Radial Kohn-Sham solver – core orbitals in hybrid calculations

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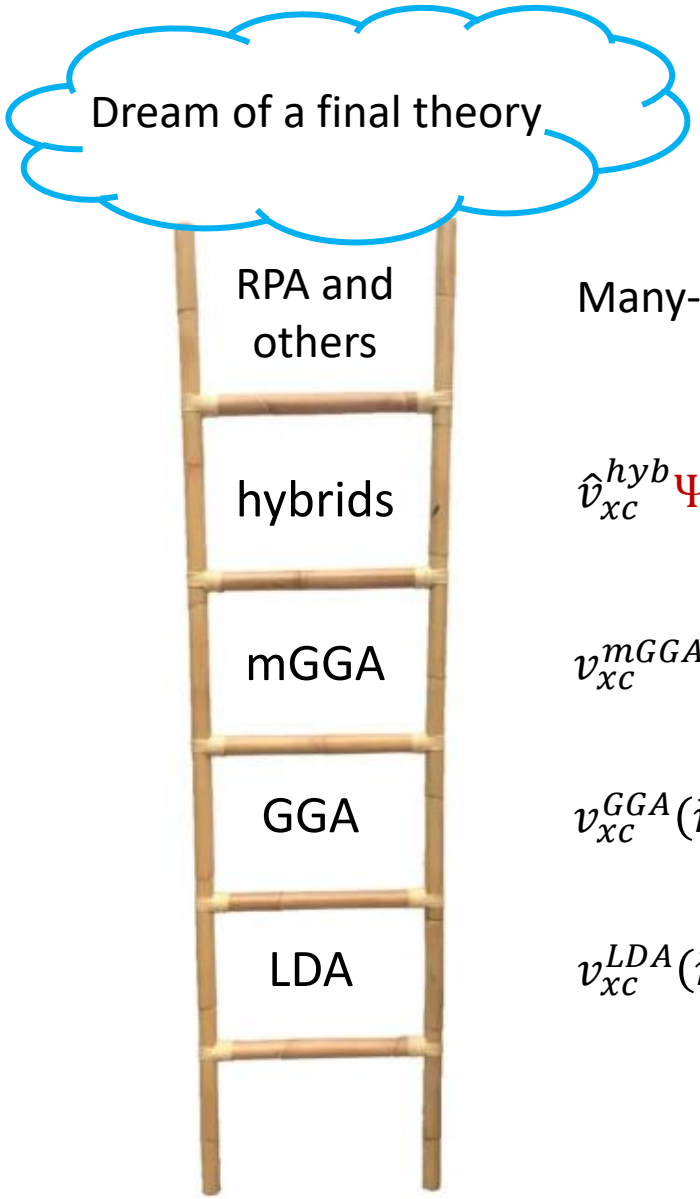
How exciting! 2023
2023.08.09

Theory classification in DFT



Many-body perturbation theory etc.

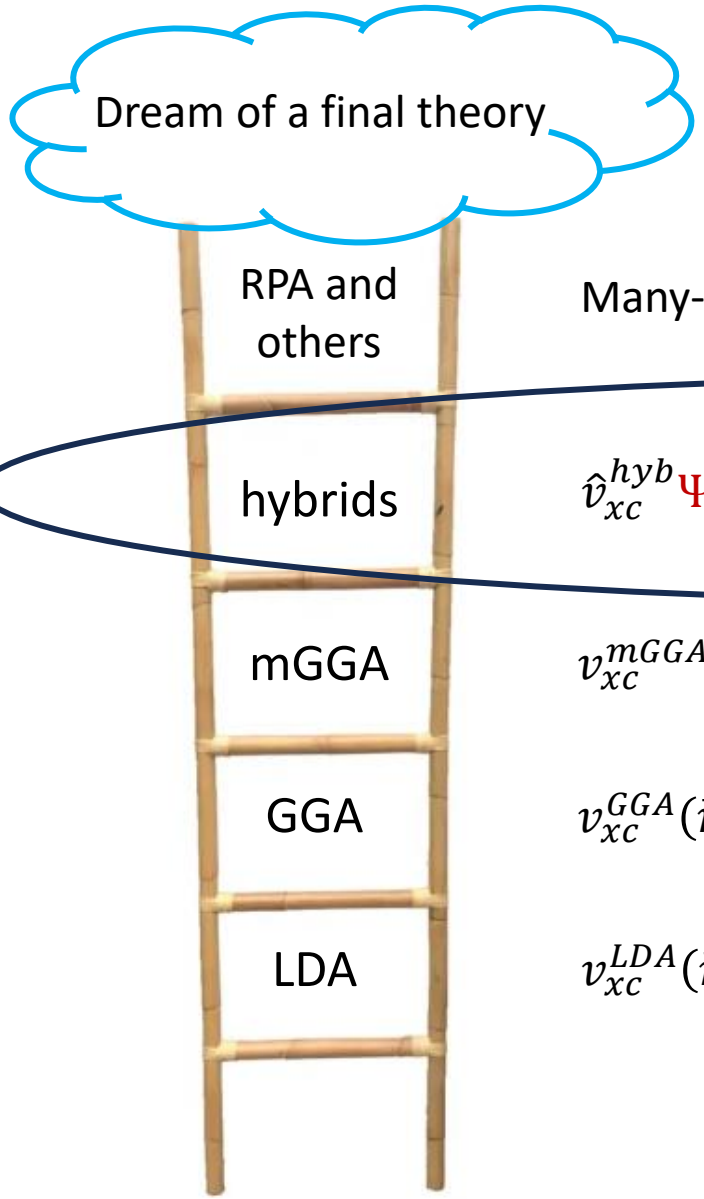
$$\hat{v}_{xc}^{hyb}\Psi(\vec{r}) = \alpha \sum_n^{occ} \Psi_n(\vec{r}) \int \frac{\Psi_n^*(\vec{r}')\Psi(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3\vec{r}' + (1-\alpha)\, v_x^{GGA}(\vec{r}) + v_c^{GGA}(\vec{r})$$

$$v_{xc}^{mGGA}(\vec{r}) = v_{xc}(\rho(\vec{r}), \nabla\rho(\vec{r}), \nabla^2\rho(\vec{r}))$$

$$v_{xc}^{GGA}(\vec{r}) = v_{xc}(\rho(\vec{r}), \nabla\rho(\vec{r}))$$

$$v_{xc}^{LDA}(\vec{r}) = v_{xc}(\rho(\vec{r}))$$

Theory classification in DFT



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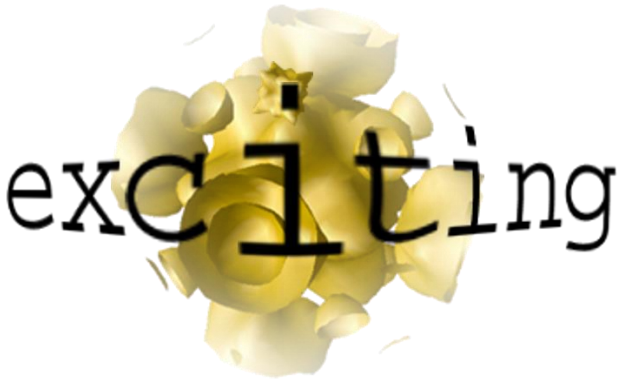
Some improvements needed in LAPW method



