




PAW datasets for meta-GGA calculations

Natalie Holzwarth – Wake Forest University, Winston-Salem NC USA
natalie@wfu.edu

PHYSICAL REVIEW B **105**, 125144 (2022)

Cubic spline solver for generalized density functional treatments of atoms and generation of atomic datasets for use with exchange-correlation functionals including meta-GGA

N. A. W. Holzwarth ¹, Marc Torrent ², Jean-Baptiste Charraud,² and Michel Côté ³

¹*Department of Physics, Wake Forest University, Winston-Salem, North Carolina 27109, USA*

²*CEA, DAM, DIF, F91297 Arpajon, and Université Paris-Saclay, CEA, Laboratoire Matière en Conditions Extrêmes, 91680 Bruyères-le-Châtel, France*

Acknowledgements: NSF Grant DMR-224295 and WFU High Performance Computing Facility; Collaboration with Marc Torrent and with Michel Côté (and their students)

Topics for discussion

- Motivation for meta-GGA
- Numerical challenges of SCAN and R2SCAN
- PAW datasets for R2SCAN
- Do we need them or can we “cheat” and just use PAW datasets for other exchange-correlation functionals?
- Do the PAW and norm-conserving formalisms behave in the same way in this regard?

ATOMPAW

INFO

DATASETS

CONTRIBUTERS

CONTACT INFO

NAWH Web

PHYSICS Web

WFU Web

ATOMPAW

Download source code and example files:

- [atompaw-4.2.0.3.tar.gz](#) (5.6mb) 06/09/2023 Corrections introduced by Marc Torrent for improving backward compatibility with JTH LDA and GGA datasets. Additions introduced by Josef Zwanziger to calculate Lamb shift. Corrections introduced by Natalie Holzwarth for improving some metaGGA analysis with [libxc software database \(with version 6.2.0\)](#).
- [atompaw-4.2.0.2.tar.gz](#) (5.6mb) 10/17/2022 Updated version of pwscfinterface.F90 in consultation with Quantum Espresso developers (thanks to Iurii Timrov) for compatibility with QE-7.1. Marc Torrent added improvements to the compilation system and updated the libxc interface subroutines.
- [atompaw-4.2.0.1.tar.gz](#) (5.7mb) 5/26/2022 Minor corrections including compatibility with intel compiler (thanks to Josef Zwanziger) and some adjustments to the all-electron self-consistency.

In collaboration with François Jollet and Marc Torrent since ~ 2000

Motivation and brief history –

- ❑ **As density functional theory develops, new exchange correlation functionals are frequently proposed and, thanks to Libxc (Marques et al. *Comp. Phys. Comm.* 183, 2272 (2012), Lehtola et al. *Software X* 7, 1 (2018)), they can be incorporated into various codes.**
- ❑ **The meta-GGA functional form adds the kinetic energy density into the functional; considerable improvements in DFT prediction of materials properties has been reported within the context of “generalized” DFT (Yang et al. *PRB* 93, 205205 (2016))**
- ❑ **“SCAN” form of meta-GGA -- “Strongly Constrained and Appropriately Normed Semilocal Density Functional” (Sun et al. *PRL* 115, 036402 (2015)) demonstrates improved materials prediction for a variety of systems; ~2300 citations as of June 2400.**

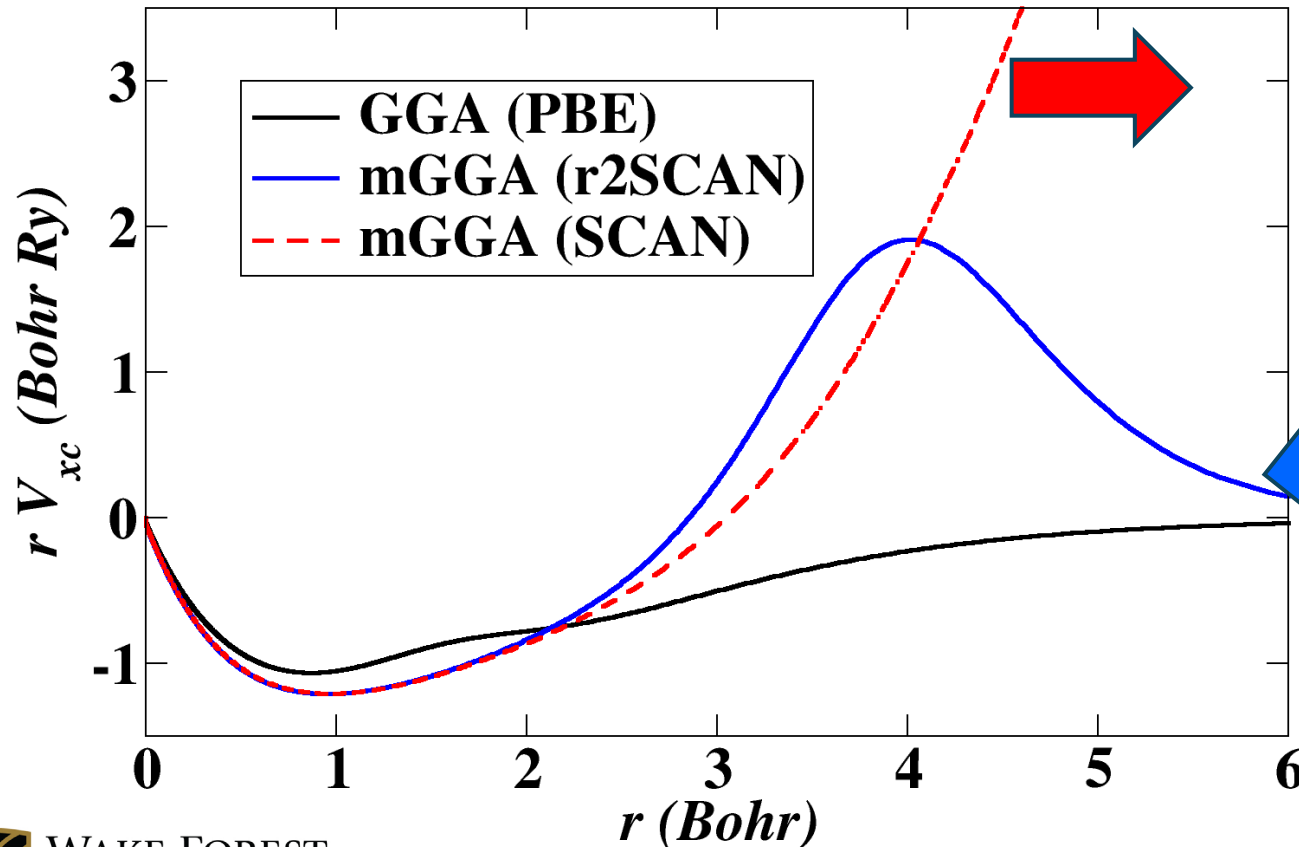
Motivation and brief history – continued –

- ❑ However, most of the SCAN results were obtained using codes with localized basis sets or VASP which appears to use a special form of SCAN functional.
- ❑ Several authors reported numerical difficulties in using plane wave codes with the SCAN functional (Yao et al. JCP 146, 224105 (2017), Bartók et al. JCP 150, 161101 (2019) & rSCAN)
- ❑ We found that the exchange-correlation potentials for the SCAN form analytically diverges in regions of space where the radial wavefunction decreases exponentially.
- ❑ A revised functional was introduced by the Tulane and Temple groups (“Accurate and Numerically Efficient r2SCAN Meta-Generalized Gradient Approximation”, Furness et al., J. Phys. Chem. Lett 11, 8208 (2020)); ~400 citations as of June 2024.

