

# Progress on self-consistent meta-gga PAW datasets from ATOMPAW



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## **Outline**

- 1. Motivation and brief history**
- 2. Numerical issues associated with SCAN functional**
- 3. Self-consistent atomic solver and results for r2SCAN**
- 4. Pseudopotential construction methods for meta-GGA and results for r2SCAN**
- 5. Summary and outlook**

## To do list

- Develop a self-consistent all electron atomic solver for the generalized Kohn-Sham equations needed to evaluate exchange-correlation functionals having the meta-GGA form.**
  
- Adapt pseudization schemes for basis and projector functions for use in the generalized Kohn-Sham formalism.**
  
- Test and evaluate.**

## 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; >950 citations as of 5/2021.

## 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 effective 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)).

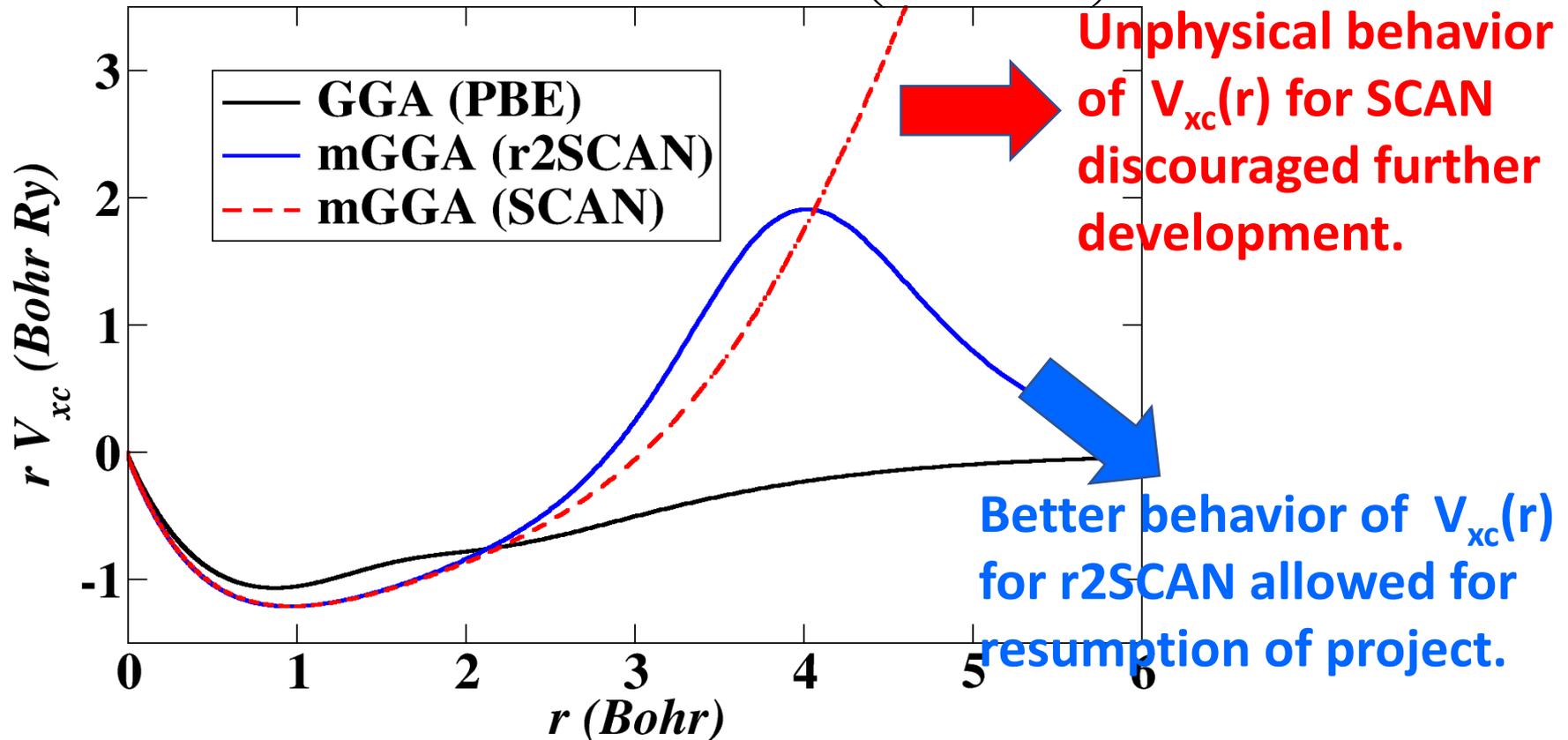
# Functional form of $V_{xc}(r)$ for textbook model of He atom

thanks to L. Schiff,  
Quantum Mechanics  
(1955)

$$n(r) = \frac{2A^3}{\pi} e^{-2Ar}$$

$$A = \frac{27}{16} \text{ Bohr}^{-1}$$

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



With the introduction of the r2SCAN functional,  
work on developing a self-consistent atomic solver for meta-GGA  
formalism resumed.

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

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

**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 for spherical atom

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

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

occupancy for state  $n_i l_i$

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

Self-consistent generalized Kohn-Sham equations:

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

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

# Differential equations to solve numerically

Method 1: Coupled first order equations --

$$\frac{dy_1(r)}{dr} = z_{12}(r)y_2(r) \quad \frac{dy_2(r)}{dr} = z_{21}(r)y_1(r)$$



in **ATOMPAW**

with  $y_1(r) = \varphi_{nl}(r)$        $y_2(r) = (1 + V_\tau(r)) \frac{d\varphi_{nl}(r)}{dr}$

$$z_{12}(r) = \frac{1}{(1 + V_\tau(r))} \quad z_{21}(r) = (1 + V_\tau(r)) \frac{l(l+1)}{r^2} + \frac{dV_\tau(r)}{dr} \frac{1}{r} + \frac{2m}{\hbar^2} (V_{\text{eff}}(r) - \epsilon_{nl})$$

Method 2: Transformed second order equation --

Let  $\varphi_{nl}(r) = \frac{y_{nl}(r)}{\sqrt{1 + V_\tau(r)}} \equiv y_{nl}(r)e^{x(r)}$  where  $x(r) = -\frac{1}{2} \ln(1 + V_\tau(r))$

$$\frac{d^2 y_{nl}(r)}{dr^2} + \left( \frac{d^2 x(r)}{dr^2} + \frac{2}{r} \frac{dx(r)}{dr} - \left( \frac{dx(r)}{dr} \right)^2 - \frac{l(l+1)}{r^2} - \frac{2m}{\hbar^2} \left( \frac{V_{\text{eff}}(r) - \epsilon_{nl}}{1 + V_\tau(r)} \right) \right) y_{nl}(r) = 0$$

