Development of self-consistent pseudopotentials and PAW datasets for meta-GGA exchange-correlation functionals

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Manuscript accepted for publication in PRB: *"A cubic spline solver for generalized density functional treatments of atoms and the generation of atomic datasets for use with exchange-correlation functionals including the meta generalized gradient approximation"*

Three points:

1. Examined self-consistent electronic structure of spherical atoms using the meta-GGA exchange-correlation functionals, focusing on "r2SCAN" (Furness, et al. JPCL 11, 8208 (2020)) -- analyzed with generalized Kohn-Sham equations. ➔ Propose slight modification "r2SCAN01"

2. Developed a general-purpose ODE solver for second order differential eigenvalue equations, with or without first order derivatives, based on the cubic spline interpolation formalism. ➔The resultant "splinesolver" algorithm is particularly efficient for converging the self-consistent electronic structure of spherical atoms, including those using meta-GGA functionals.

3. Adapted PAW construction methods for use with meta-GGA functionals. ➔Preliminary results are promising; available in ATOMPAW code

**Part 1:** **Some perspective –**

- **Use of meta-GGA exchange-correlation functionals increased with the introduction of the SCAN formulation (Sun, et al. PRL 115, 036402 (2015))**

  SCAN → "Strongly Constrained and Appropriately Normed"

  - **SCAN paper has ~ 1300 citations mostly showing improved property representation; continuing discussion are being presented at this meeting**
  - **Several authors have identified numerical issues due to functional parameter choices in the design of the SCAN functional form**
    - **Apparently, the difficulties are not apparent when electronic wavefunctions are represented with fixed localized basis functions; plane wave codes (other than VASP) have difficulty**
    - **SCAN: $V_{xc}(r)$ diverges for r → ∞ for the electron density of a H atom for example**
    - **rSCAN: Bartôk and Yates, JCP 150, 161101 (2019)**
    - **r2SCAN: Furness, et al. JPCL 11, 8208 (2020) – corrects numerical issues of SCAN**

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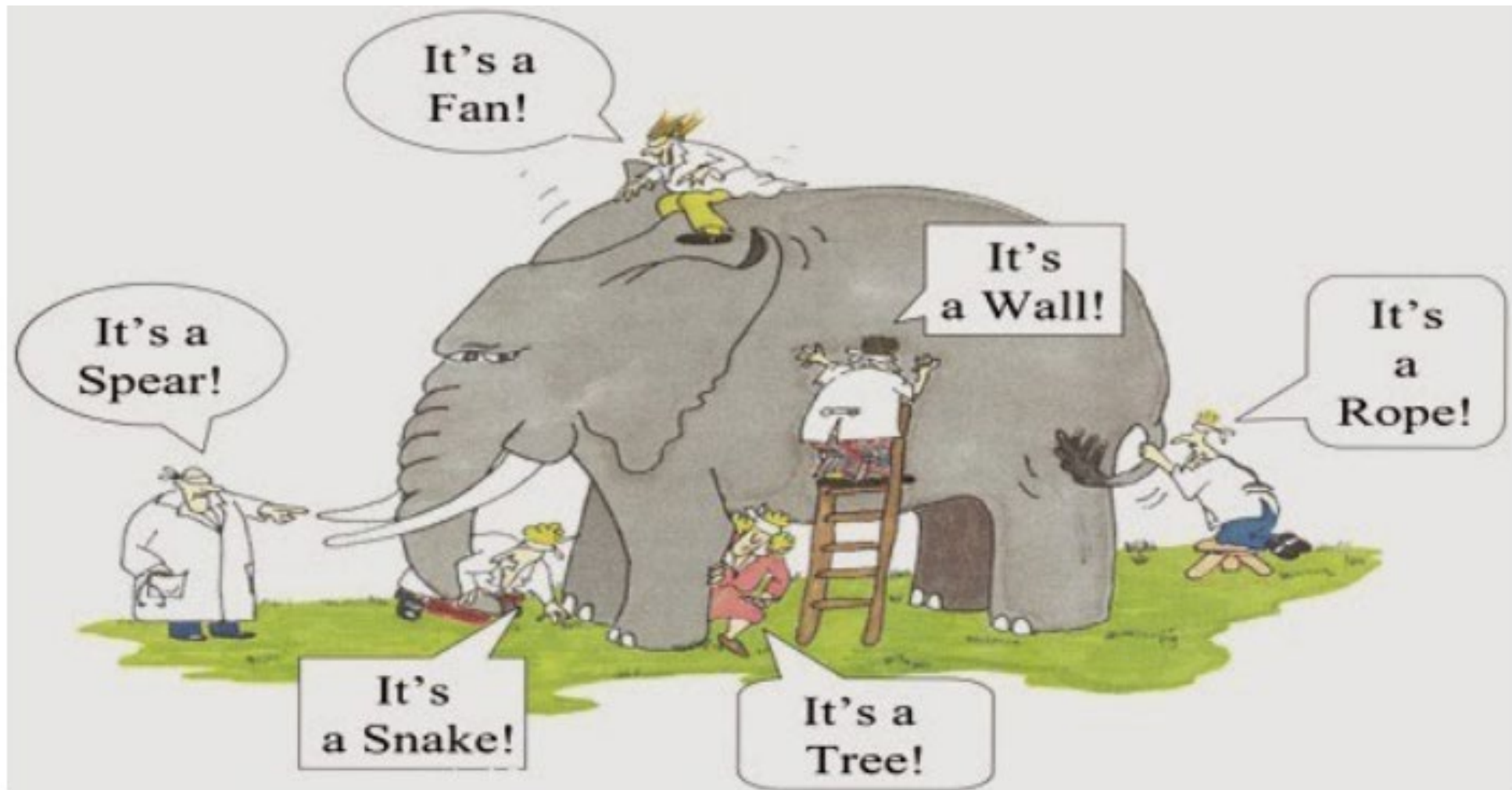
The Blind Men and the Elephant

