Recent advances in development of single-point orbital-free kinetic energy functionals

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Electronic Structure Methods Survey -

Goal: Forces on nuclei for MD.

- *ab-initio* **wave function methods**:
  $\hat{H} \rightarrow$ system of SCF Eqns. $\rightarrow \{\psi_i\} \rightarrow E[\{\psi_i\}, \{\mathbf{R}_I\}] \rightarrow \mathbf{F}_I = -\nabla_I E$.
  Slow, scales as $\geq O(N^4)$.

- **Kohn-Sham density functional theory (DFT) methods**:
  $E_{xc}^{approx}[n] \rightarrow$ system of KS Eqns. $\rightarrow$
  $\{\phi_i\},\ n \rightarrow T_s[\{\phi_i\}] \rightarrow E[\{\phi_i\}, n, \{\mathbf{R}_I\}] \rightarrow \mathbf{F}_I = -\nabla_I E$.
  The exact, explicit density functional for non-interacting kinetic energy (KE), T_s, is not known $\rightarrow$ orbitals are used.
  Slow, scales as $O(N^4)$ (order-N methods are approximate).

- **Orbital-free DFT (OF-DFT) methods**:
  $T_s^{approx}[n] \rightarrow$ single Euler-Lagrange Eqn. $\rightarrow n \rightarrow E[n, \{\mathbf{R}_I\}] \rightarrow \mathbf{F}_I = -\nabla_I E$.
  Relatively fast, may scale approximately as $O(N)$.

- **Classical; semi-empirical parametrical**
  Classical: $\{\mathbf{R}_I\} \rightarrow E[\{\mathbf{R}_I\}] \rightarrow \mathbf{F}_I = -\nabla_I E$.
  Semi-empirical parametrical: $\{\mathbf{R}_I\} \rightarrow$ parametric $\hat{H} \rightarrow$
  $\{\psi_i\} \rightarrow E[\{\psi_i\}, \{\mathbf{R}_I\}] \rightarrow \mathbf{F}_I = -\nabla_I E$.
  Fast, but not universal, not reliable especially for states far from equilibrium.

OF-DFT: Basics -

Kohn-Sham noninteracting kinetic energy (KE) is minimum KE of one-determinant wave function for density n

$$T_{\rm s}[\{\phi_i\}_{i=1}^N] = 2\sum_{i=1}^{N_e/2}\int \phi_i^*(\mathbf{r})(-\frac{1}{2}\nabla^2)\phi_i(\mathbf{r})d^3\mathbf{r} \equiv \int t_{\rm orb}(\mathbf{r})d^3\mathbf{r}.$$

The difference between interacting and noninteracting KE

$$T_{\rm c} = \langle\Psi|\hat{T}|\Psi\rangle - T_{\rm s}$$

is included in XC functional $E_{\rm xc}[n]$. Kohn-Sham DFT orbital dependent total energy functional:

$$E^{\text{KS-DFT}}[\{\phi_i\}_{i=1}^N, n] = T_s[\{\phi_i\}_{i=1}^N] + E_{\rm ne}[n] + E_{\rm H}[n] + E_{\rm xc}[n] + E_{\rm ion}\ .$$

In OF-DFT, $T_s[\{\phi_i\}_{i=1}^N] \to T_{\rm s}[n]$, and tot. energy becomes explicit functional of n:

$$E^{\text{OF-DFT}}[n] = T_s[n] + E_{\rm ne}[n] + E_{\rm H}[n] + E_{\rm xc}[n] + E_{\rm ion}\ .$$

OF-DFT: Basics -

Electron density $n(\mathbf{r})$ is the sole variable. There is a single Euler equation:

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_{\mathrm{KS}}([n];\mathbf{r}) = \mu \, ; \quad \text{where} \;\; v_{\mathrm{KS}}([n];\mathbf{r}) \equiv \frac{\delta}{\delta n(\mathbf{r})}\Big(E_{\mathrm{ne}}[n] + E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n] \Big) \, .$$

Computational cost of OF-DFT does not depend on N_e, but scales as the spatial extent of the system.