Functional form of $V_{xc}(r)$ for textbook model of He atom thanks to L. Schiff, Quantum Mechanics (1955)

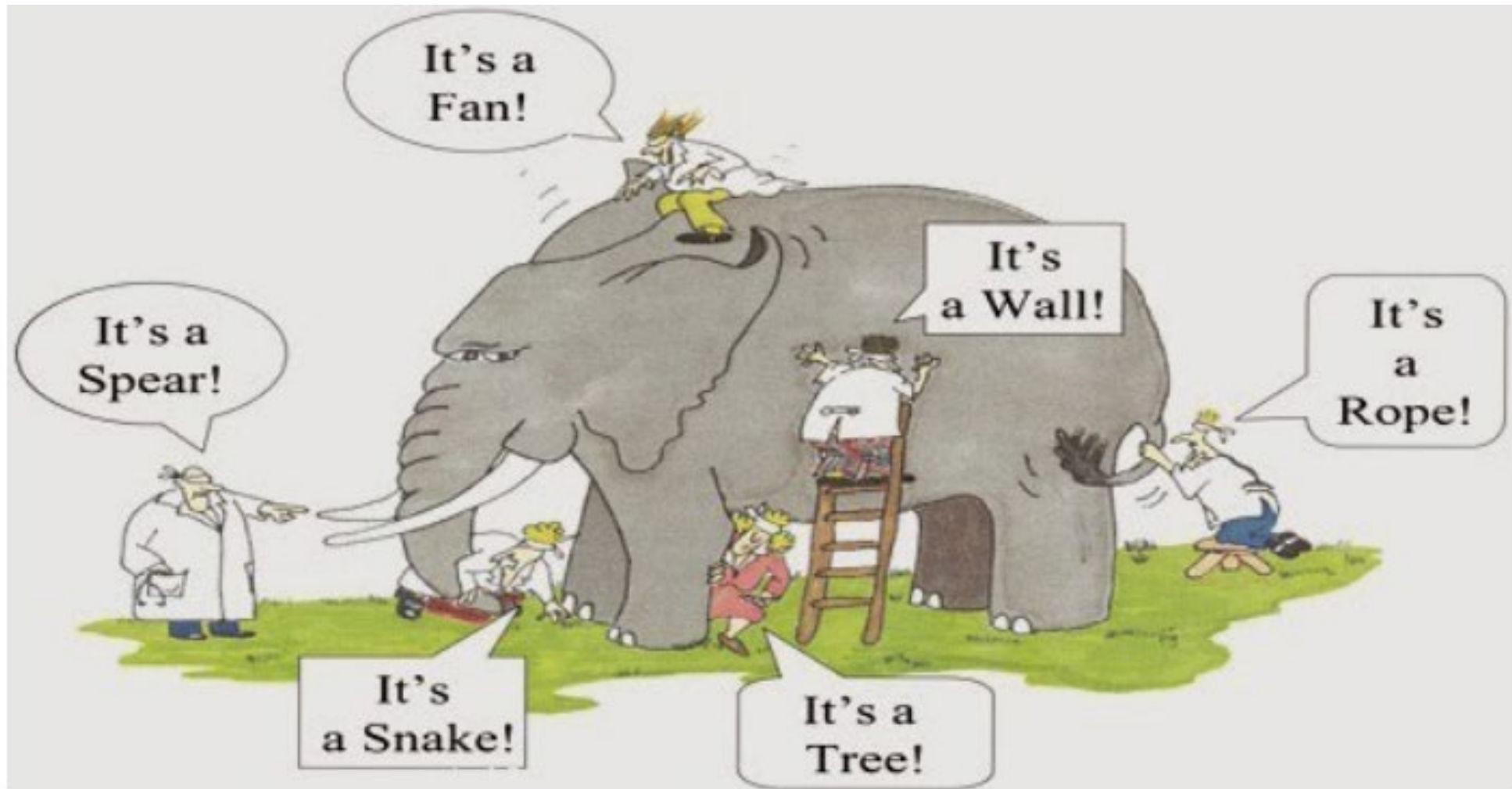
$$n(r) = \frac{2A^3}{\pi} e^{-2Ar} \quad A = \frac{27}{16} \text{ Bohr}^{-1}$$

$$\tau(r) = \frac{\hbar^2}{2m} A^2 \left(\frac{2A^3}{\pi} e^{-2Ar} \right)$$



Unphysical behavior of $V_{xc}(r)$ for SCAN discouraged further development.

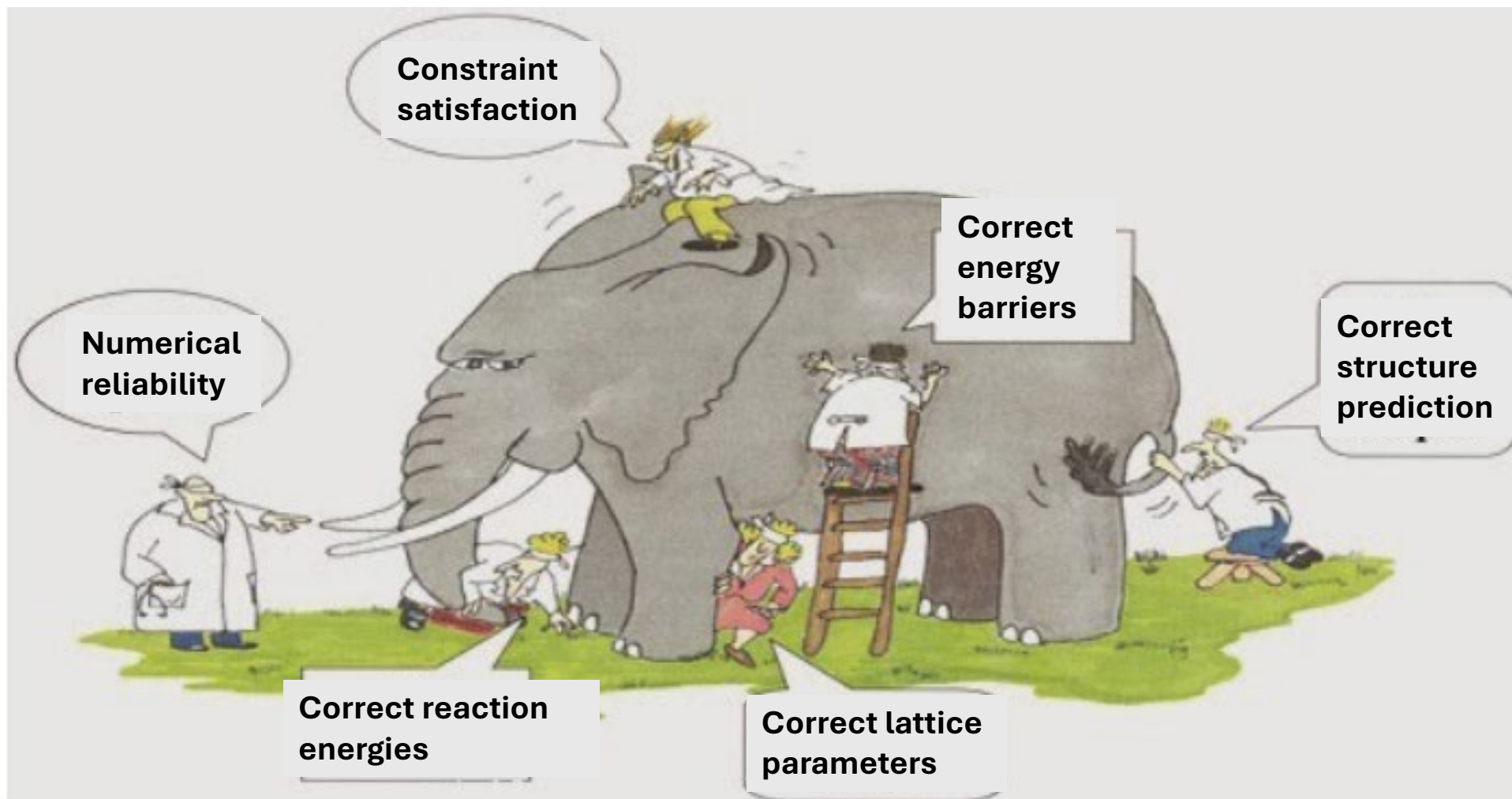
Better behavior of $V_{xc}(r)$ for r2SCAN allowed for resumption of project.