Adapted story – elephant⬅➡DFT theory & computation
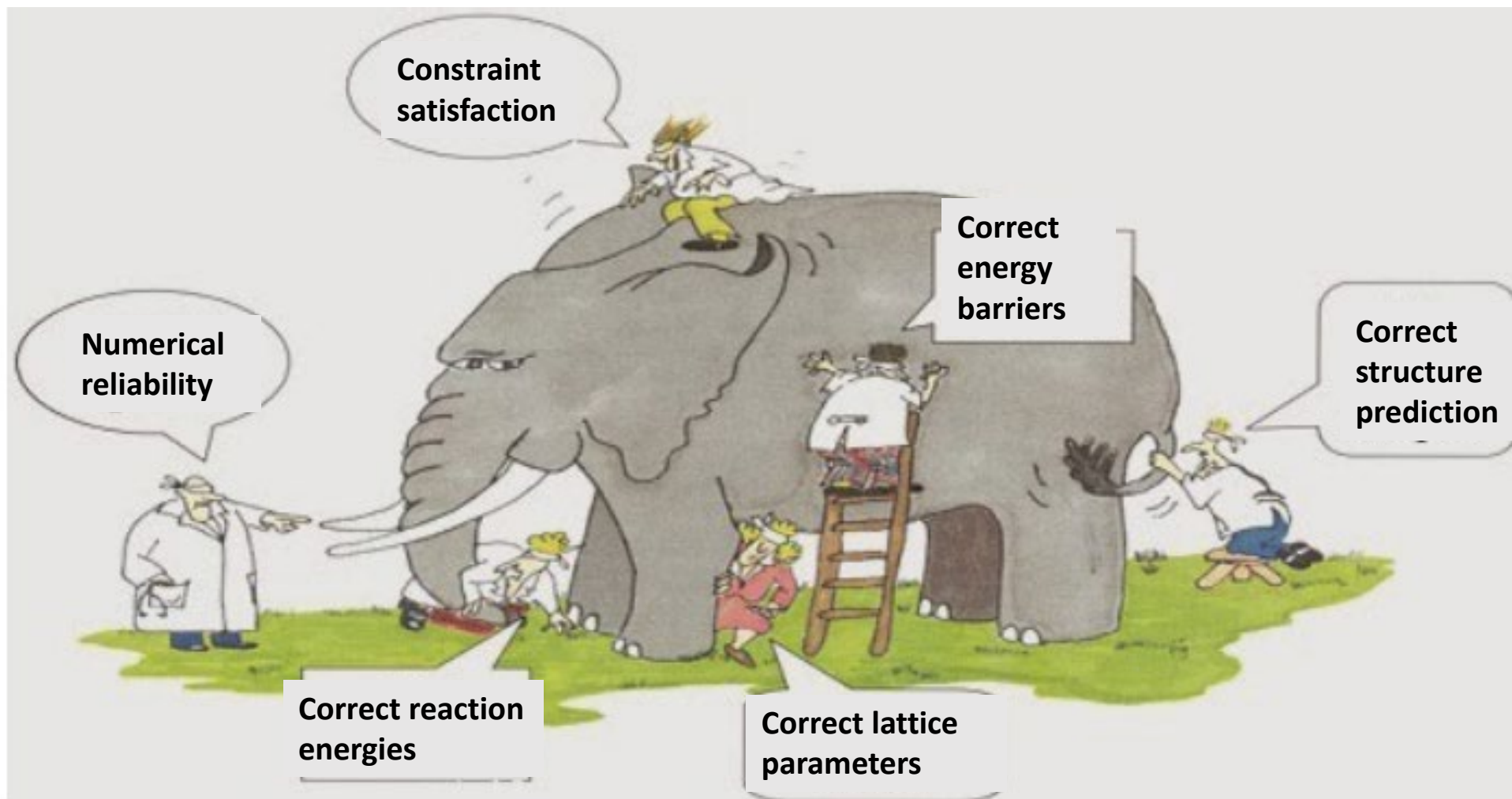
Condensed matter scientists and the ideal exchange-correlation functional

Systematic equations --

General form of the exchange-correlation functional:

$$E_{xc} = \int d^3 r \, f_{xc}(n(\mathbf{r}), \sigma(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}))$$

In terms of single particle states $\Phi_i(\mathbf{r})$ having occupancy w_i,

kinetic energy density

$$n(\mathbf{r}) \equiv \sum_i w_i |\Phi_i(\mathbf{r})|^2 \qquad \sigma(\mathbf{r}) \equiv \nabla n(\mathbf{r}) \cdot \nabla n(\mathbf{r}) \qquad \tau(\mathbf{r}) = \frac{\hbar^2}{2m} \sum_i w_i |\nabla \Phi_i(\mathbf{r})|^2$$

The generalized Kohn-Sham equations take the form

$$H(\mathbf{r}) = -\frac{\hbar^2}{2m}\left(\nabla^2 + \nabla \cdot (V_\tau(\mathbf{r})\nabla)\right) + V_{\text{eff}}(\mathbf{r}) \qquad \text{where} \quad V_\tau(\mathbf{r}) \equiv \frac{\partial f_{xc}}{\partial \tau}$$

dimensionless "kinetic potential"

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{electron-nucleus}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