## Some further details –

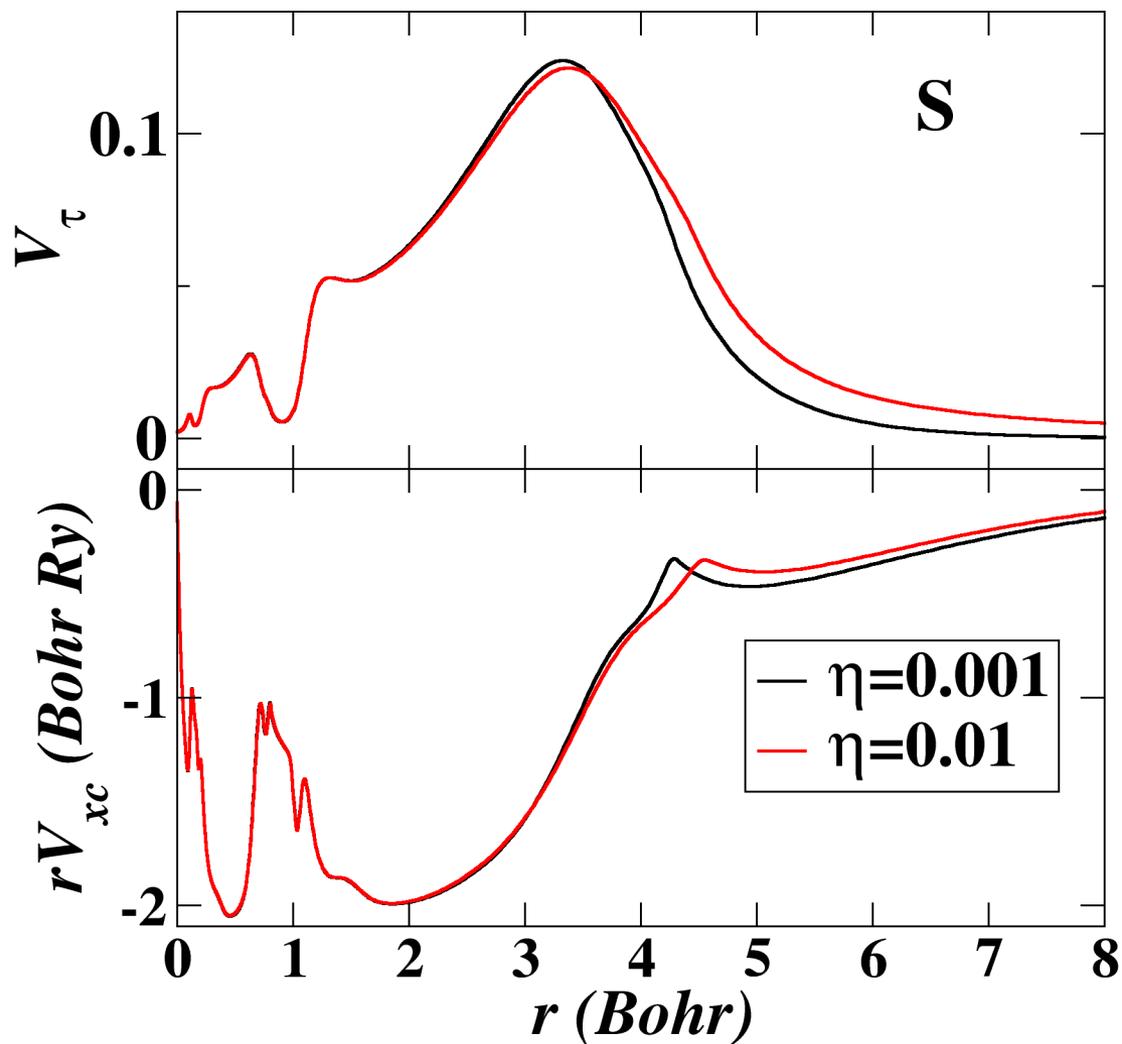
In developing the self-consistent atomic solver, we found some further numerical issues with r2SCAN which could be ameliorated by making one further small change in the formulation.

$$\bar{\alpha} \equiv \frac{\tau - \tau_W}{\tau_{\text{unif}} + \eta \tau_W} \quad \tau_W = \frac{|\nabla n|^2}{8n} \quad \tau_{\text{unif}} = \frac{3n}{10} (3\pi^2 n)^{2/3}$$