<https://medium.com/betterism/the-blind-men-and-the-elephant-596ec8a72a7d>

The Blind Men and the Elephant

Adapted story – elephant \leftrightarrow DFT theory & computation



Condensed matter scientists and the ideal exchange-correlation functional

Systematic equations --

General form of the exchange-correlation functional:

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

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

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

The generalized Kohn-Sham equations take the form

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

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

dimensionless “kinetic potential”

$$V_{xc}(\mathbf{r}) = \frac{\partial f_{xc}}{\partial n} - \nabla \cdot \left(2 \frac{\partial f_{xc}}{\partial \sigma} \nabla n \right) + \nabla^2 \left(\frac{\partial f_{xc}}{\partial (\nabla^2 n)} \right)$$

Some details for a spherical atom --

$$\Phi_i(\mathbf{r}) = \frac{\varphi_{n_i l_i}(r)}{r} Y_{l_i m_i}(\hat{\mathbf{r}})$$

occupancy for state $n_i l_i$

$$n(r) = \frac{1}{4\pi r^2} \sum_{n_i l_i} w_{n_i l_i} |\varphi_{n_i l_i}(r)|^2 \quad \tau(r) = \frac{\hbar^2}{2m} \frac{1}{4\pi r^2} \sum_{n_i l_i} w_{n_i l_i} \tau_{n_i l_i}(r)$$

$$\tau_{n_i l_i}(r) = \left(\frac{d\varphi_{n_i l_i}(r)}{dr} - \frac{\varphi_{n_i l_i}(r)}{r} \right)^2 + l_i(l_i + 1) \left(\frac{\varphi_{n_i l_i}(r)}{r} \right)^2$$

Self-consistent generalized Kohn-Sham equations:

$$\left(H(r) - \epsilon_{n_i l_i} \right) \varphi_{n_i l_i}(r) = 0$$

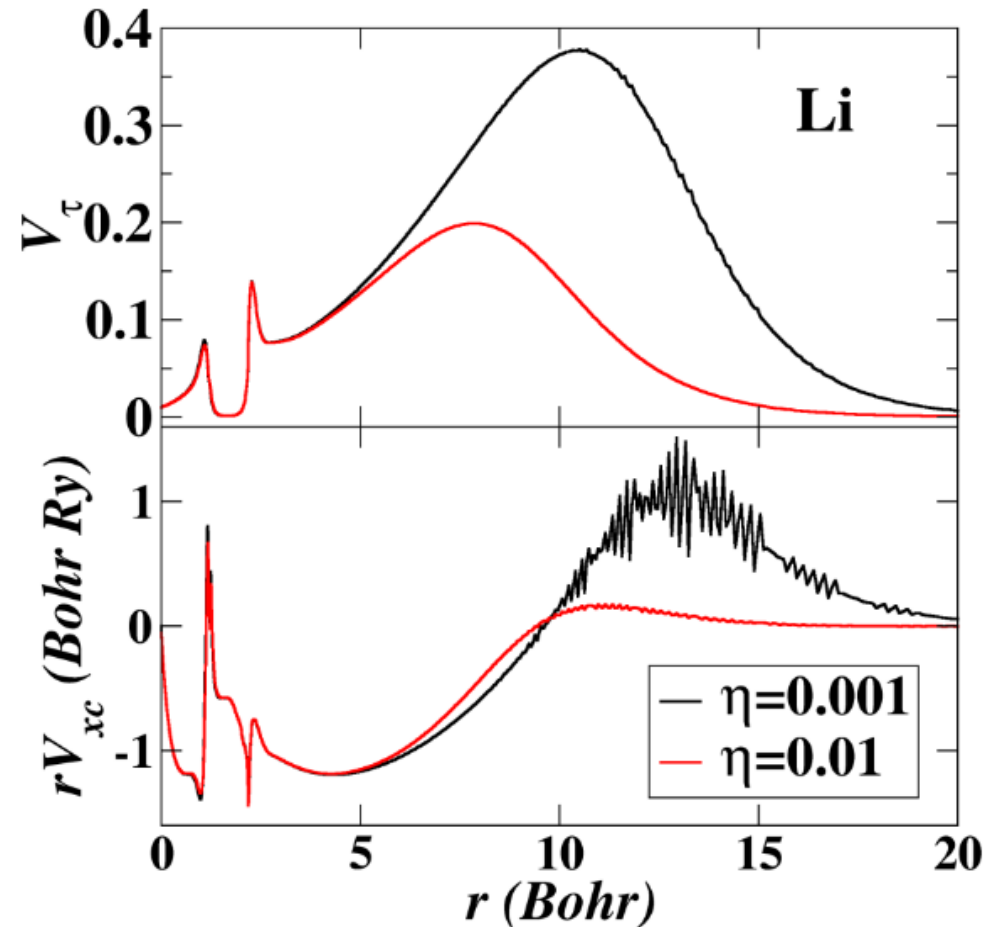
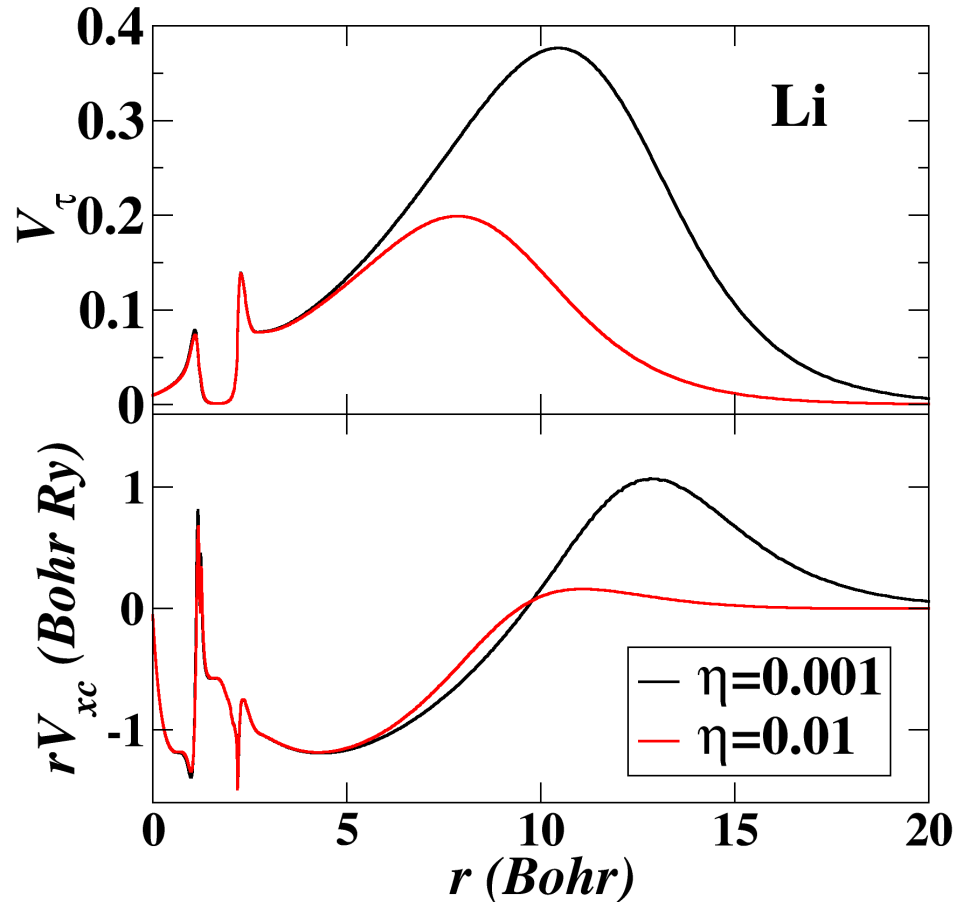
$$H(r) = -\frac{\hbar^2}{2m} \left(\left(1 + V_\tau \right) \left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right) + \frac{dV_\tau}{dr} \left(\frac{d}{dr} - \frac{1}{r} \right) \right) + V_{\text{eff}}(r)$$

Some details regarding functional forms associated with kinetic energy density $\tau(r)$

$$\bar{\alpha} \equiv \frac{\tau - \tau_W}{\tau_{\text{unif}} + \eta \tau_W} \quad \text{where} \quad \tau_W = \frac{|\nabla n|^2}{8n}$$