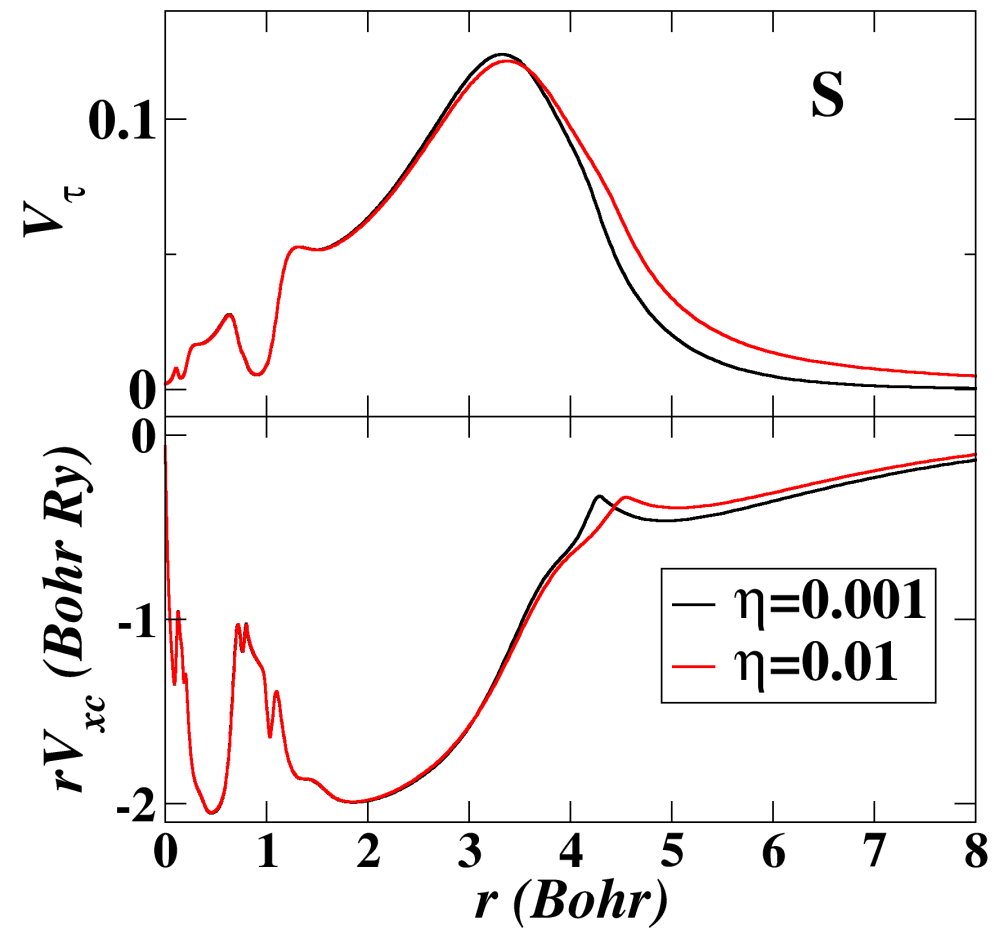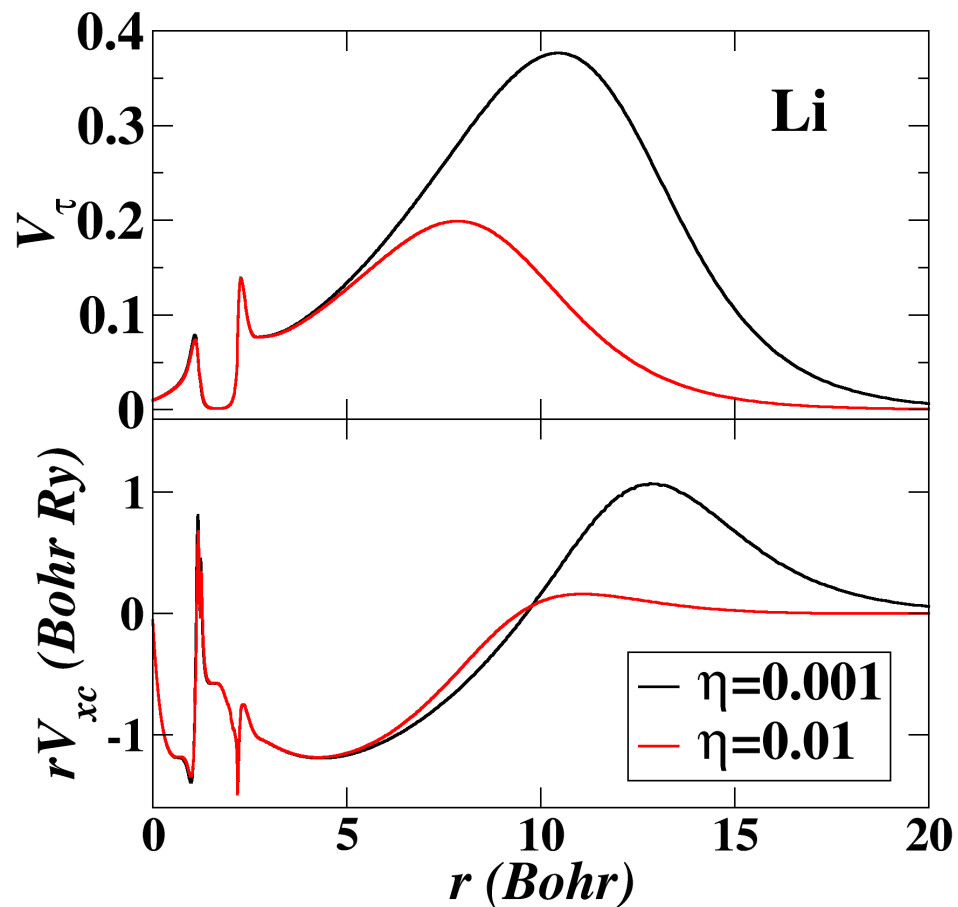$$V_{xc}(\mathbf{r}) = \frac{\partial f_{xc}}{\partial n} - \nabla \cdot \left(2 \frac{\partial f_{xc}}{\partial \sigma} \nabla