All-electron LAPW basis set

Core orbitals:

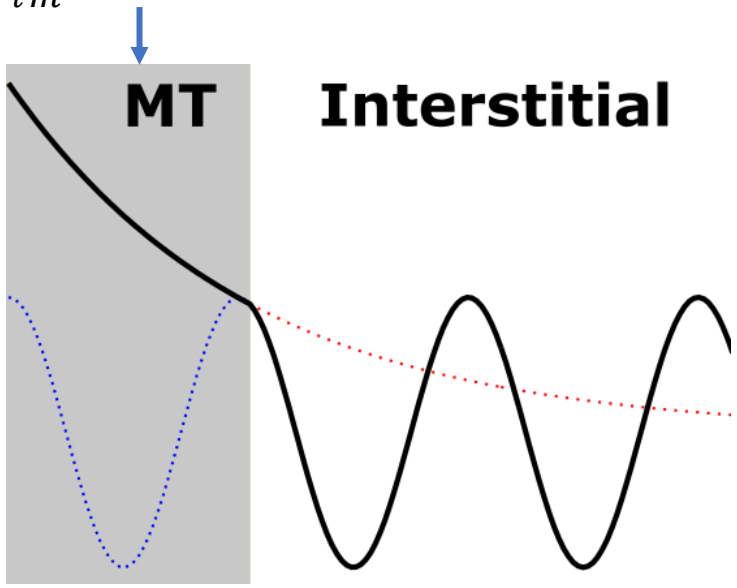
$u_{n\ell}(r)Y_{\ell m}(\hat{r})$

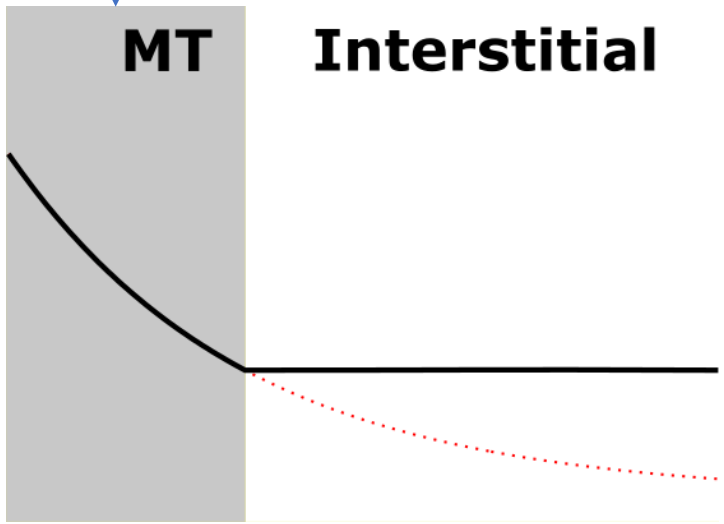
LAPW basis set in MT:

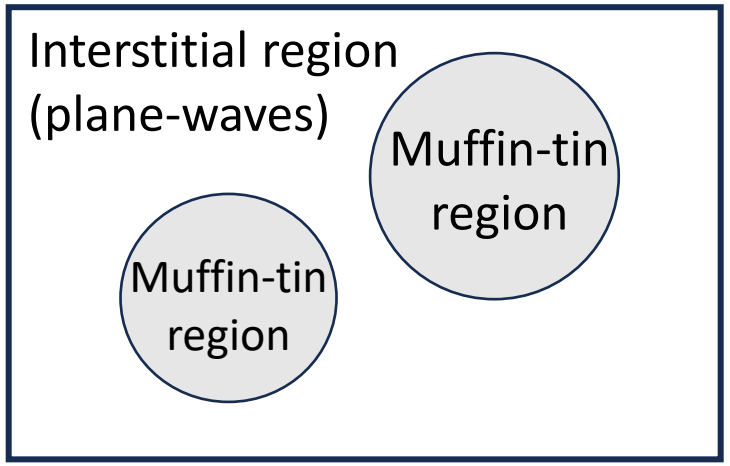
$$\sum_{\ell m}(A_{\ell m}u_{\ell}(r;\epsilon_{\ell}) + B_{\ell m}\dot{u}_{\ell}(r;\epsilon_{\ell}))Y_{\ell m}(\hat{r})$$

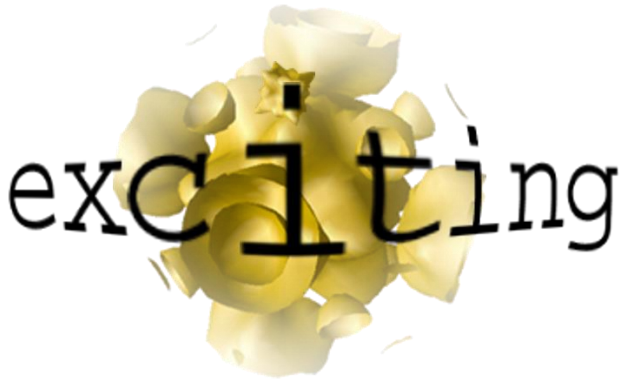
Local orbitals:

$(a_v u_{\ell}(r;\epsilon_{\ell}) + b_v \dot{u}_{\ell}(r;\epsilon_{\ell}))Y_{\ell m}(\hat{r})$