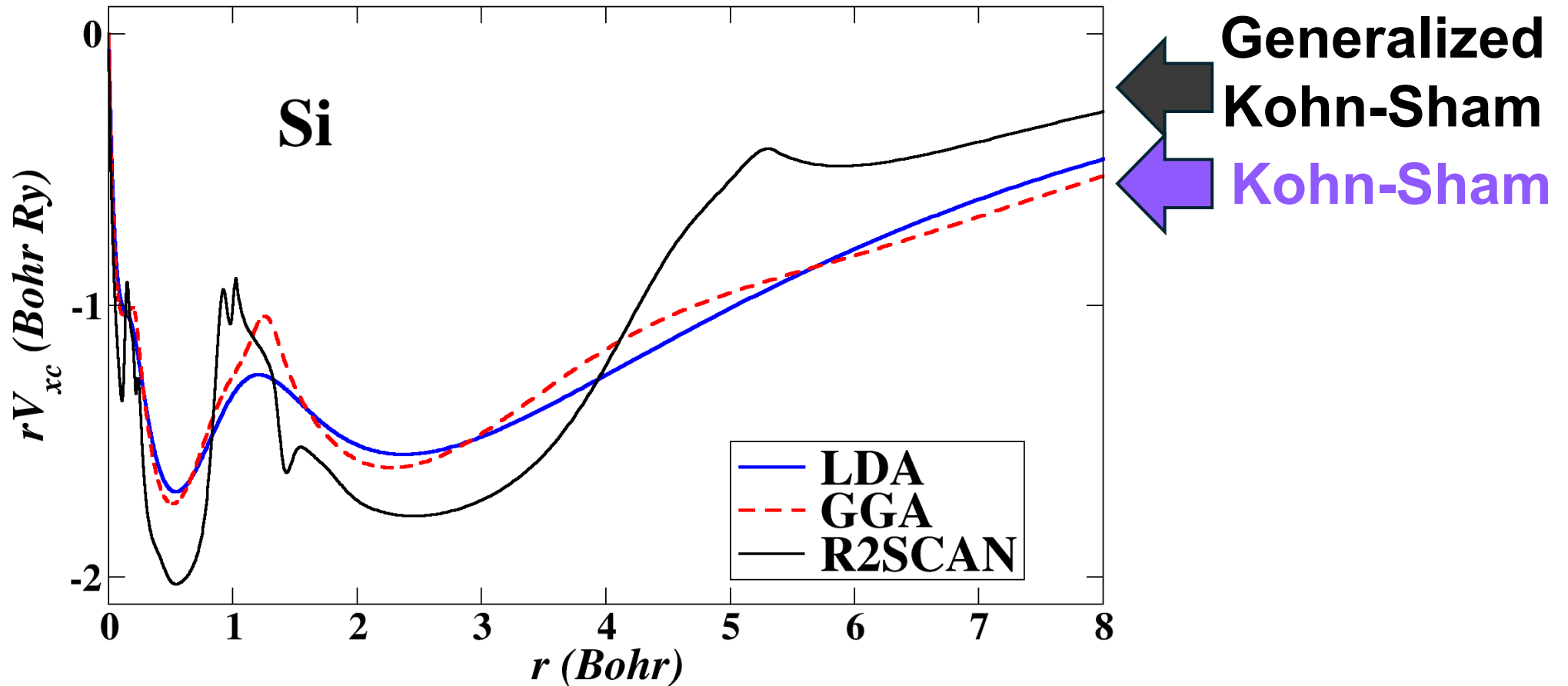
$$\tau_{\text{unif}} = \frac{3n}{10} (3\pi^2 n)^{2/3}$$

Original r2SCAN $\eta=0.001$
r2SCAN01 $\eta=0.01$

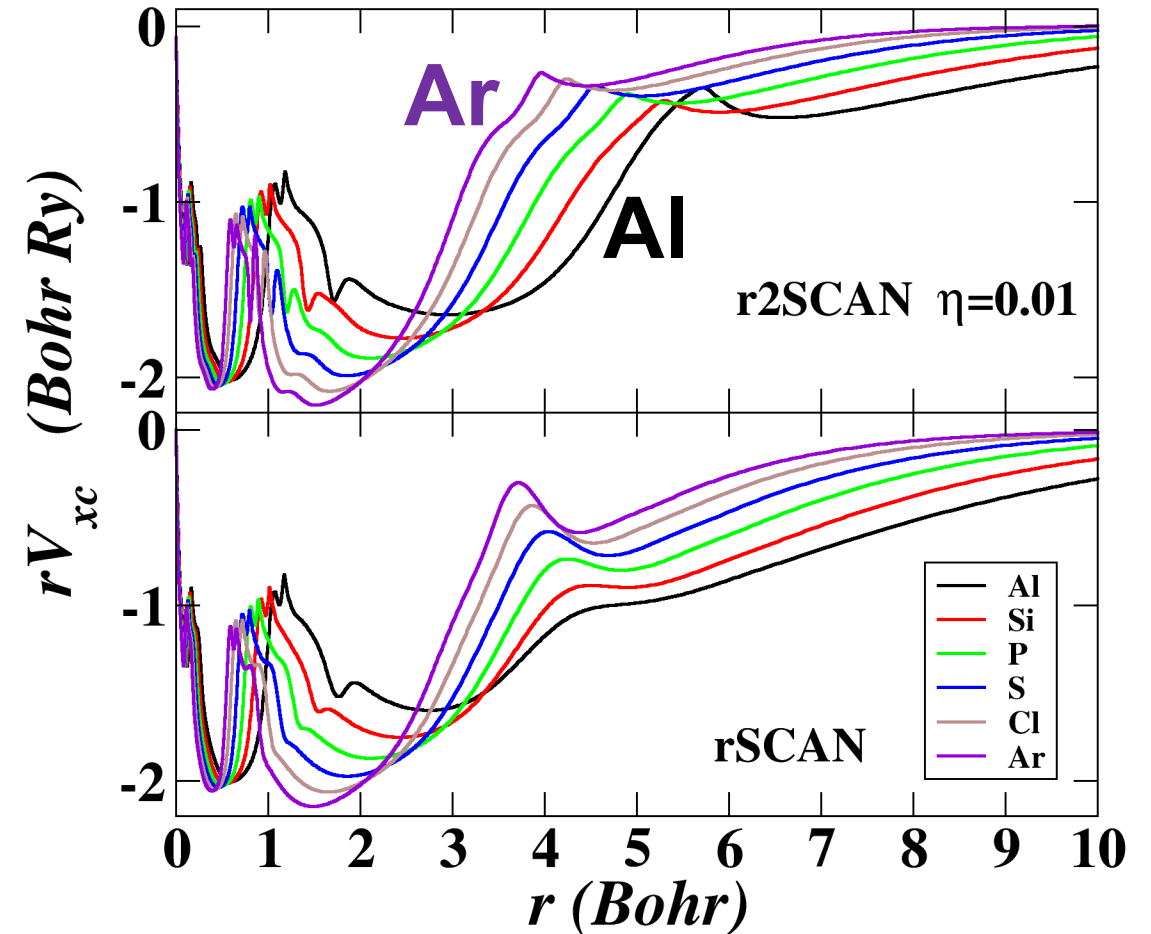
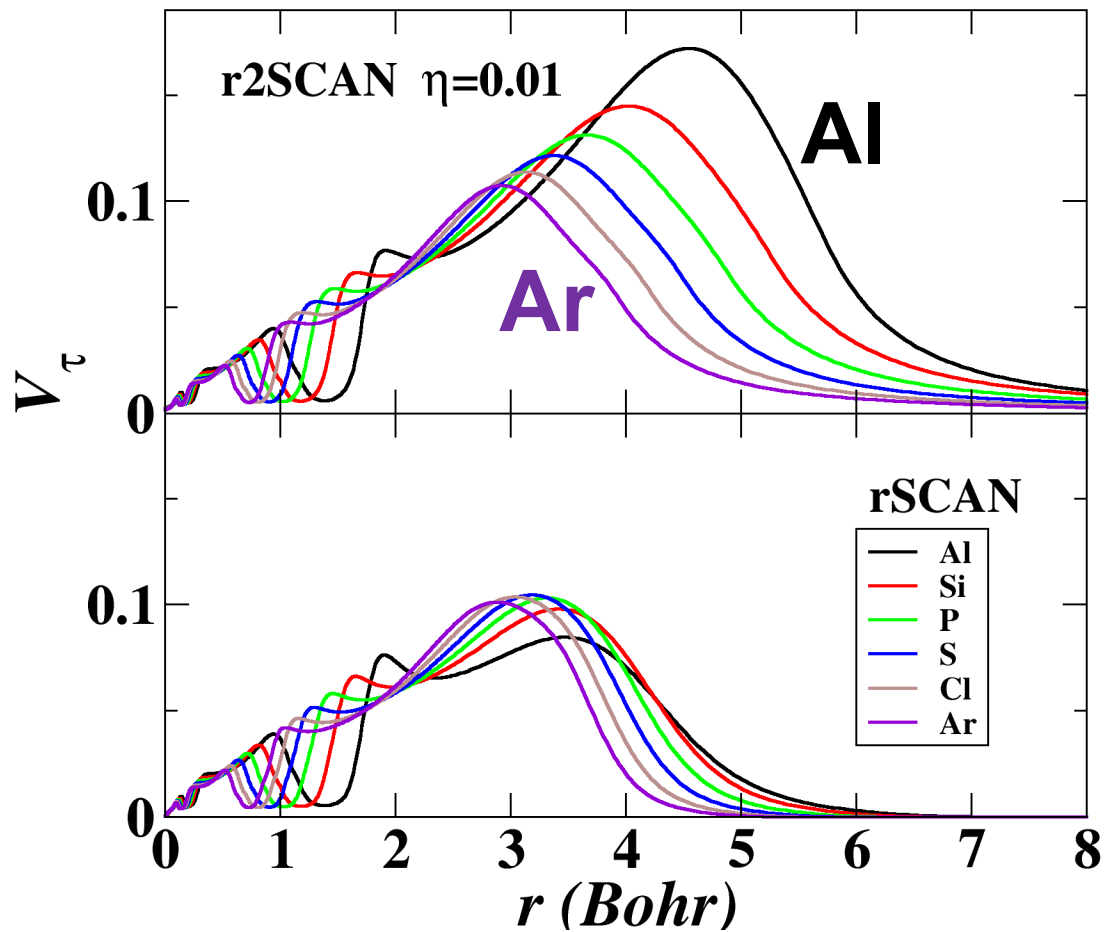