n\right) + \nabla^2 \left(\frac{\partial f_{xc}}{\partial (\nabla^2 n)}\right)$$
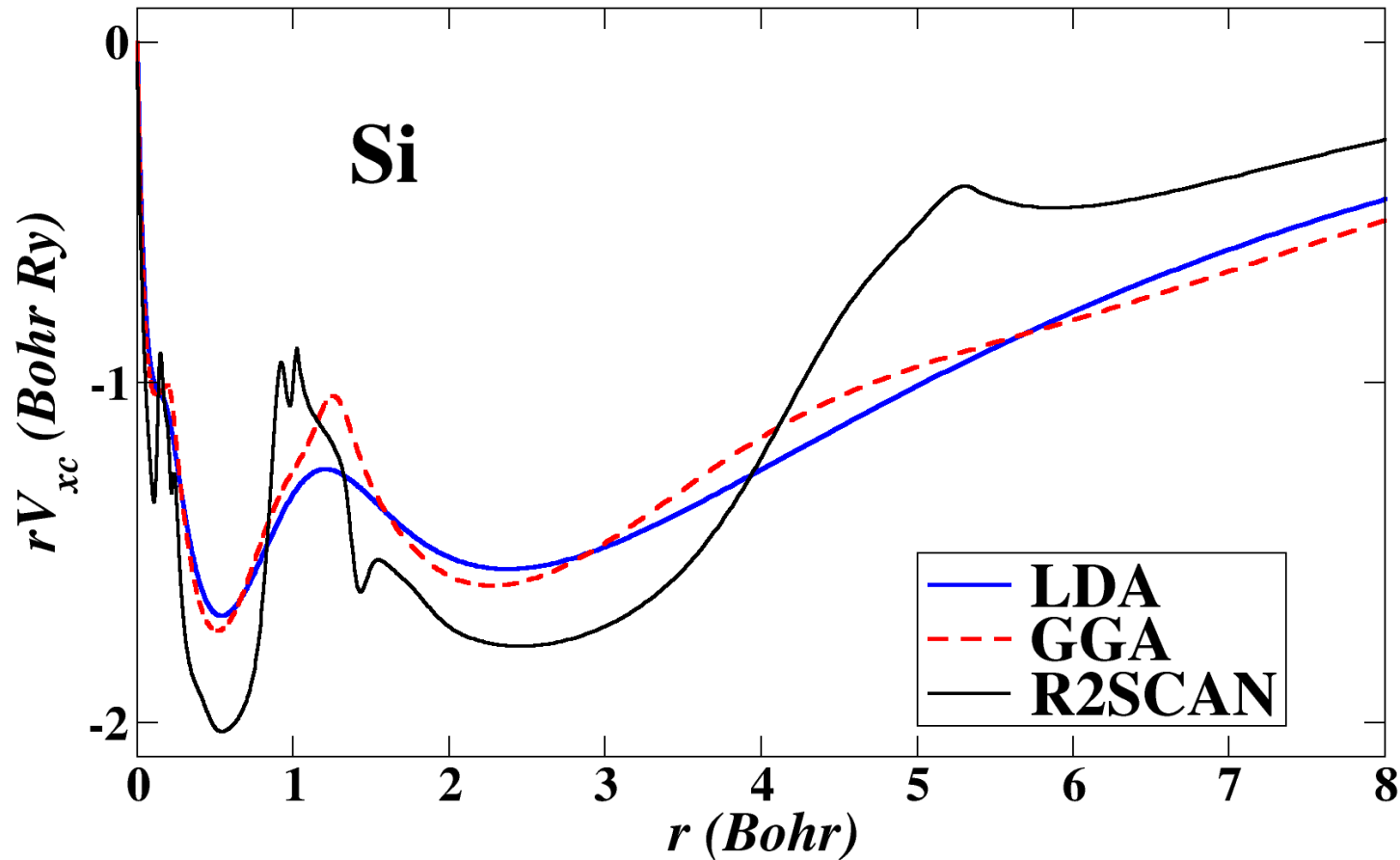
Some details regarding functional forms associated with kinetic energy density $\tau(r)$