Original choice:  $\eta=0.001$

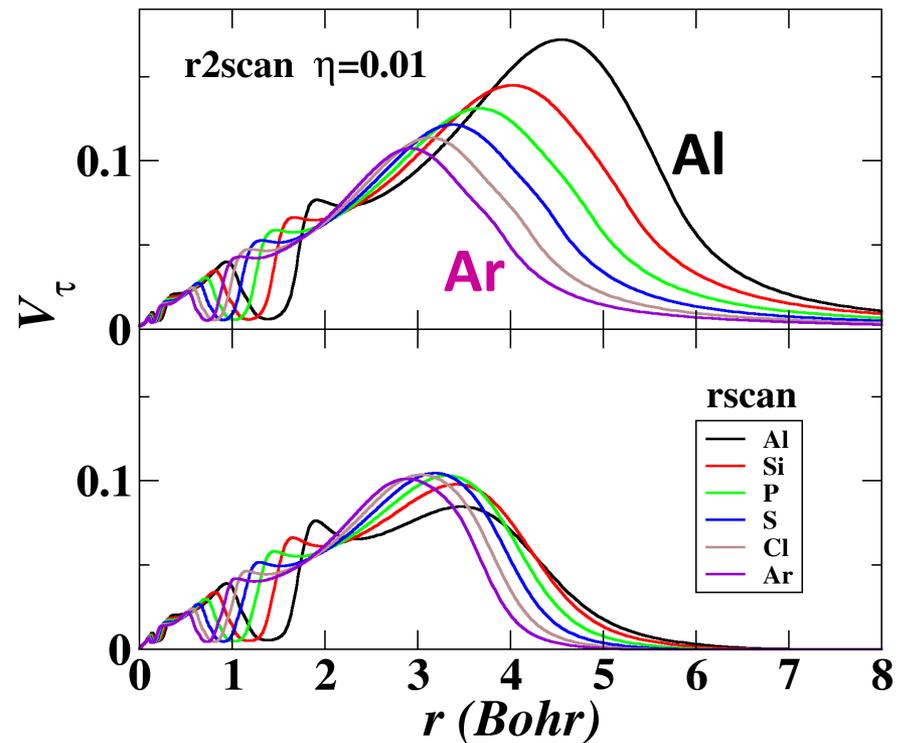
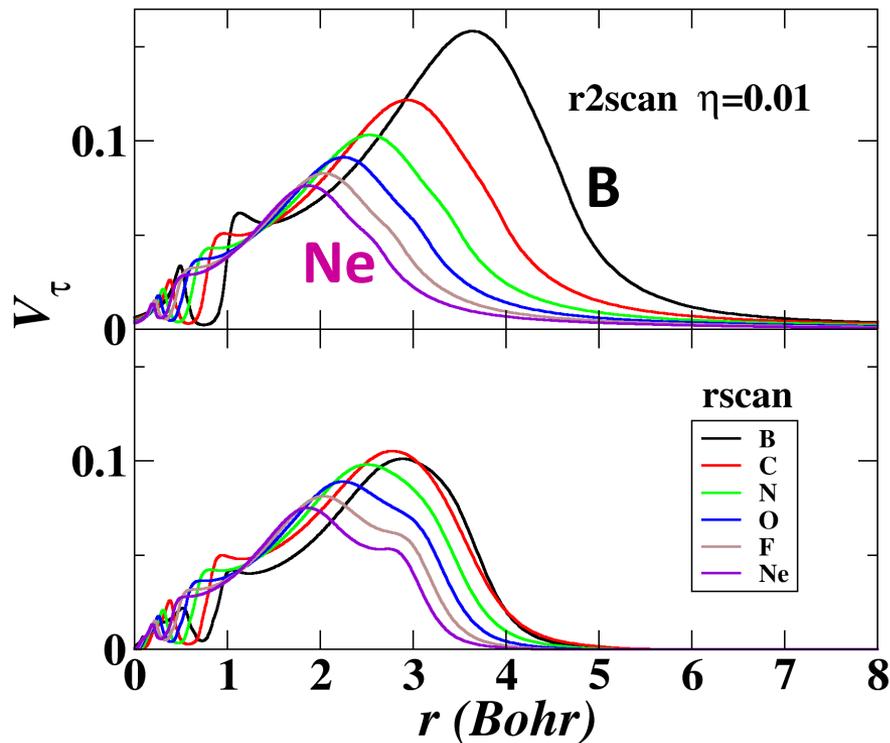
Better numerics:  $\eta = 0.01$

# Comparison of self-consistent r2SCAN potentials for atomic S with $\eta=0.01$ and $\eta=0.001$ .



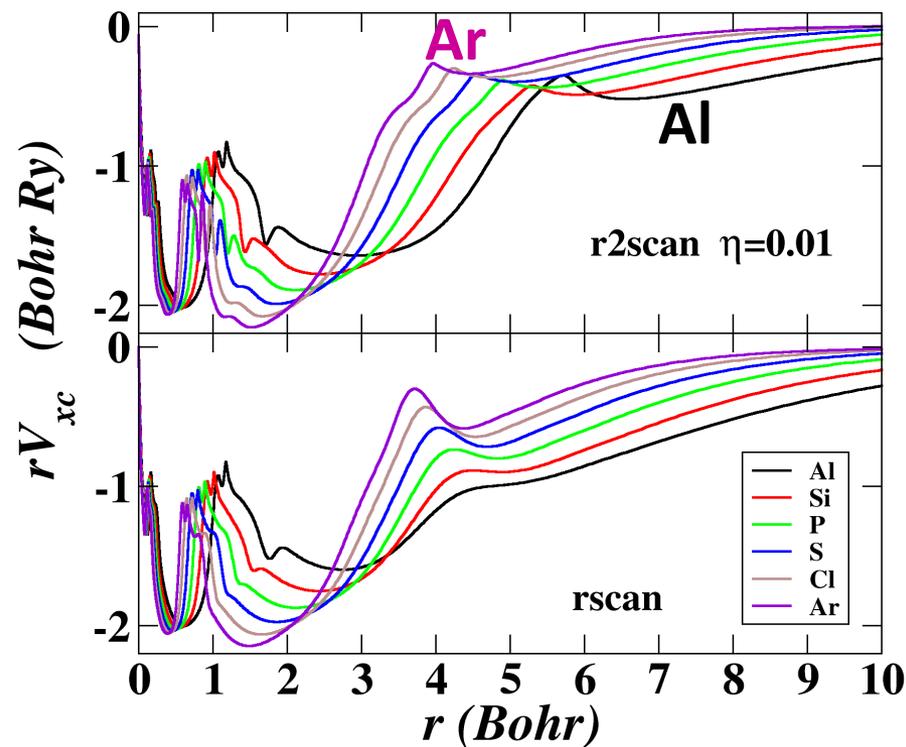
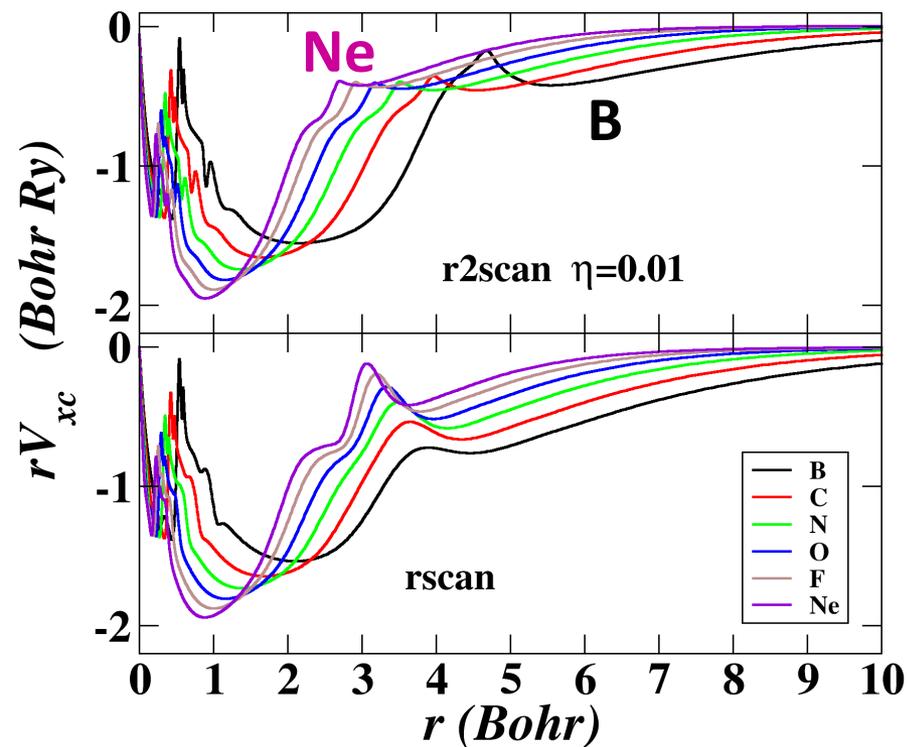
# Some results for $V_\tau(r)$

comparing r2SCAN  $\eta=0.01$  (Furness, 2020)  
with rSCAN (Bartók, 2019)