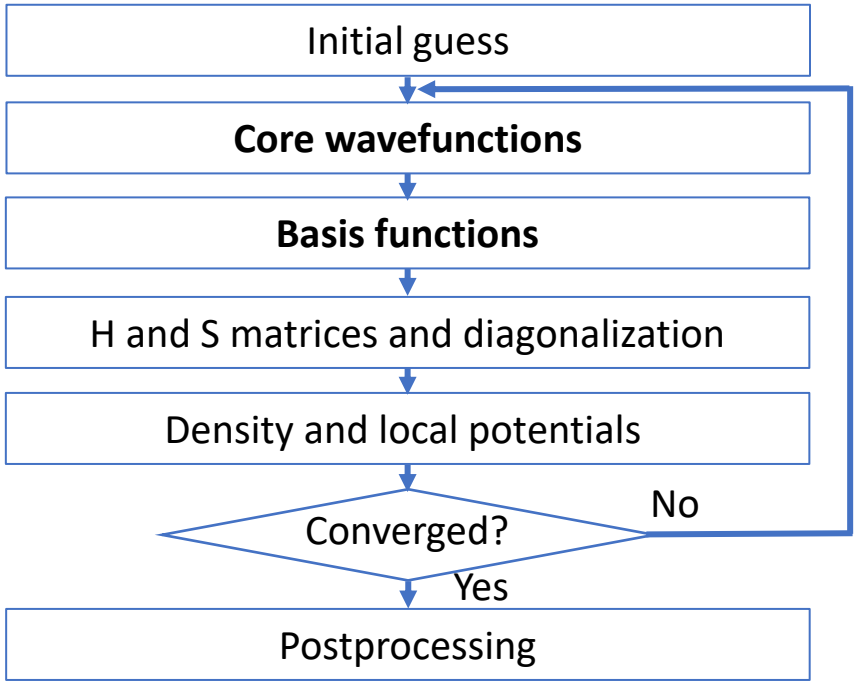




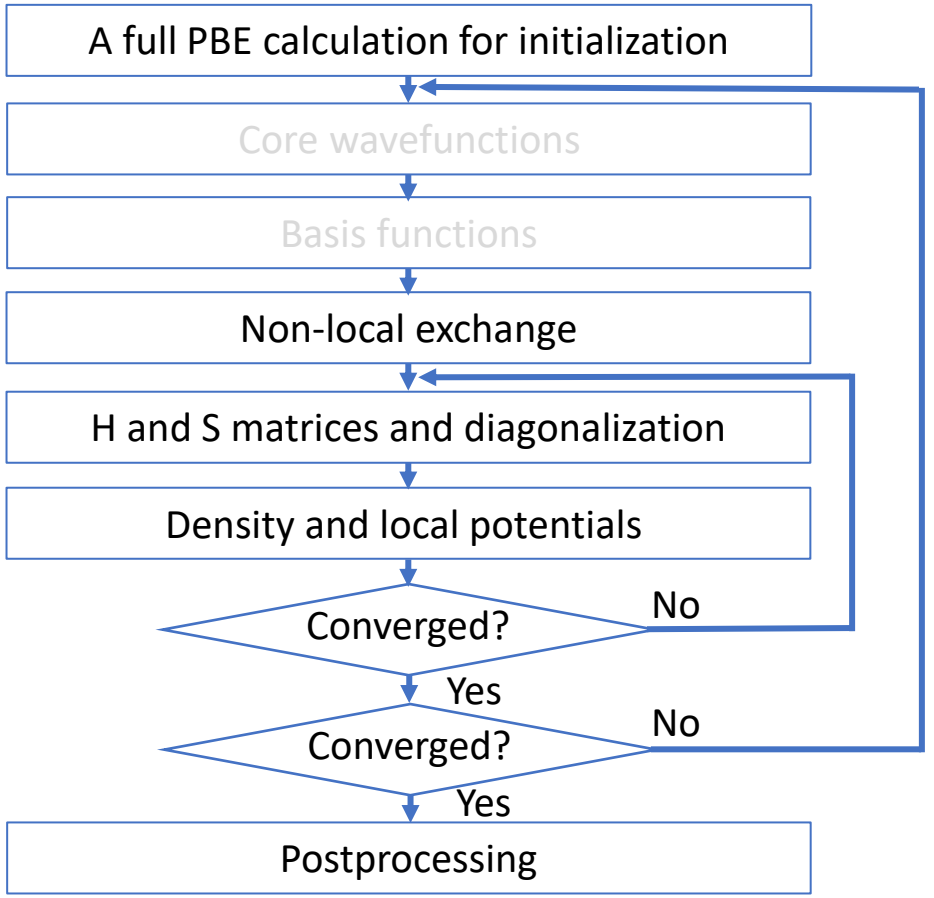


Workflow in `exciting` with local and hybrid functionals

LDA or GGA

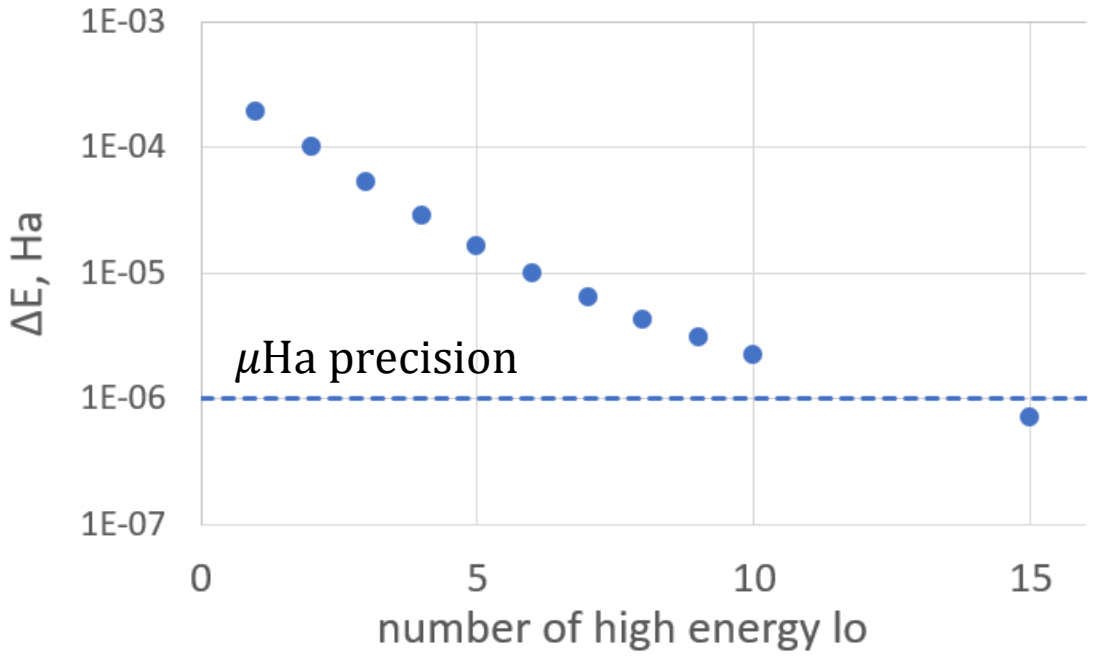


Hybrid functionals



Convergence of HF calculation with respect to the size of PBE LAPW+lo basis set