$$\overline{\alpha} \equiv \frac{\tau - \tau_W}{\tau_{\text{unif}} + \eta \tau_W} \quad \text{where} \quad \tau_W = \frac{|\nabla n|^2}{8n} \quad \tau_{\text{unif}} = \frac{3n}{10}\left(3\pi^2 n\right)^{2/3}$$
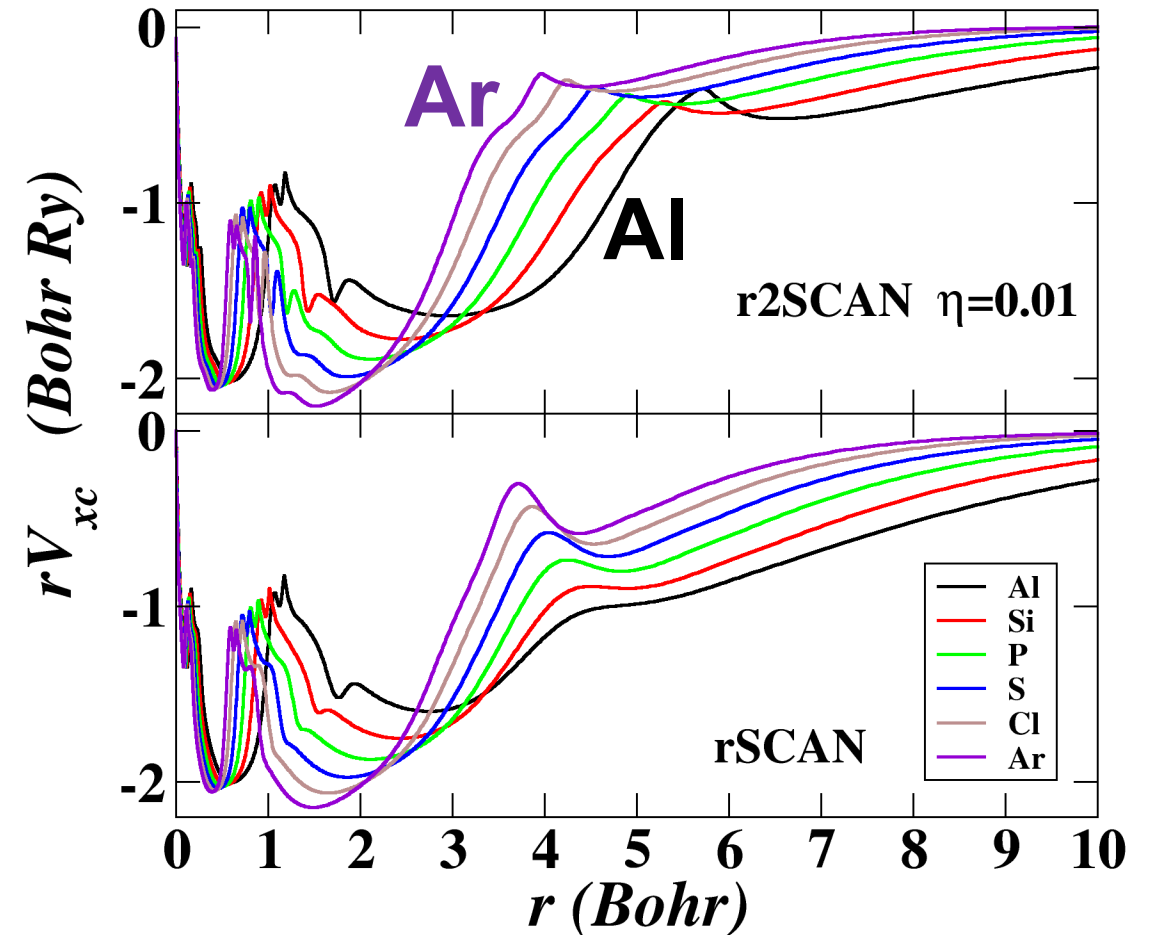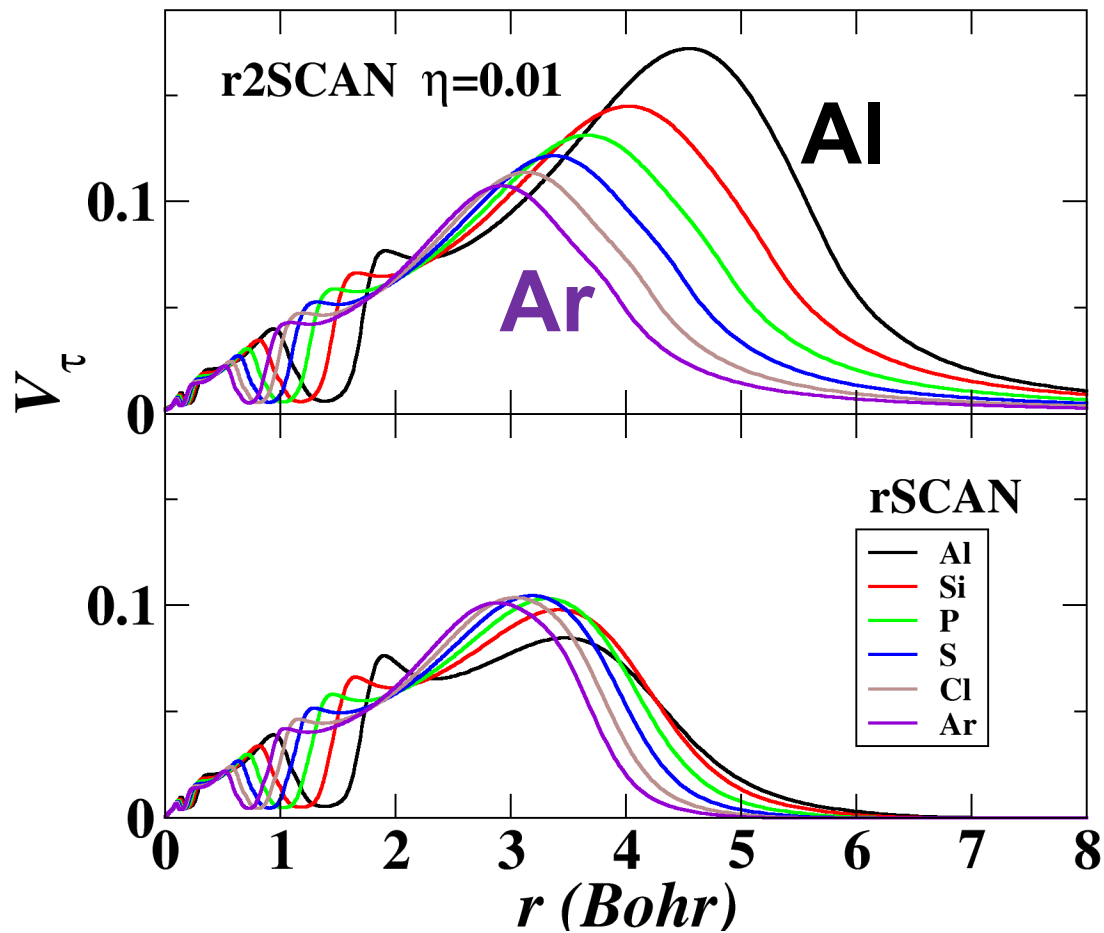
Original r2SCAN $\eta=0.001$
r2SCAN01 $\eta=0.01$