**Instability for
a coarser
mesh.**

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



Numerical methods for converging self-consistent equations

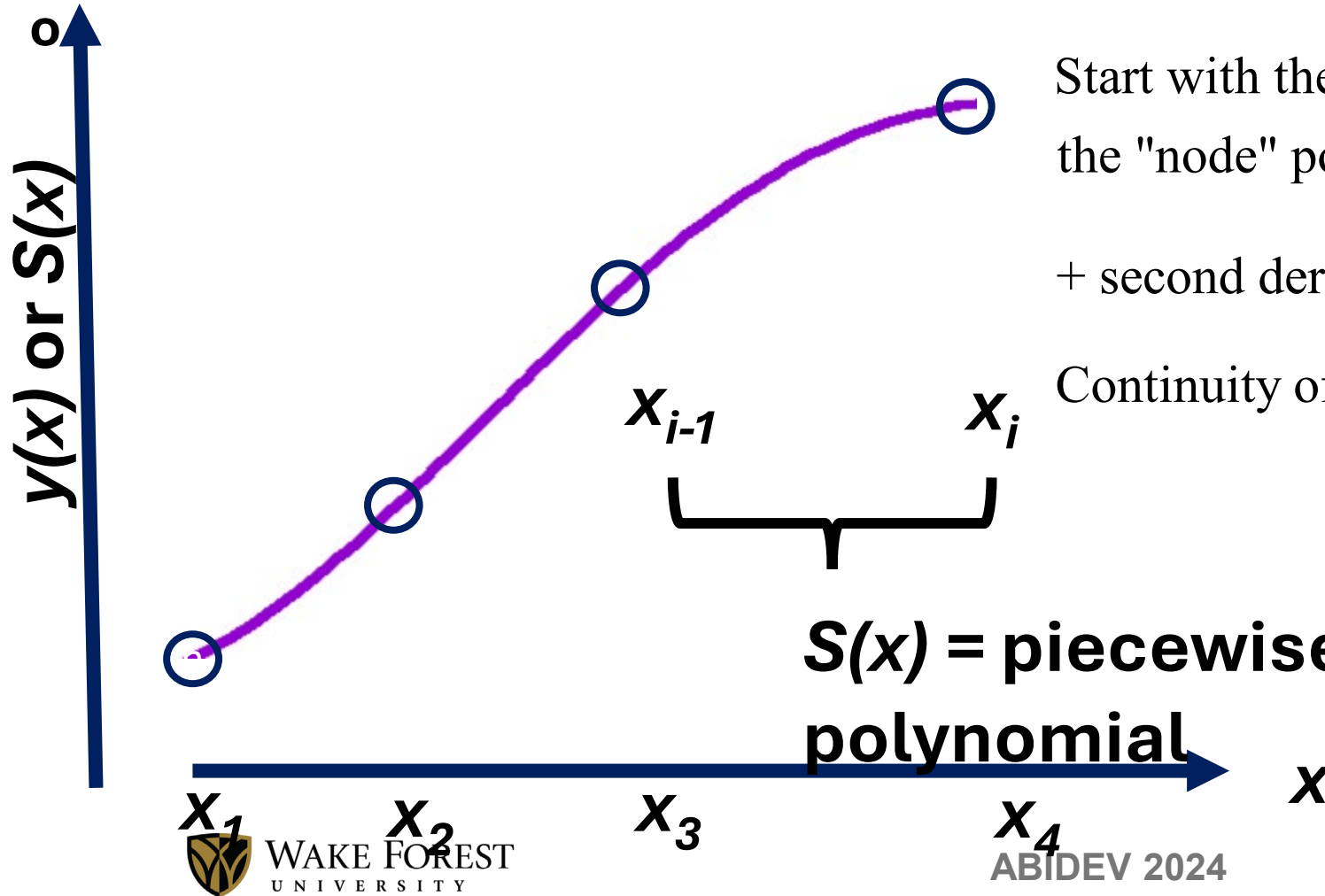
$$H(r) = -\frac{\hbar^2}{2m} \left((1 + V_\tau) \left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right) + \frac{dV_\tau}{dr} \left(\frac{d}{dr} - \frac{1}{r} \right) \right) + V_{\text{eff}}(r)$$

$$\left(H(r) - \epsilon_{n_i l_i} \right) \varphi_{n_i l_i}(r) = 0$$

- Finite difference methods tend to generate instabilities
- Developed a cubic spline scheme that seems to work better.

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



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:

$$\mathbf{FM} = \mathbf{Gy} \quad (n \times n \text{ matrices})$$

S(x) = piecewise continuous cubic polynomial

Spline interpolation between the node points $x_{i-1} \leq x \leq x_i$:

For $h_i \equiv x_i - x_{i-1}$: $S''(x) = M_{i-1} \frac{x_i - x}{h_i} + M_i \frac{x - x_{i-1}}{h_i}$

$$S'(x) = -M_{i-1} \frac{(x_i - x)^2}{2h_i} + M_i \frac{(x - x_{i-1})^2}{2h_i} + \frac{y_i - y_{i-1}}{h_i} - \frac{(M_i - M_{i-1})h_i}{6}$$

$$S(x) = M_{i-1} \frac{(x_i - x)^3}{6h_i} + M_i \frac{(x - x_{i-1})^3}{6h_i} + \left(y_{i-1} - \frac{M_{i-1}h_i^2}{6} \right) \frac{x_i - x}{h_i} + \left(y_i - \frac{M_i h_i^2}{6} \right) \frac{x - x_{i-1}}{h_i}$$

Note that automatically $S''(x_i) = M_i$ and $S(x_i) = y_i$

Ensure first derivative continuity at each interior node point:

$$\frac{h_i}{h_{i+1} + h_i} M_{i-1} + 2M_i + \frac{h_{i+1}}{h_{i+1} + h_i} M_{i+1} = \frac{6}{h_{i+1} + h_i} \left(\frac{y_{i+1} - y_i}{h_{i+1}} - \frac{y_i - y_{i-1}}{h_i} \right) \rightarrow \text{Matrix form: } \mathbf{FM} = \mathbf{Gy}$$

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

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

- 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 $FM = Gy$ so that the differential eigenvalue equation on the nodes becomes a linear algebraic eigenvalue problem.**

$$\Lambda y = \varepsilon y$$

Some details

$$A(x) \frac{d^2 y}{dx^2} + B(x) \frac{dy}{dx} + V(x)y = \varepsilon y$$

Note that $\frac{d^2 y_i}{dx^2} = M_i$

$$\frac{dy_i}{dx} = \frac{y_{i+1} - y_i}{h_{i+1}} - \frac{M_{i+1} + 2M_i}{6} h_{i+1}$$

and $\mathbf{FM} = \mathbf{G}y$

For $B(x) \equiv 0$:

$$\mathbf{\Lambda} = A(x_i) (\mathbf{F}^{-1} \mathbf{G}) + V(x_i)$$

For $B(x) \neq 0$,

$\mathbf{\Lambda}$ is more complicated.