He



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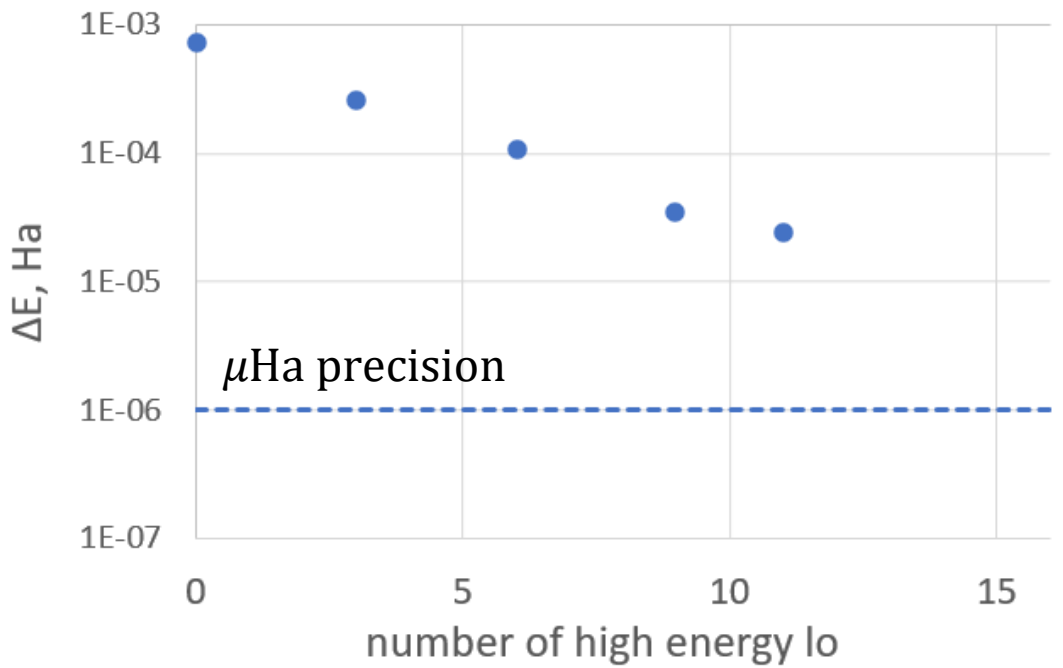

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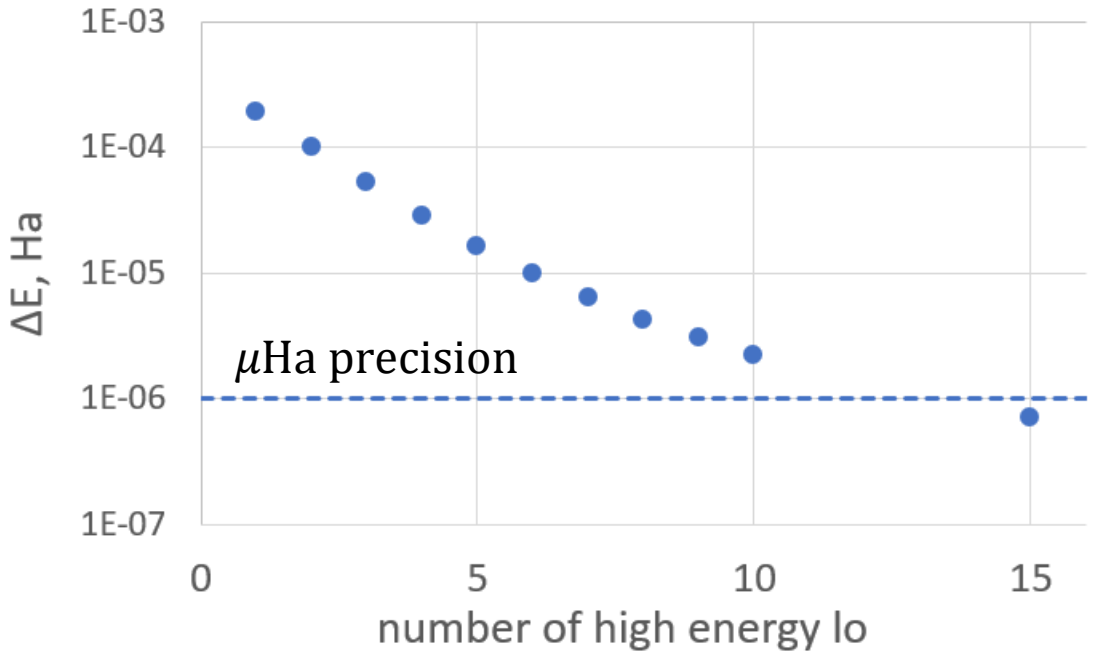

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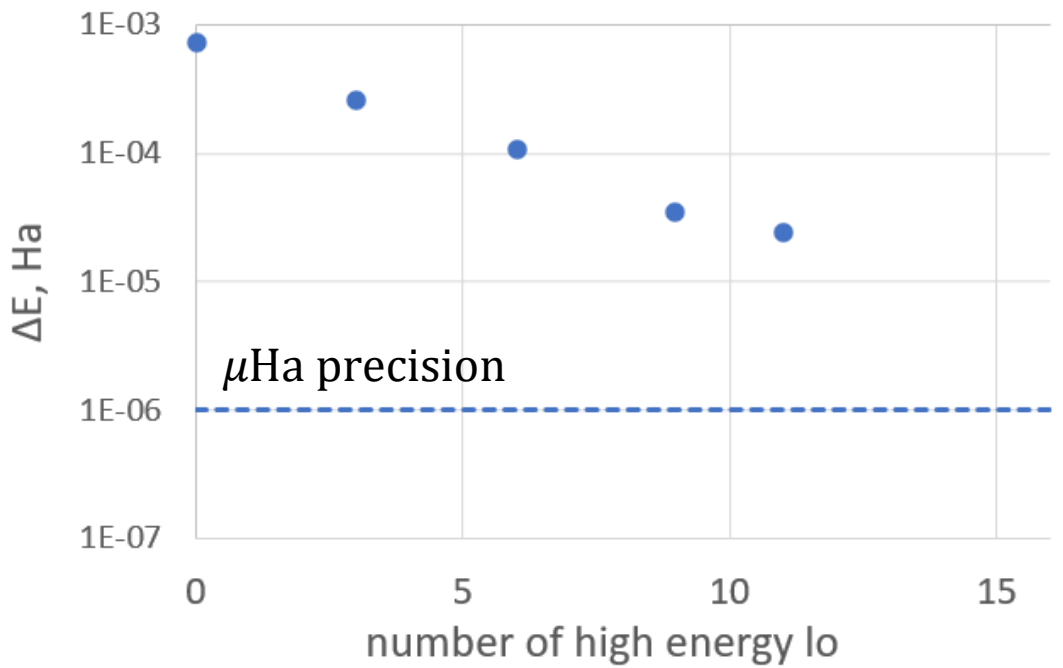