# Comparison of self-consistent $V_{xc}(r)$ for a Si atom with different functional forms

Comparison of self-consistent $V_\tau(r)$ and $V_{xc}(r)$ for atoms in the 3rd row of the periodic table

Spline solver algorithm

Cubic spline interpolation -- J. H. Ahlberg, The theory of splines and their applications (1967) and Carl de Boor, A practical Guide to Splines (1978) – based on representing a one-dimensional function by a piecewise continuous polynomial of order 3.
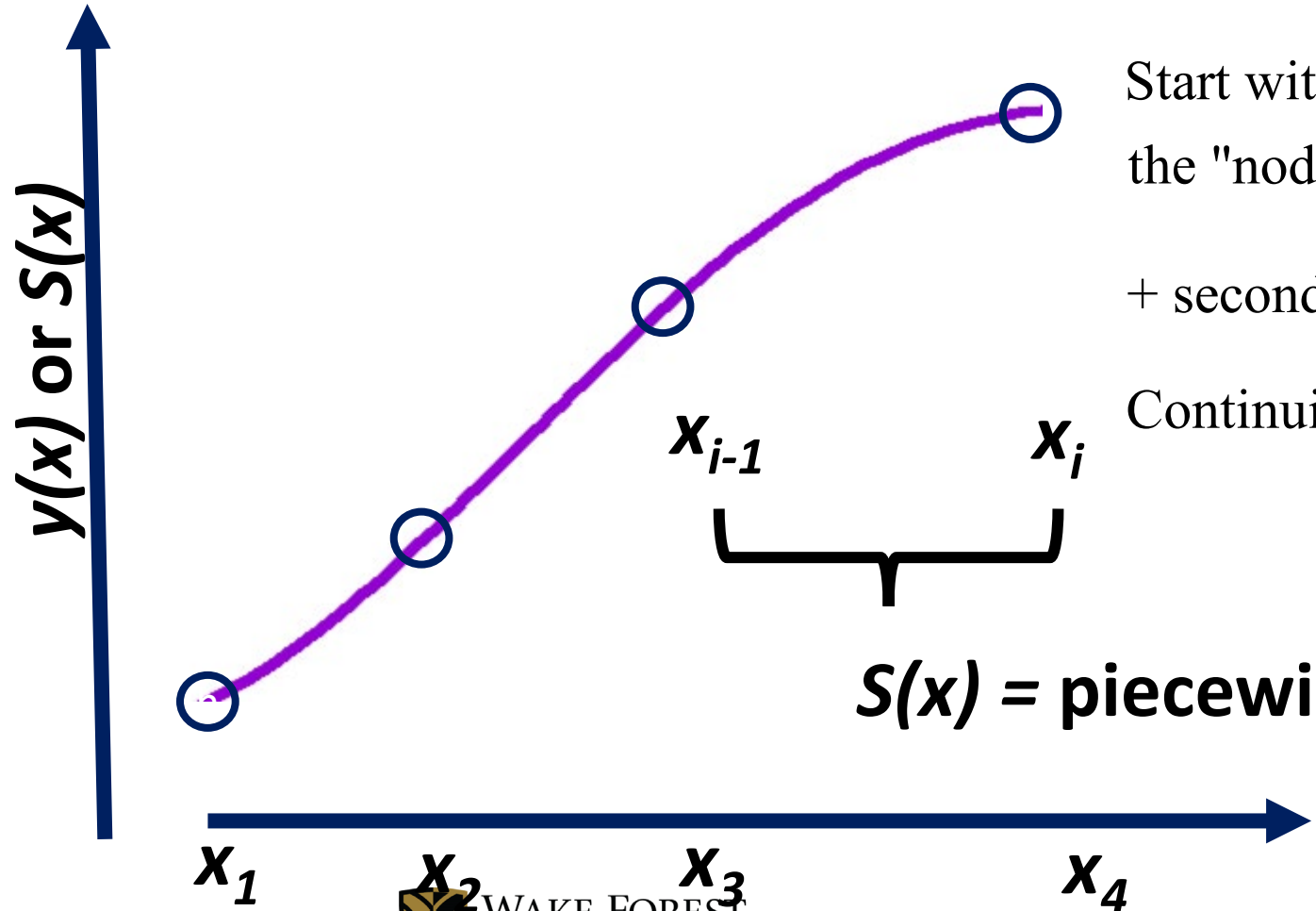
Start with the value of the function on the "node" points:

$$y_i \equiv y(x_i) = S(x_i)$$

+ second derivatives:

$$M_i \equiv \frac{d^2 y(x_i)}{dx^2} = \frac{d^2 S(x_i)}{dx^2}$$

Continuity of first derivatives at interior node points:

$$\mathbf{F}M = \mathbf{G}y \quad (n \times n \text{ matrices})$$

S(x) = piecewise continuous cubic polynomial

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Connection to second order differential eigenvalue equations --

Consider a differential eigenvalue problem; $A(x), B(x), V(x)$ are known:

$$A(x)\frac{d^2 y}{dx^2} + B(x)\frac{dy}{dx} + V(x)y = \varepsilon y \qquad \text{need to find } y(x) \text{ and } \varepsilon$$

