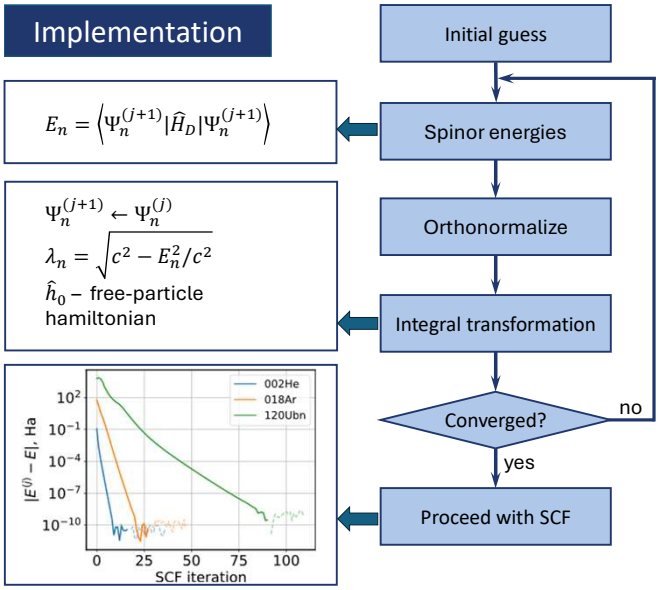
Why do we need it?

- The usual approach with outward integration doesn't work with non-local potentials.
- High quality relativistic reference data for hybrid functionals with range separation for verifying other codes.
- Implementation of core orbitals in linearized augmented plane waves:
  - hybrid functionals are typically implemented with PBE cores,
  - access to better quality core energies, for example, for x-ray absorption spectroscopy simulations.

We use a similar approach to our scalar-relativistic atomic solver [1] and rewrite the Dirac equation as an integral equation:

$$\Psi_n(\boldsymbol{r}) = \frac{1}{c^2}\int\left(\left(E_n + \hat{h}_0\right)\frac{e^{-\lambda_n|\boldsymbol{r}-\boldsymbol{r}'|}}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|}\right)\hat{V}\Psi_n(\boldsymbol{r}')d^3r'.$$

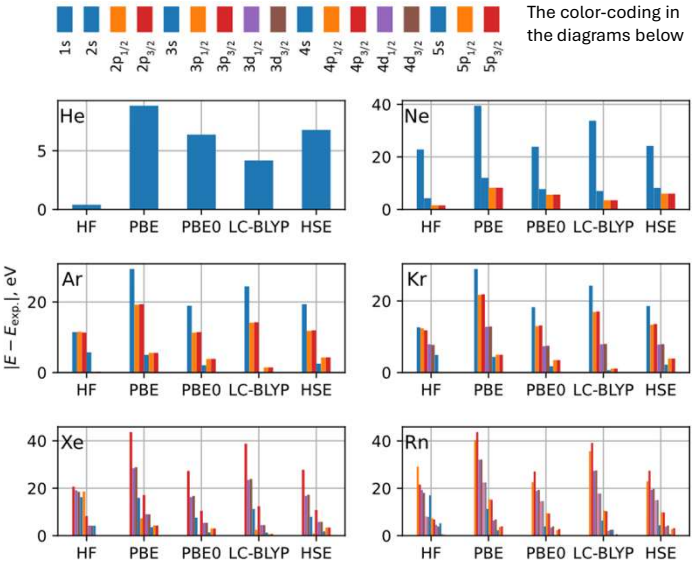
Implementation



Electron removal energies

We calculate the total Dirac-Fock energies for atoms with closed (sub)shell and find perfect agreement with the data published by Visscher and Dyall [2]. However, our calculations provide more significant digits, i.e. at least up to 10^{-8} Ha.

Next, we compare orbital energies in noble-gas atoms with experimental electron removal energies (respective shell edges) [3]. The deviation from the experimental data is shown in the diagram below. The orbitals with removal energy <1 keV are shown.



Conclusions

- Among the 5 considered methods, the Hartree-Fock method shows the best agreement between one-electron orbital energies and experimental data.
- None of the methods performs fully satisfactory in this sense.

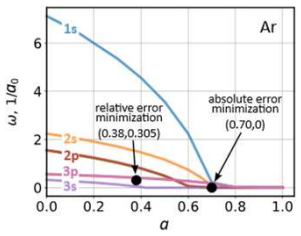
Optimal hybrids

We ask ourselves: is it possible to pick a set of parameters for a hybrid functional that results in orbital energies in *perfect* agreement with the experimental data? We fit the electron-removal energies by varying pameters a and ω in the density functional of the following form :

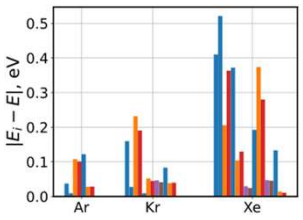
$$E_{xc} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) + E_x^{HF,LR}(\omega) + E_c^{PBE}$$

We minimize the root mean squares of the (i) absolute errors and (ii) relative errors w.r.t. experimental data.

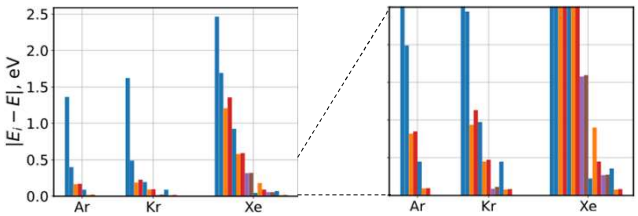
Parameters yielding the optimal or ideal agreement with Expt.



Errors after minimizing absolute errors for each atom



Errors after minimizing relative errors for each atom



Conclusions

- Fitting to experimental electron removal energies leads to greatly reduced errors showing a potential for a method within the hybrid-functionals framework that works specifically for orbital energies.
- Fitting for an individual atom works reasonably well. Is there a way to choose the parameters that work for all atoms?
- The developed code can be used for assessing emerging hybrid functionals such as those with local mixing or local range separation.

References

[1] J. Užulis, and A. Gulans, *J. Phys. Commun.* **6**, 085002 (2022)
[2] L. Visscher, and K.G. Dyall, Atomic Data and Nuclear Data Tables **67**, 207 (1997)
[3] Lotz W, *J. Opt. Soc. Am.* **106**, 206-210 (1970)

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