Why do we need μHa precision?

- LAPW is a *gold standard* method – it can produce benchmark data.
- To validate method and implementation.

Radial solver for basis functions point by point $(u_i \rightarrow u_{i+1})$ outwards integration

$$-\frac{1}{2}\frac{d^2}{dr^2}u(r) + \frac{l(l+1)}{2r^2}u(r) + v^{\mathrm{L}}(r)u(r) = \varepsilon u(r) \qquad u(r) = \psi(r)r$$

- First point initial value $u_1 = r_1^{\ell+1}$

- Solve ODE point by point $(u_i \rightarrow u_{i+1})$

(by splitting 2-nd order dif. eq. in two coupled 1-st. order dif. eq.)

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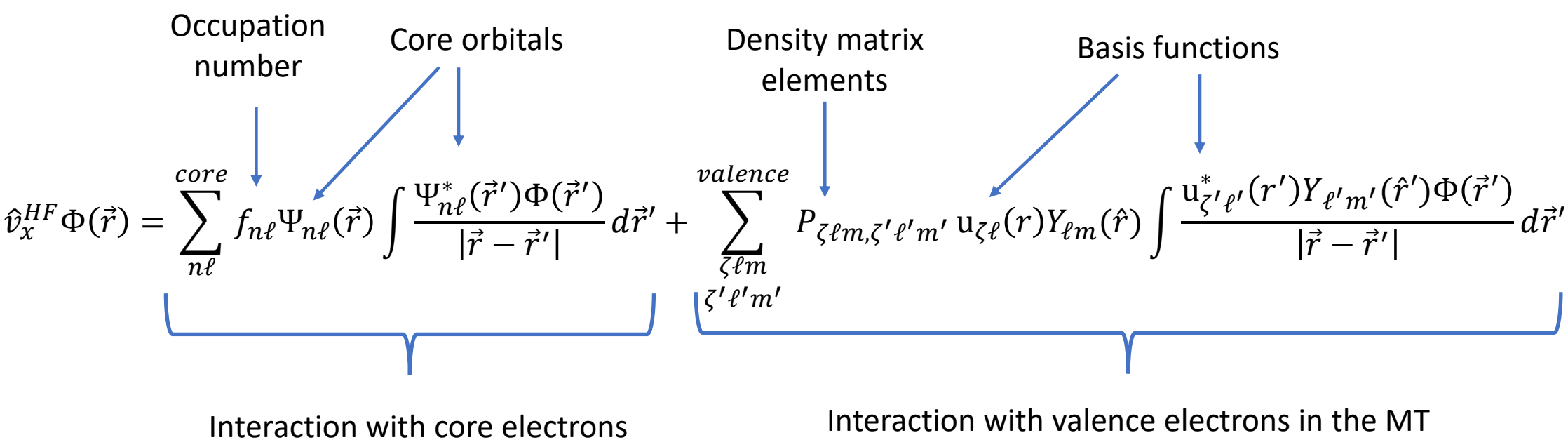
$$-\frac{1}{2}\frac{d^2}{dr^2}u(r) + \frac{l(l+1)}{2r^2}u(r) + v^{\mathrm{L}}(r)u(r) + \hat{v}_x^{NL}u(r) = \varepsilon u(r)$$

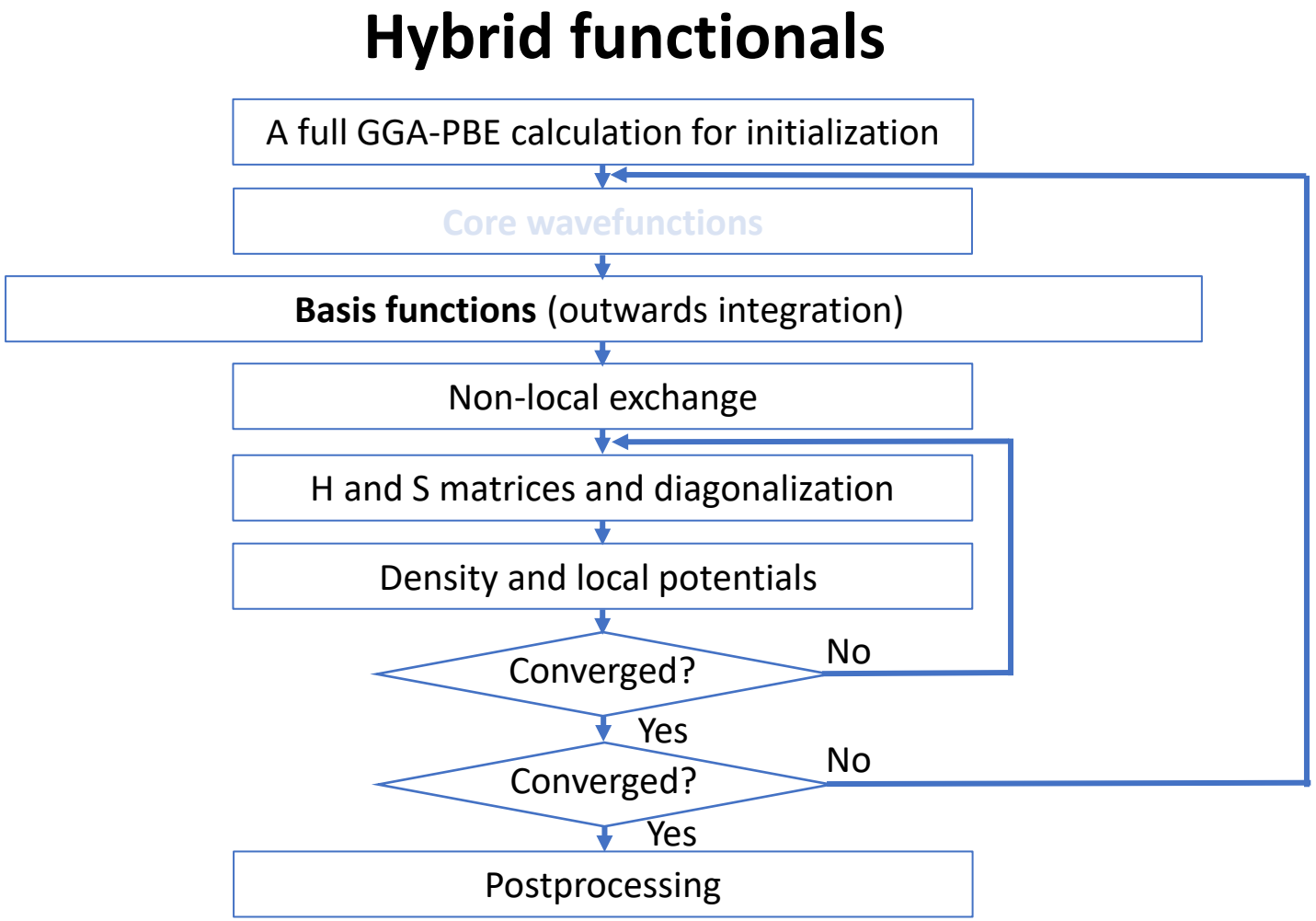
We don't have this function yet.