1. **Discretize** $x \rightarrow x_i$ $y_i = y(x_i)$
2. **Represent** *y(x)* **in terms of a cubic spline interpolation**
3. **Use the spline relations for first and second derivatives and the relation F***M***=G***y* **so that the differential eigenvalue equation on the nodes becomes a linear algebraic eigenvalue problem.** $$\Lambda y = \varepsilon y$$

➔**In practice, only a few eigenvalues/vectors are needed in each self-consistency iteration; more efficient than Hartree's numerical methods.**
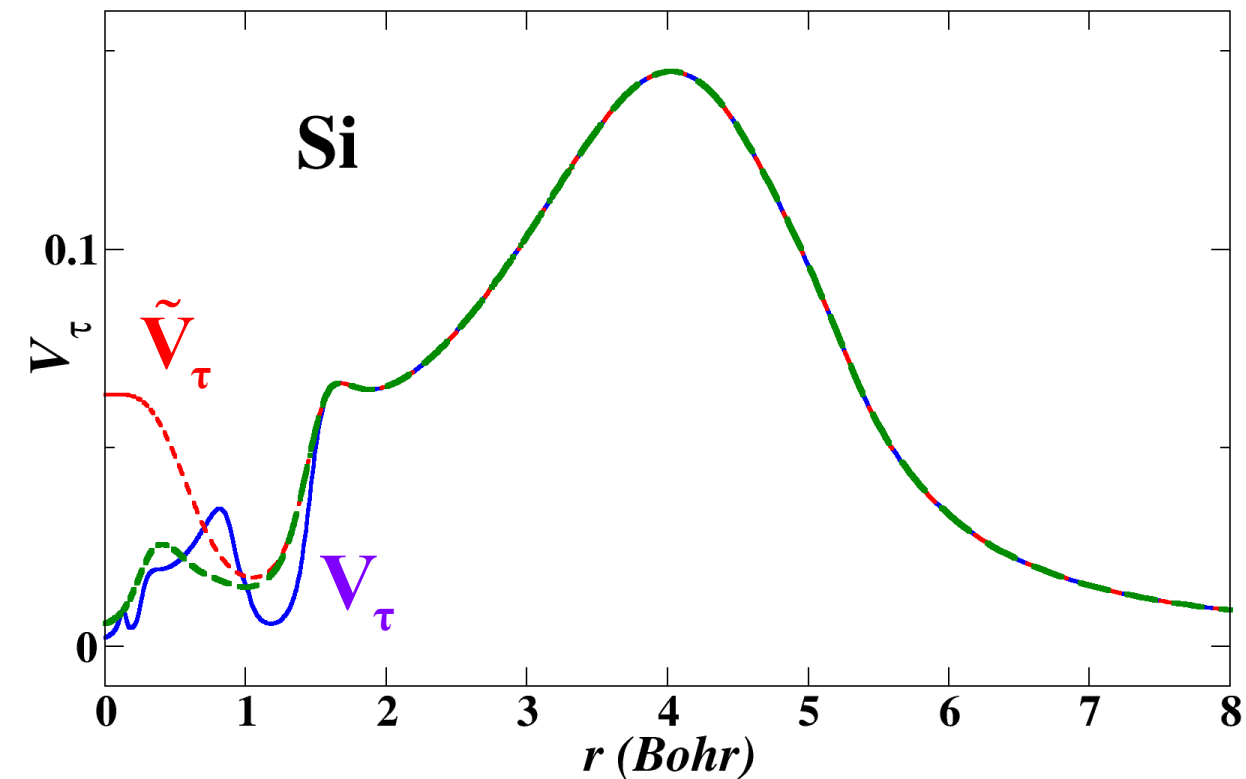
Pseudization schemes

Full GKS equations: $H(\mathbf{r})\Phi(\mathbf{r}) = \left(-\dfrac{\hbar^2}{2m}\left(\nabla^2 + \nabla \cdot \left(V_\tau(\mathbf{r})\nabla \right) \right) + V_{\text{eff}}(\mathbf{r}) \right)\Phi(\mathbf{r}) = \varepsilon\Phi(\mathbf{r})$