All evaluations are at the n interior node points.

\Rightarrow Differential equation becomes $\mathbf{\Lambda}y = \varepsilon y$ **$\leftarrow n \times n$ matrix eigenvalue equation**


More details

Radial mesh -- $r(x) = a_0 (e^x - 1)$

discretization -- $x = ih$ for $i = 1, 2, \dots, n$; $i = 0$ is treated specially

$$r(x) = a_0 (e^x - 1) \qquad y(x) = e^{-x/2} \phi(r(x))$$

By design, $y(x = 0) = 0$ and $y(x = x_{n+1}) = 0$

For $0 \leq x \leq x_1$, $y(x) = Cx^{l+1}$  **This behavior alters the first row of F and G matrices**

Linear eigenvalue problem: $\Lambda y = \varepsilon y$

From eigenvectors y_i , $\phi(r(x))$ is determined by interpolation. Only the first few eigenvalues/vectors are needed for the self-consistency iterations. Often found to be more efficient than methods based on finite differences.

Pseudization schemes

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

$$\text{Pseudized equations: } \tilde{H}(\mathbf{r})\tilde{\Phi}(\mathbf{r}) = \left(-\frac{\hbar^2}{2m} \left(\nabla^2 + \nabla \cdot (\tilde{V}_\tau(\mathbf{r})\nabla) \right) + \tilde{V}_{\text{eff}}(\mathbf{r}) \right) \tilde{\Phi}(\mathbf{r}) = \varepsilon\tilde{\Phi}(\mathbf{r})$$

$$\text{Constraint: } \tilde{H}(\mathbf{r}) = H(\mathbf{r}) \quad \text{for } r \geq r_c$$

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 $r \leq r_c$.

Construction of PAW datasets

Frozen core approximation:

All electron treatment

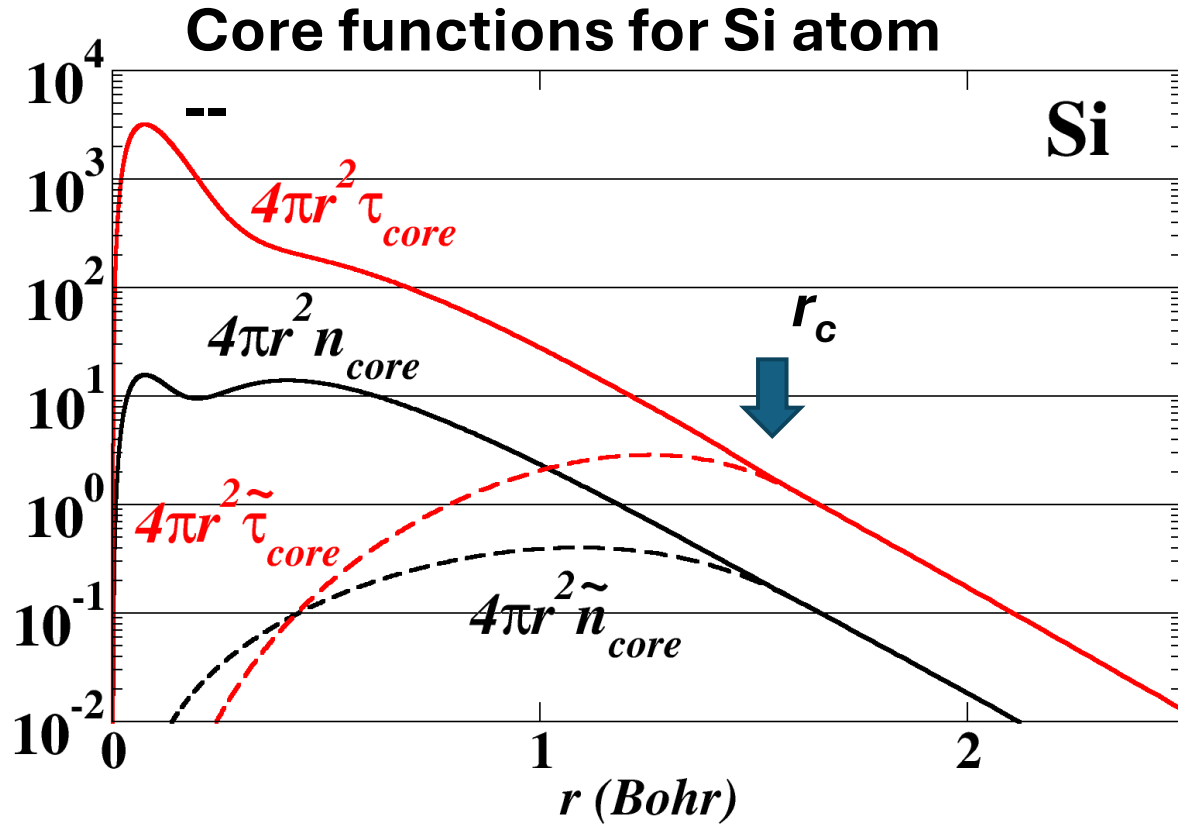
$$n_{core}(r) + n_{vale}(r)$$

$$\tau_{core}(r) + \tau_{vale}(r)$$

Pseudo electron treatment

$$\tilde{n}_{core}(r) + \tilde{n}_{vale}(r)$$

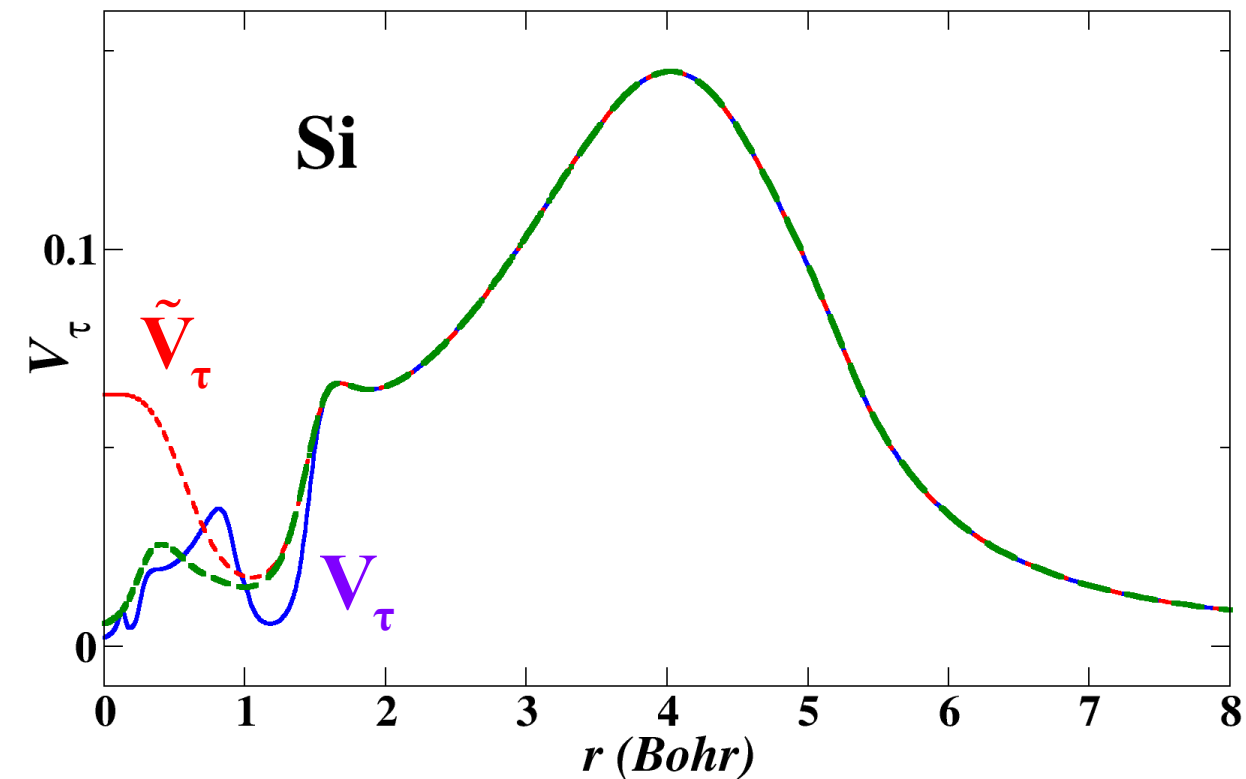
$$\tilde{\tau}_{core}(r) + \tilde{\tau}_{vale}(r)$$