$$-\frac{1}{2}\frac{d^2}{dr^2}u^{(i)}(r) + \frac{l(l+1)}{2r^2}u^{(i)}(r) + v^{\mathrm{L}}(r)u^{(i)}(r) + \hat{v}_x^{NL}u^{(i-1)}(r) = \varepsilon u^{(i)}(r)$$

Exact exchange in radial solver

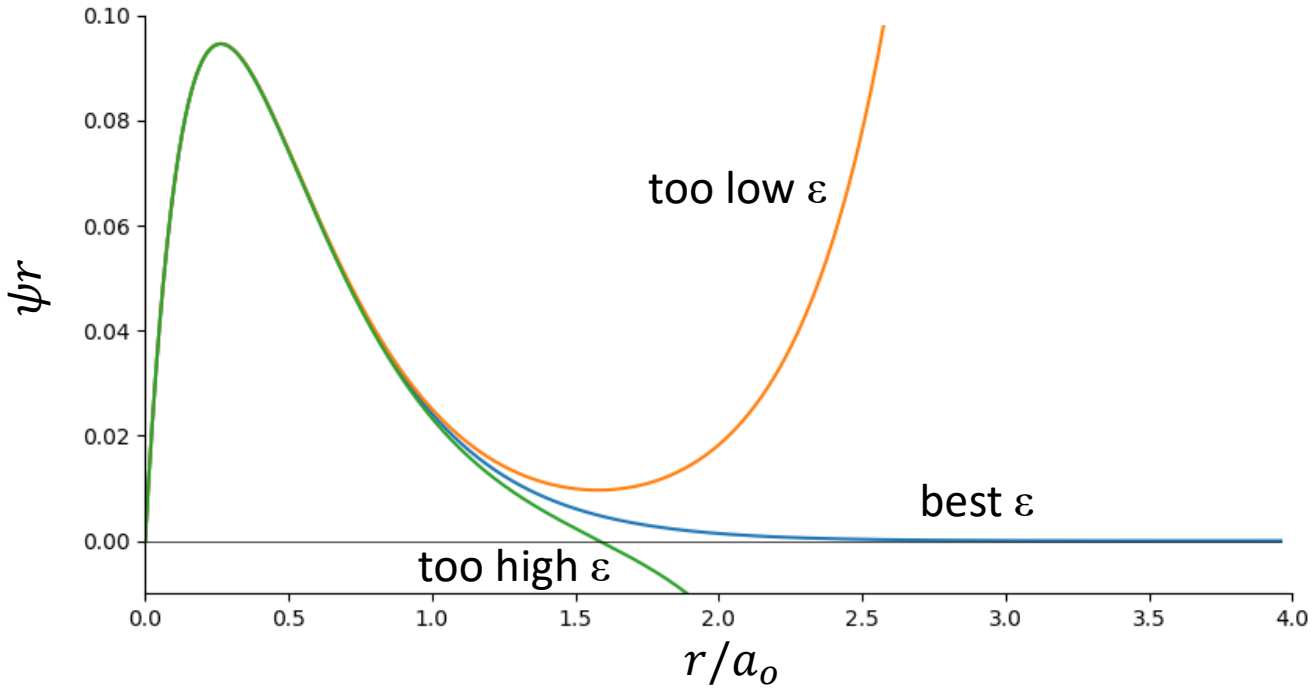


Workflow in exciting with hybrid functionals



Radial solver for core orbitals point by point $(u_i \rightarrow u_{i+1})$ outwards integration

$$-\frac{1}{2}\frac{d^2}{dr^2}u^{(i)}(r) + \frac{l(l+1)}{2r^2}u^{(i)}(r) + v^{\mathrm{L}}(r)u^{(i)}(r) + \hat{v}_x^{NL}u^{(i-1)}(r) = \varepsilon u^{(i)}(r)$$