Pseudized equations: $\tilde{H}(\mathbf{r})\tilde{\Phi}(\mathbf{r}) = \left(-\dfrac{\hbar^2}{2m}\left(\nabla^2 + \nabla \cdot \left(\tilde{V}_\tau(\mathbf{r})\nabla \right) \right) + \tilde{V}_{\text{eff}}(\mathbf{r}) \right)\tilde{\Phi}(\mathbf{r}) = \varepsilon\tilde{\Phi}(\mathbf{r})$
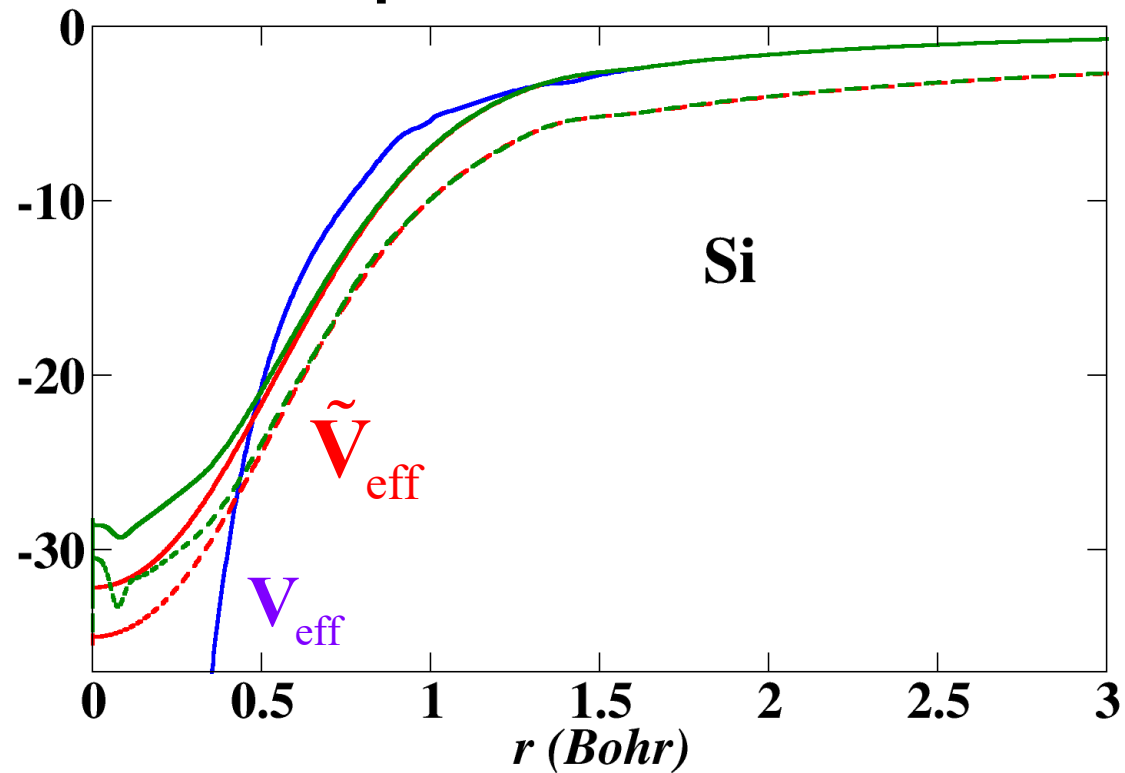
Constraint: $\quad \tilde{H}(\mathbf{r}) = H(\mathbf{r}) \quad$ for $\; r \geq r_c$

For the exchange-correlation terms, this can be accomplished by replacing the full electron density $n(\mathbf{r})$ and full kinetic energy density $\tau(\mathbf{r})$ by smooth analogs $\tilde{n}(\mathbf{r})$ and $\tilde{\tau}(\mathbf{r})$ in the range $r \leq r_c$.
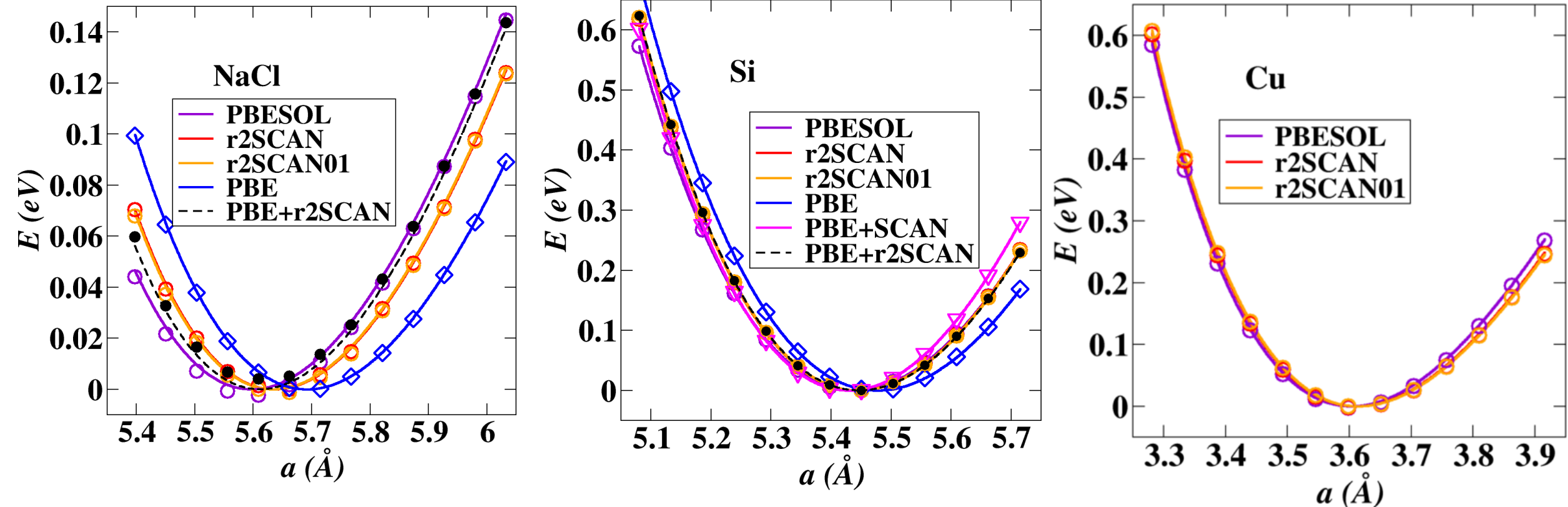
Example pseudization of kinetic potential

Example pseudization of effective potential

(dashed lines represent unscreened potentials)

Some binding energy curves obtained using ABINIT with PAW datasets

Detailed convergence studies needed before making definitive conclusions.

Summary and conclusions –

- r2SCAN exchange-correlation functional developed by Furness et al. (2020) appears be a useful addition to the library of DFT possibilities; looking forward to further analyses and simulations

- Splinesolver algorithm is a promising general purpose method for efficient evaluation of second order differential eigenvalue equations, with or without first order derivative contributions, particularly useful for self-consistent iterations

- From the all-electron atomic solutions, PAW pseudization schemes for use in the generalized Kohn-Sham equations are fairly straight forward and implemented ATOMPAW code. Further optimization and convergence studies are needed.

Thank you for your attention