# Some results for $V_{xc}(r)$

comparing r2SCAN  $\eta=0.01$  (Furness, 2020)  
with rSCAN (Bartók, 2019)



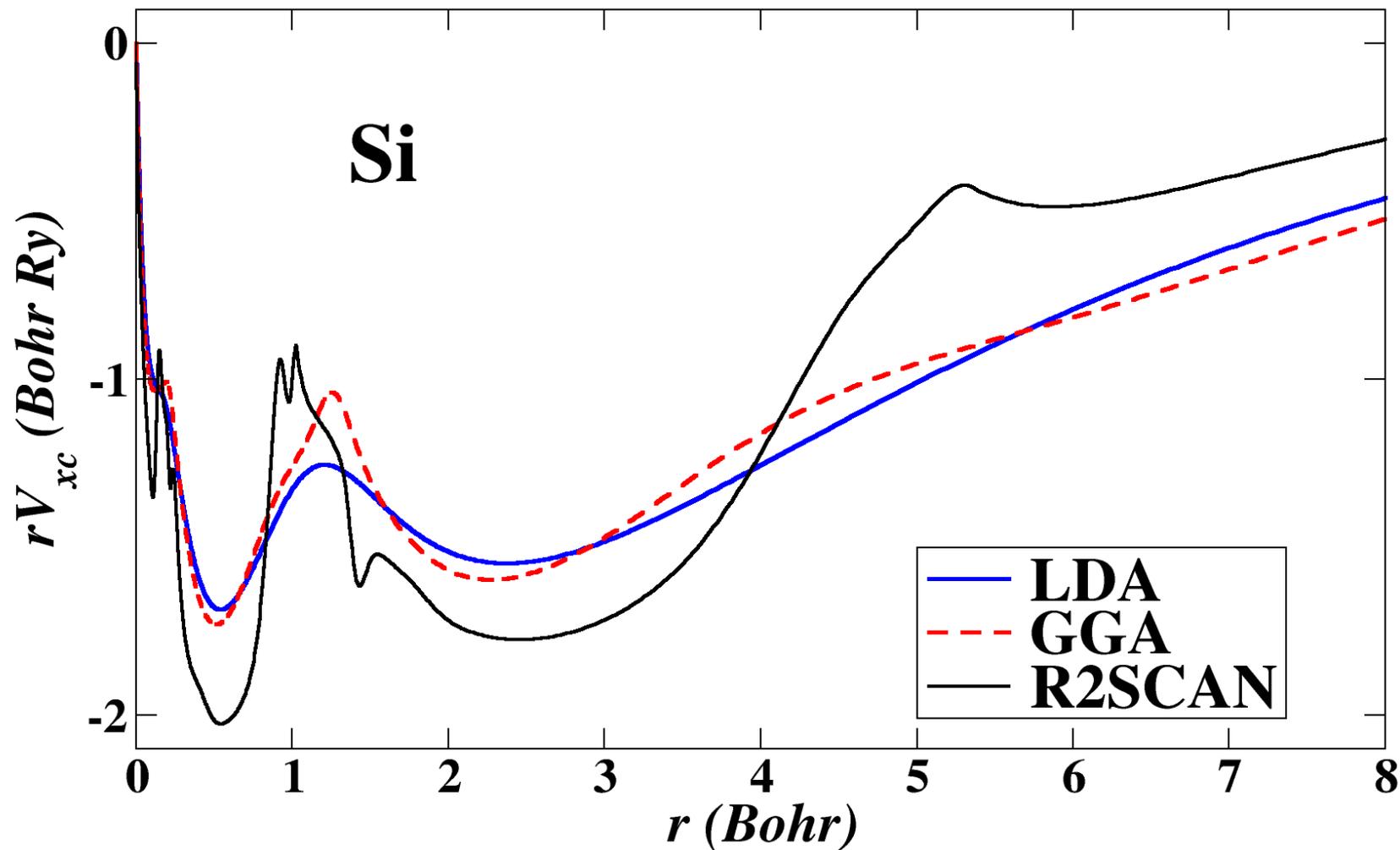
# Self-consistent total energy results

TABLE I. Total energy results (in Ry) calculated for the rscan ( 14) and r2scan 15 functionals for various atoms, comparing rscan and r2scan using  $\eta = 0.01$  and  $\eta = 0.001$ . The column "  $\Delta r2scan$ " lists the difference in the two r2scan formulations. Atoms for which the solver did not converge are indicated with "'\_'" .

Atom	rscan	r2scan( $\eta = 0.01$ )	r2scan( $\eta = 0.001$ )	$\Delta r2scan$
H	-0.906	-0.906	–	–
He	-5.810	-5.810	–	–
Li	-14.933	-14.932	–	–
Be	-29.302	-29.299	–	–
B	-49.231	-49.218	-49.216	-0.002
C	-75.533	-75.511	-75.508	-0.004
N	-108.885	-108.855	-108.850	-0.005
O	-149.961	-149.920	-149.914	-0.006
F	-199.426	-199.373	-199.366	-0.008
Ne	-257.945	-257.879	-257.870	-0.009
Na	-324.572	-324.494	–	–
Mg	-400.192	-400.100	–	–
Al	-484.765	-484.653	-484.639	-0.014
Si	-578.754	-578.625	-578.610	-0.015
P	-682.480	-682.335	-682.318	-0.017
S	-796.263	-796.100	-796.082	-0.019
Cl	-920.417	-920.236	-920.216	-0.020
Ar	-1055.257	-1055.057	-1050.035	-0.022

**Find that self-consistency is hard to achieve for some atoms with the  $\eta=0.001$  version of r2SCAN.**

# How does the r2scan $V_{xc}(r)$ compare with other functionals?



# Construction of PAW datasets

Frozen core approximation:

All electron treatment

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

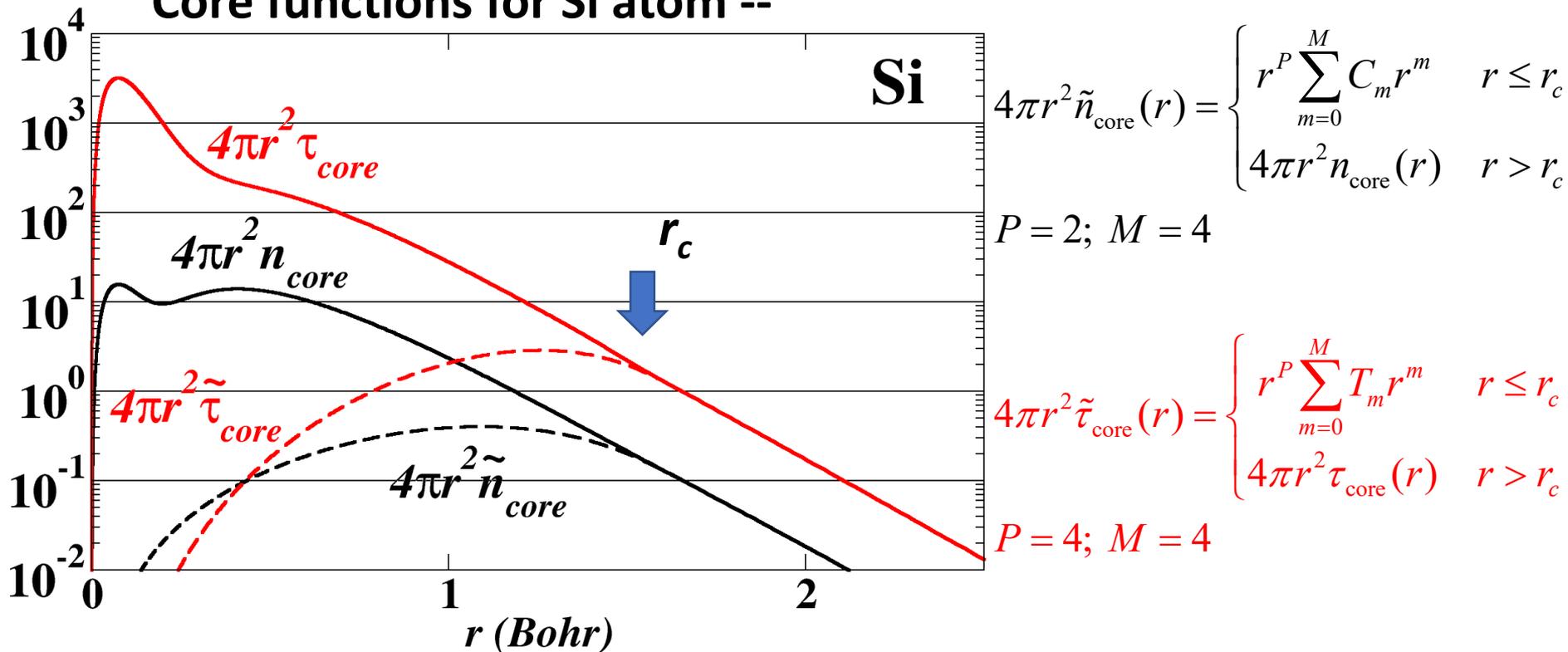
$$\tau_{core}(r) + \tau_{vale}(r)$$

Pseudo electron treatment

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

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

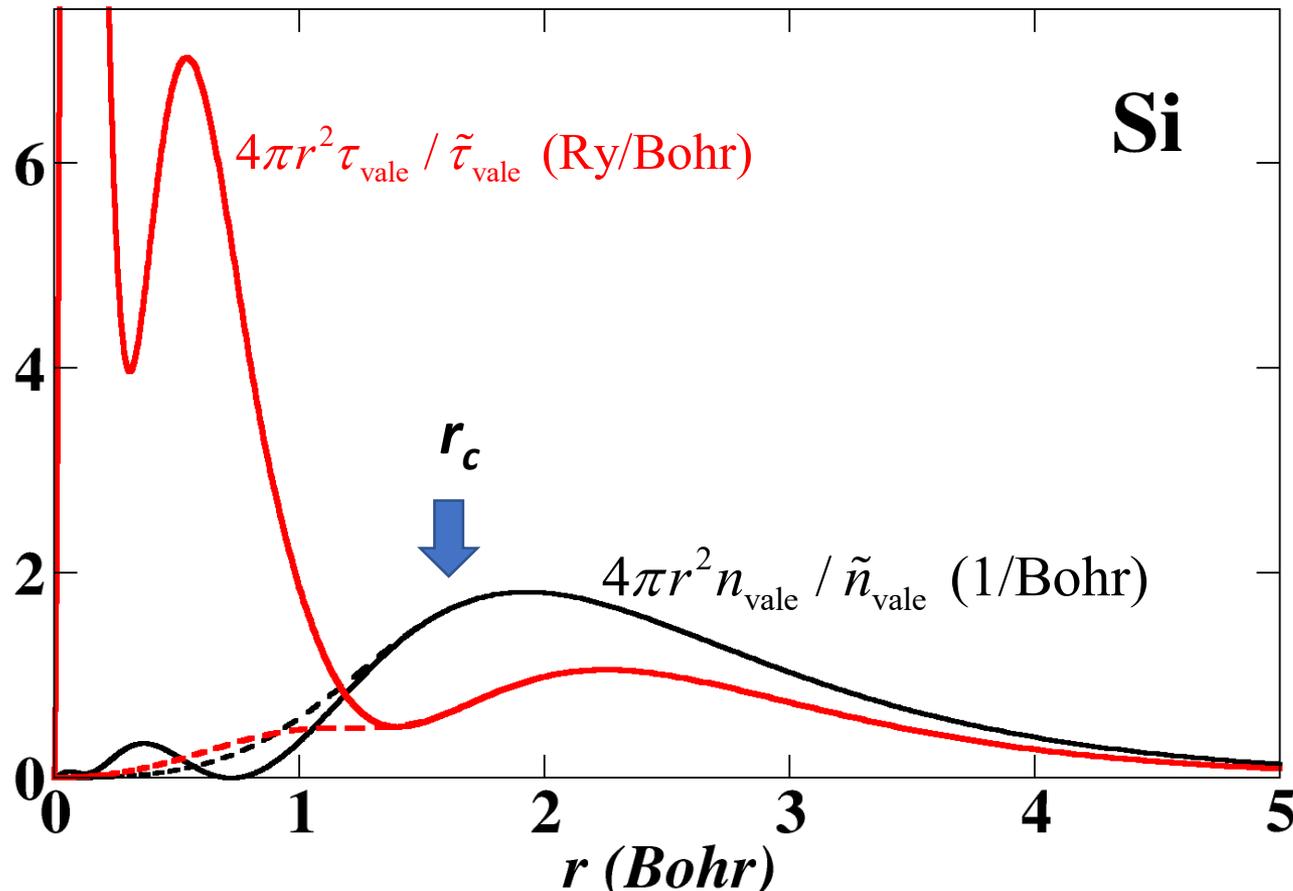