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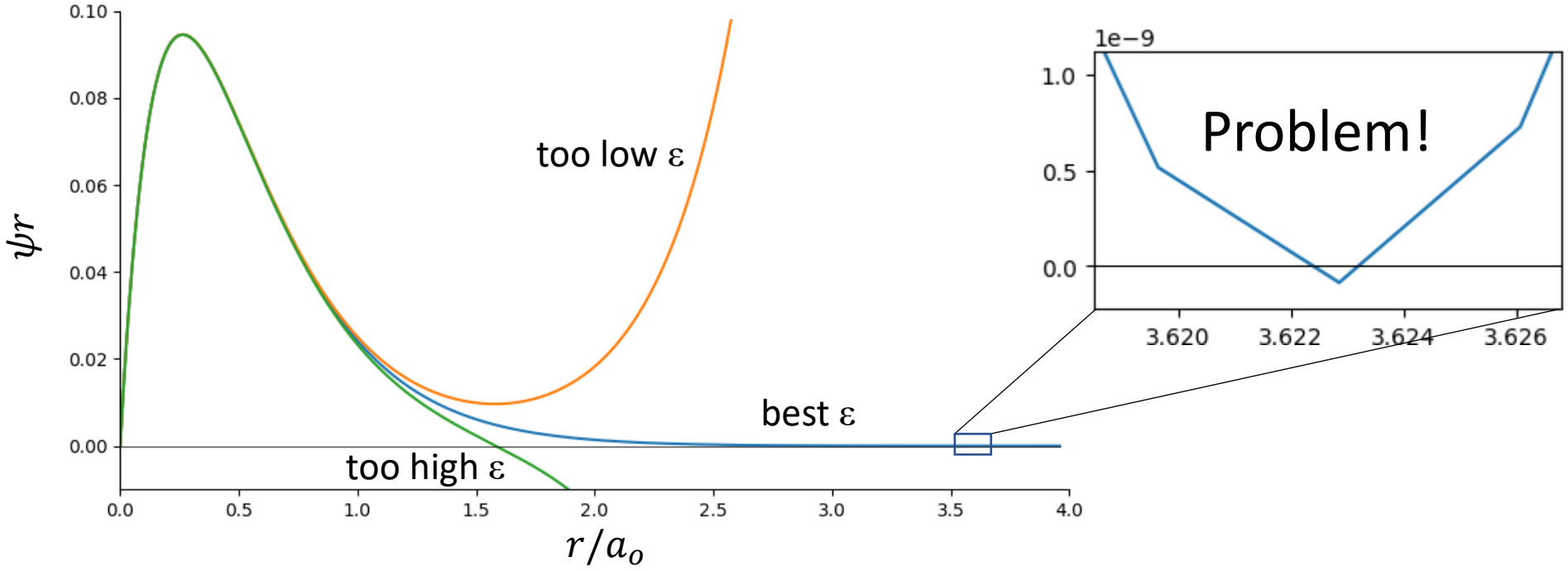

Radial solver - integral equation approach

$$-\frac{1}{2}\nabla^2\Psi_{\mathrm{nl}m}\,(\vec{r}) + \hat{v}\Psi_{\mathrm{nl}m}(\vec{r}) = \varepsilon\Psi_{nlm}(\vec{r})$$

$$(\nabla^2+2\varepsilon)\Psi_{nlm}(\vec{r}) = 2\hat{v}\Psi_{nlm}(\vec{r})$$

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Screened
Poisson eq.

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$$(\nabla^2+2\varepsilon)\Psi^{(i)}_{nlm}(\vec{r}) = 2\hat{v}\Psi^{(\mathrm{i}-1)}_{\mathrm{nlm}}(\vec{r})$$ ← Screened Poisson eq.

$$\Psi^{(\mathrm{i})}_{nlm}(\vec{r}) = 2\int_0^\infty d^3r'\; G(\vec{r},\vec{r}')\hat{v}\Psi^{(\mathrm{i}-1)}_{\mathrm{nlm}}(\vec{r}')$$ ← Green's function method

Radial solver - integral equation approach

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Green's function method

$$G(\vec{r},\vec{r}') = \frac{e^{-\lambda|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} = 4\pi\lambda\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i_l(\lambda r_<)k_l(\lambda r_>)Y^*_{lm}(\hat{r})Y_{lm}(\hat{r}')$$

Modified Spherical Bessel Functions

Radial solver - integral equation approach

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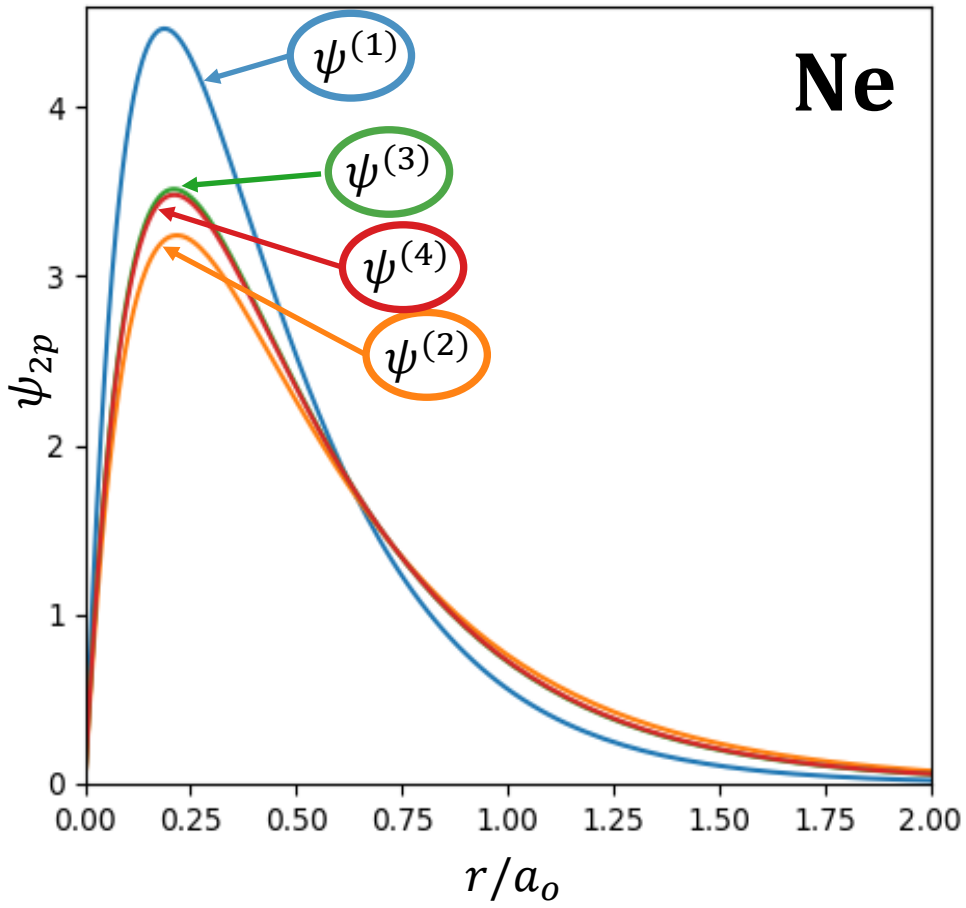
Modified Spherical Bessel Functions



Radial solver via integral equation approach

A stand-alone atomic solver for closed shell atoms.