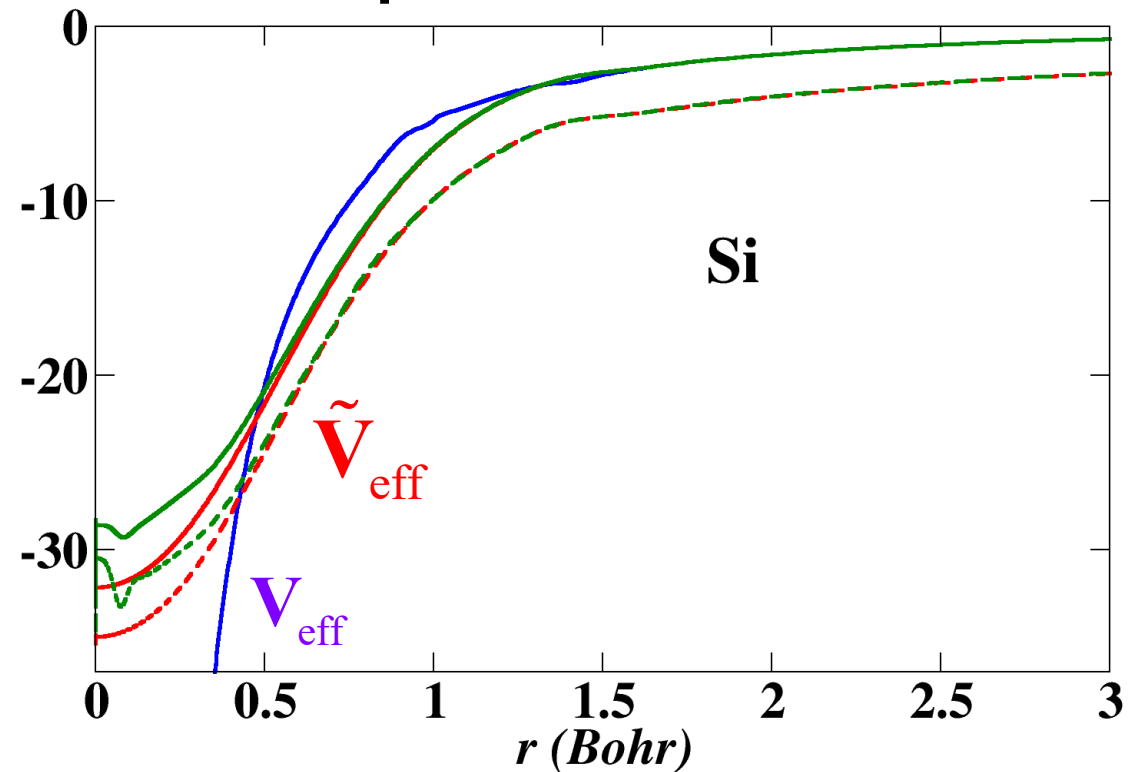
Note:

- For Coulombic (Hartree terms) the core is included in the local pseudopotential
- For $V_{xc}(r)$, the non-linear core corrections are important

Example pseudization of kinetic potential



Example pseudization of effective potential



(dashed lines represent unscreened potentials)

Atompaw input files for C

LDA

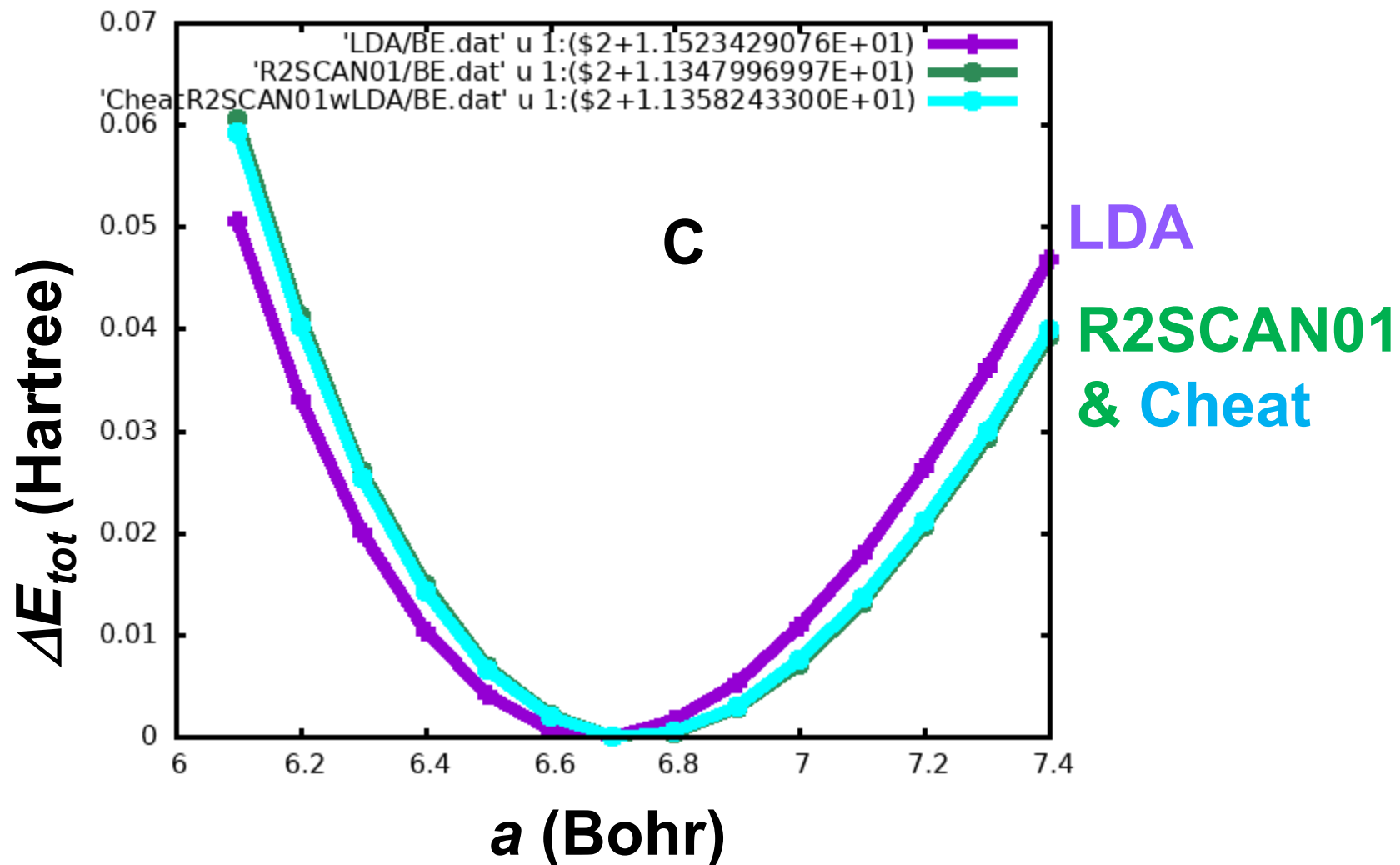
```
C 6
XC_LDA_X+XC_LDA_C_PW loggrid 2001
2 2 0 0 0
2 1 2
0 0 0
c
v
v
1
1.3 1.1 1.3 1.0
y
16
n
y
12
n
MODRRKJ VANDERBILTORTHO BESSELSHAPE
2 0 MTROULLIER
1.3
1.3
1.3
1.3
ABINITOUT
default
XMLOUT
default
```