## Core functions for Si atom --



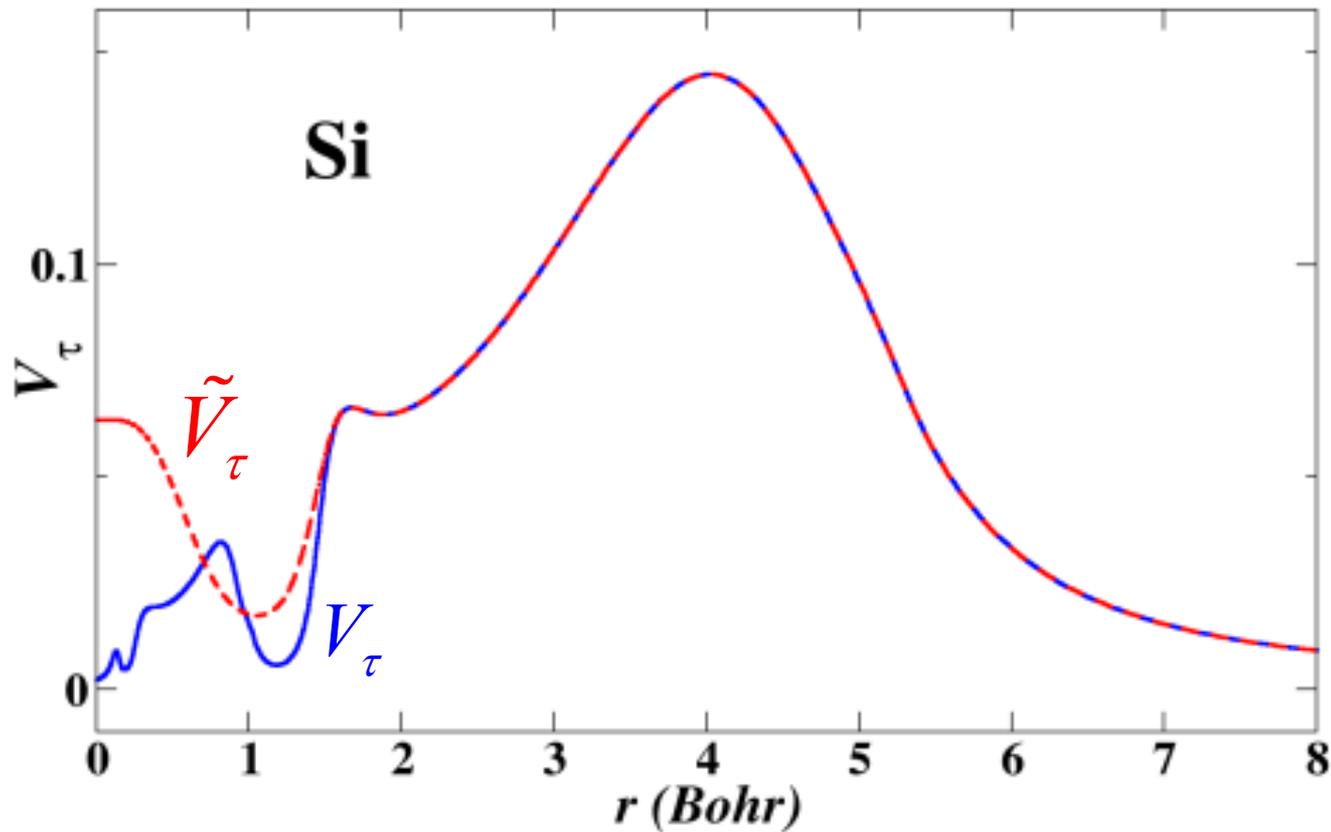
# Construction of PAW datasets -- continued

The datasets are focused on the valence electrons and there are many formulations which can be adopted for use with the generalized Kohn-Sham PAW equations (although some schemes may be more difficult).