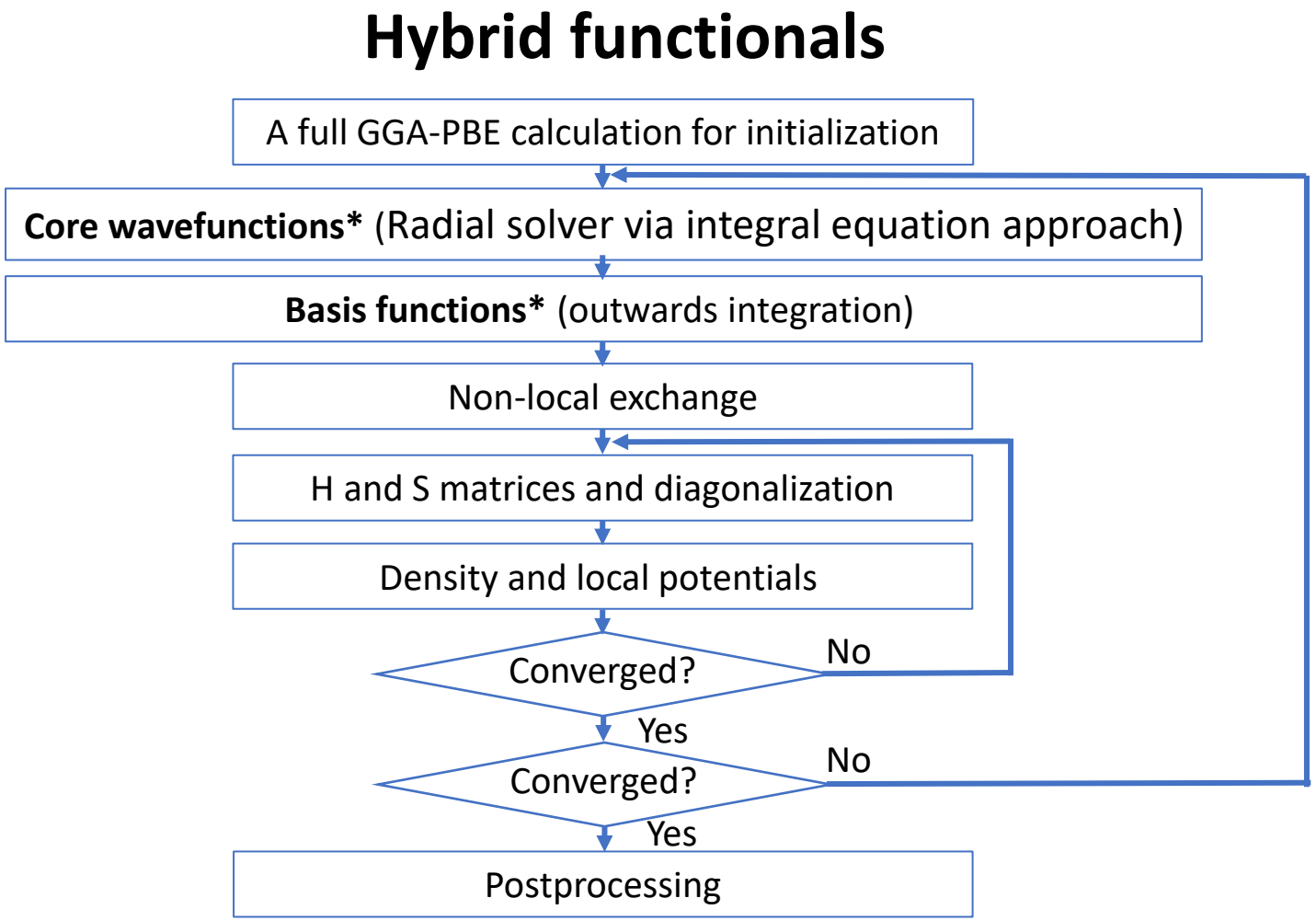
- Can solve Kohn-Sham equation for atoms with spherically symmetric density - closed shell or open shell with predefined fractional occupation numbers.
- Supports spin-polarized systems (calculations with separated spin channels).
- Up to 14-digit precision for the total energy in Hartee-Fock case.
- Interface with libxc (local LDA and GGA functionals).
- Hybrid exchange-correlation functionals and range-separated hybrids (erf kernel).
- Supports non-relativistic [1] and scalar-relativistic Hamiltonians within the zero-order regular approximation (ZORA).
- Point and Gaussian charge distribution model of nucleus.
- A verification tool for other DFT codes.

GitHub

https://github.com/gulans/atom-HF

[1] J. Užulis and A. Gulans, Journal of Physics Communications **6**, 085002 (2022);

Workflow in exciting with hybrid functionals



* - not included in latest exciting neon version.

Basis functions with non-local exchange

Total energy deviation from exact HF total energies with PBE and HF core orbitals and different types of LAPW+lo basis set.

	MT=2.0 a_0				MT=1.5 a_0
Core type	PBE	HF	HF	HF	HF
Radial basis type	PBE	PBE	HF	HF + 1lo	HF + 1lo
Atom	$\Delta E, \mu\mathrm{Ha}$	$\Delta E, \mu\mathrm{Ha}$	$\Delta E, \mu\mathrm{Ha}$	$\Delta E, \mu\mathrm{Ha}$	$\Delta E, \mu\mathrm{Ha}$
He	527	527	0	0	0
Be	706	706	0	0	0
Ne		3999	177	4	12
Ar		-1425	40	39	2
Kr		8869	23	8	20
Xe		-92	4	2	34

Acknowledgments

Work has been financed from projects:

- **”Strengthening of the capacity of doctoral studies at the University of Latvia within the framework of the new doctoral model”**, identification No. 8.2.2.0/20/I/006.
- **Precise Fock Exchange (PREFEX)** by the Latvian Council of Science (No. LZP-2020/2-0251)
- **NOMAD CoE** (European Union’s Horizon 2020, grant agreement No. 951786.)

Advisor: **Andris Guļāns**

Summary

- **The integral equation approach** is a highly precise method for solving the radial problem with hybrid functionals. We apply it in `exciting` for calculating **core orbitals**.

- We extend the existing **outward integration radial solver** in `exciting` to **generate radial basis functions** compatible with hybrid functionals.

- We combine both ingredients to be able to calculate meaningful Hartree-Fock energies (the same Hamiltonian applied everywhere and no double-counting errors).

- The Hartree-Fock total energies can be converged systematically with the errors within a **few µHa**.

- The **correct core state eigenvalues** allows to use hybrid calculations in a core electron spectroscopy.