R2SCAN01

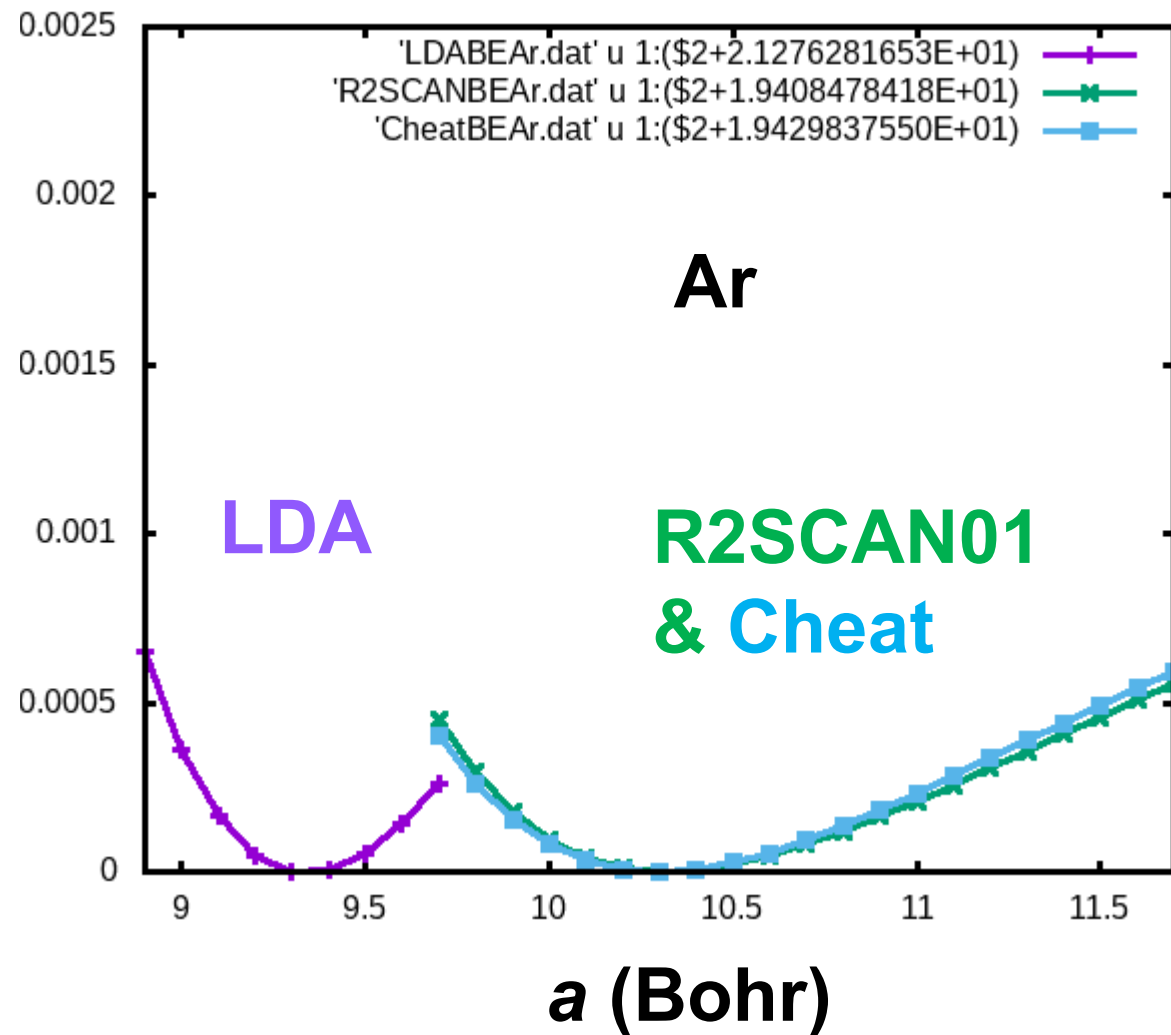
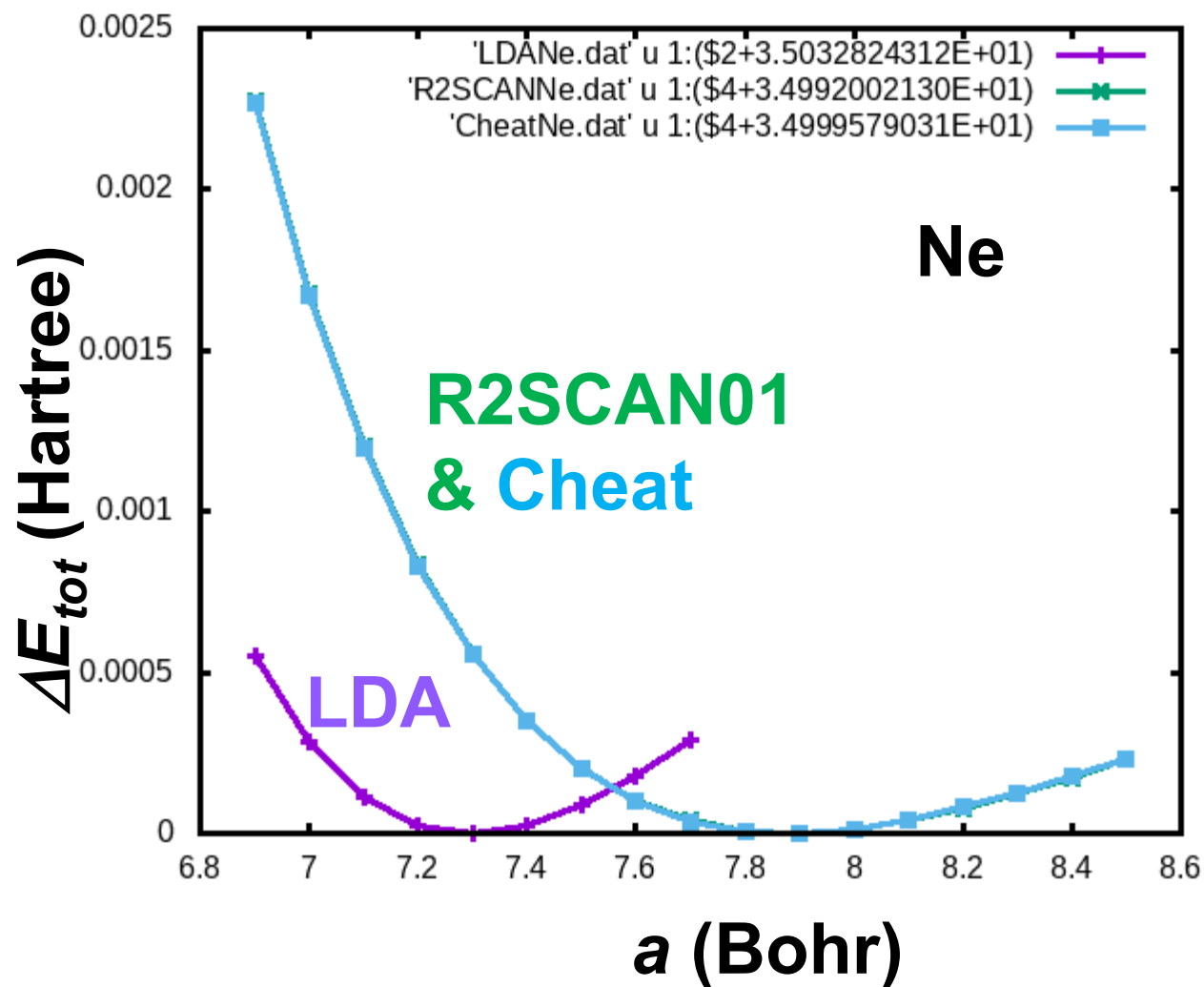
```
C 6
WTAU XC_MGGA_X_R2SCAN01+XC_MGGA_C_R2SCAN01 splr00.1d0 splns600 loggrid 2001
2 2 0 0 0
2 1 2
0 0 0
c
v
v
1
1.3 1.1 1.3 1.0
y
16
n
y
12
n
MODRRKJ VANDERBILTORTHO BESSELSHAPE
2 0 MTROULLIER
1.3
1.3
1.3
1.3
ABINITOUT
default
XMLOUT
default
```

→WTAU XC_MGGA_X_R2SCAN01+XC_MGGA_C_R2SCAN01 splr00.1d0 splns600 loggrid 2001

Example – binding energy curve for C (diamond)



Example: Binding energy curves for Ne and Ar (fcc)



Outlook

- Atompaw version 4.2.0.5 is currently being debugged (minor updates and bug fixes to 4.2.0.3)**
- More testing needs to be done.**
- It would be nice to know how/why the cheating method works so well. Is it something about PAW or do NC datasets also have this property?**
- Should we try to develop R2SCAN01 datasets for elements across the periodic table or not?**
- Testing datasets on other compatible codes such as Quantum Espresso?**

Thank you!