Valence functions for Si atom

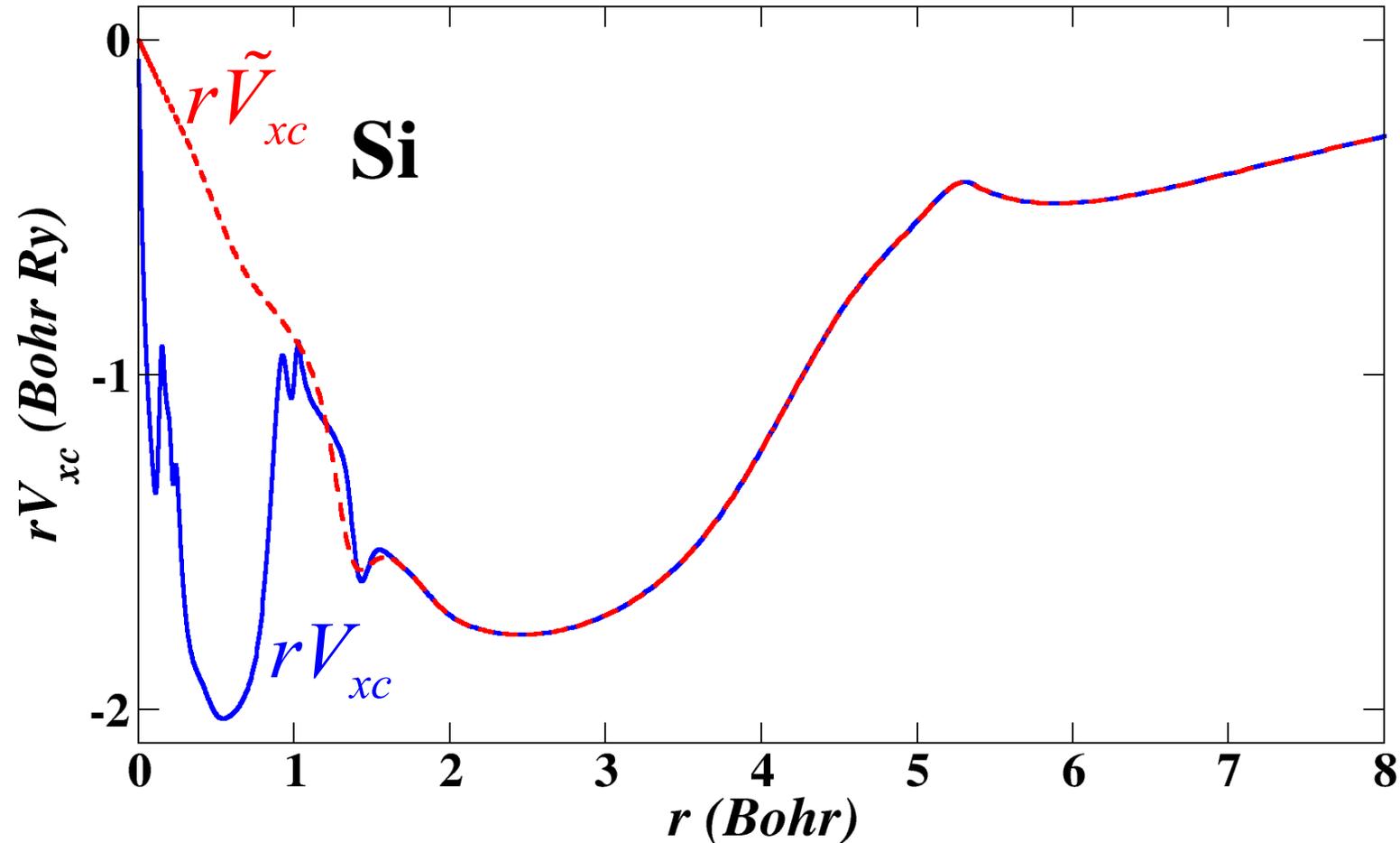


## Dimensionless kinetic potential and kinetic pseudopotential for Si for r2SCAN $\eta=0.01$



# Construction of PAW datasets -- continued

## Exchange-correlation potential and pseudopotential for Si for r2SCAN $\eta=0.01$



## Various schemes to constructed screened pseudopotential – <http://pwpaw.wfu.edu>

ATOMPAW

INFO

DATASETS

CONTRIBUTERS

CONTACT INFO

NAWH Web

PHYSICS Web

WFU Web

## ATOMPAW

### Download source code and example files:

- [atompaw-4.1.1.0.tar.gz](http://atompaw-4.1.1.0.tar.gz) (5.5mb) 1/07/2021 Francois Jollet and Marc Torrent implemented the LDA-1/2 formalism described in the publication -- [The ABINIT project: Impact, environment and recent developments](#) Additionally, solutions to the full Dirac equations for all-electron wavefunctions and densities are now available and have been used by Nils Brouwer to evaluate spin-orbit and other effects in warm dense matter.
- [Mirror site](#) for AtomPAW package on github starting with version 4.1.0.6 thanks to Marc Torrent, who also updated the instructions for installation on Mac OS.
- [atompaw-4.1.0.6.tar.gz](http://atompaw-4.1.0.6.tar.gz) (5.5mb) 6/27/2019 Francois Jollet and Marc Torrent implemented a test of the atomic pseudobasis functions for positive definite overlap matrix following a suggestion by Dr. Brecht Vestichel of Synopsys, Denmark. The eigenvalues of the overlap matrix in the basis of the projector functions are evaluated and outputted to the (case) file. If any of them are smaller than  $10^{-10}$ , the program stops with the suggestion that the pseudobasis is incomplete. Additionally, core electron and the corresponding pseudo core kinetic energy densities are now calculated and outputted to the (case).xml file for possible use by ABINIT.

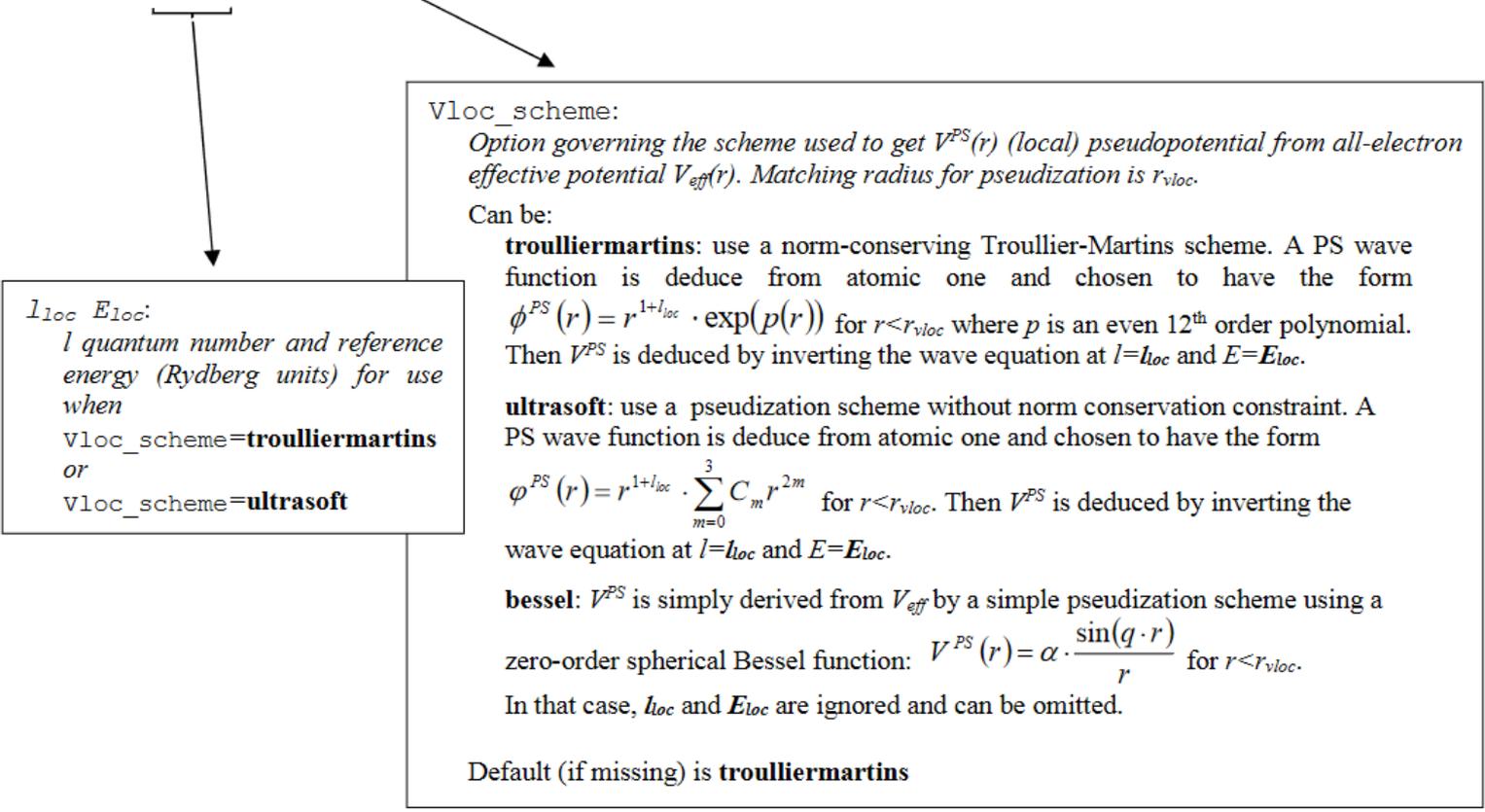
# Construction of PAW datasets -- continued

## Various schemes to constructed screened pseudopotential – $V^{PS}(r)$

<http://pwpaw.wfu.edu> specifically from Marc Torrent's

usersguide

$l_{loc}$   $E_{loc}$   $V_{loc\_scheme}$



For now, added VPSMATCHNC/VPSMATCHNNC similar to “ultrasoft” with or without norm conservation.

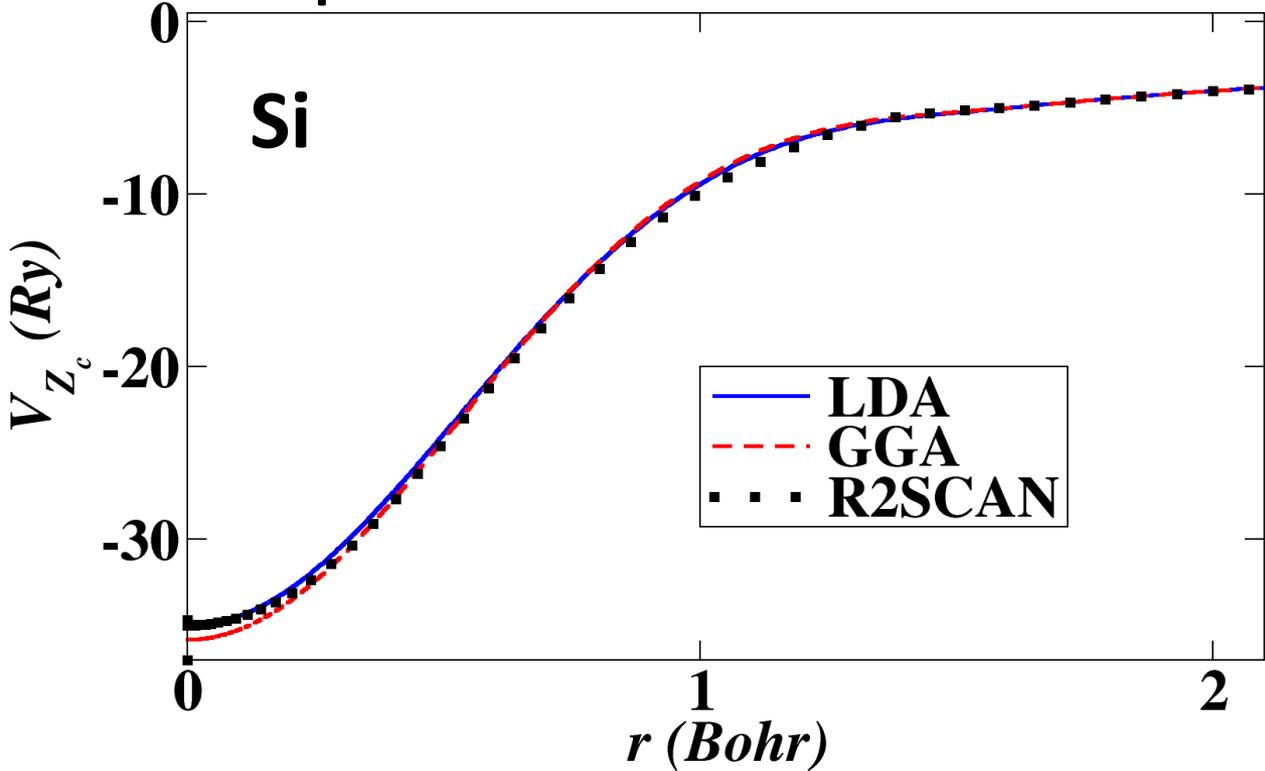
# Construction of PAW datasets -- continued

Determine ionic pseudopotential by unscreening  $V^{PS}(r)$

$$\tilde{V}_{Z_c}(r) = V^{PS}(r) - \tilde{V}_H(r) - \tilde{V}_{xc}(r) \quad \hat{n}(r) \equiv \text{unit compensation charge}$$

$$\nabla^2 \tilde{V}_H(r) = 4\pi e^2 (\tilde{n}_{\text{vale}}(r) + \Delta Q \hat{n}(r)) \quad \Delta Q \equiv \int d^3 r (n_{\text{vale}}(r) - \tilde{n}_{\text{vale}}(r))$$

**Ionic pseudopotential for Si for r2SCAN  $\eta=0.01$  in comparison with LDA and GGA**



## To do list

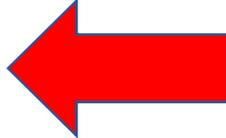
Develop a self-consistent all electron atomic solver for the generalized Kohn-Sham equations needed to evaluate exchange-correlation functionals having the meta-GGA form.

3  
4  Adapt pseudization schemes for basis and projector functions for use in the generalized Kohn-Sham formalism.

Test and evaluate.



## Additional considerations

- How sensitive are the results to the dataset? 
- Given apparently reasonable results for r2SCAN  $\eta=0.01$ , should we stick with that form or work harder on the solver? (Perhaps should also consult with Tulane/Temple developers.)
- Not all pseudization schemes are easily converted for use in generalized density functional formulation due to the dimensionless kinetic energy potential term. Which ones should we try to preserve?
- Further considerations?