The Pauli term: KE may be decomposed as:

$$T_s[n] = T_{\mathrm{W}}[n] + T_\theta[n] \, , \qquad T_\theta \geq 0 \, .$$

The non-negativity of T_θ is an important advantage of this decomposition. Euler eqn. takes the Schrödinger-like form:

$$\left\{ -\frac{1}{2}\nabla^2 + v_\theta([n];\mathbf{r}) + v_{\mathrm{KS}}([n];\mathbf{r}) \right\} \sqrt{n(\mathbf{r})} = \mu \sqrt{n(\mathbf{r})} \; ,$$

where $v_\theta([n];\mathbf{r}) = \frac{\delta T_\theta[n]}{\delta n(\mathbf{r})} \, , \;\; v_\theta(\mathbf{r}) \geq 0$ is the Pauli potential.

OF-DFT: Basics -

A formal expression for v_θ in terms of the KS orbitals:

$$v_\theta([n];\mathbf{r}) = \frac{t_\theta([n];\mathbf{r})}{n(\mathbf{r})} + \sum_{i=1}^{N}(\varepsilon_{N'} - \varepsilon_i)\frac{|\phi_i(\mathbf{r})|^2}{n(\mathbf{r})}\,,$$

where $t_\theta([n];\mathbf{r}) = t_{\rm orb}(\mathbf{r}) - n(\mathbf{r})v_{\rm W}([n];\mathbf{r})$; $v_{\rm W} \equiv \frac{\delta T_W[n]}{\delta n(\mathbf{r})} = \frac{1}{8}\left[\frac{|\nabla n|^2}{n^2} - \frac{2\,\nabla^2 n}{n}\right]$.
Born-Oppenheimer (B-O) interatomic forces, $\mathbf{F}_I = -\nabla_{\mathbf{R}_I} E^{\text{OF-DFT}}[n]$, assume the form:

$$\mathbf{F}_I^{\rm OF-DFT} = -\frac{\partial E_{\rm ion}}{\partial \mathbf{R}_I} - \int \left[v_{\rm W}([n];\mathbf{r}) + v_\theta([n];\mathbf{r}) + v_{\rm KS}([n];\mathbf{r})\right]\frac{\partial n(\mathbf{r})}{\partial \mathbf{R}_I}\,d^3\mathbf{r}\,.$$

Here there are three sources of error from approximate quantities:

(i) approximate XC in $v_{\rm KS}$
(ii) approximate v_θ (Pauli potential)
(iii) approximate density $n(\mathbf{r})$.

If we use converged KS density as input, then the major sorce of error would be approximate Pauli potential.

OF-DFT: Basics -

Pauli term in the GGA form:

$$T_\theta^{GGA}[n] = \int t_{\rm TF}([n];\mathbf{r}) F_\theta(s(\mathbf{r})) d^3\mathbf{r}\,, \quad F_\theta(s) = F_{\rm t}(s) - \frac{5}{3}s^2,$$

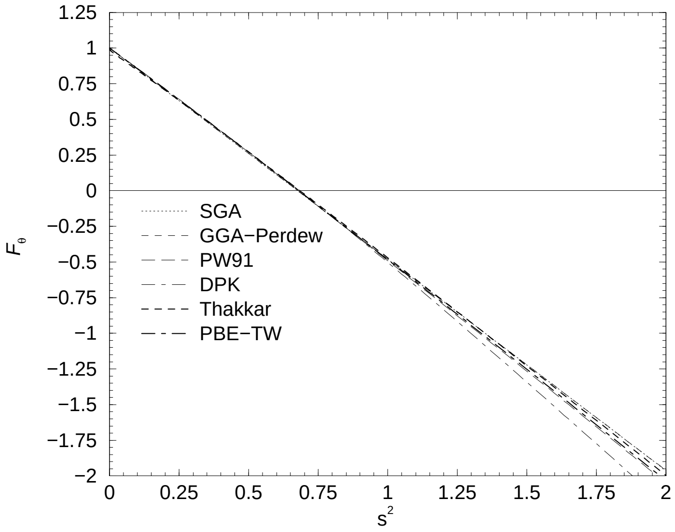
where $s \equiv \frac{|\nabla n|}{2nk_F}$. Few examples of the GGA KE functionals:

- The second-order gradient approximation (SGA).
- An ab-initio GGA proposed by Perdew (Phys. Lett. A **165**, 79 (1992)).
- The PW91 functional (by Lacks and Gordon) conjoint to the PW91 exchange (J. Chem. Phys. **100**, 4446 (1994)).
- The semi-empirical DePristo and Kress (DPK) functional: some parameters are fixed from the exact conditions and others by fitting to the KE of closed-shell atoms (Phys. Rev. A **35**, 438 (1987)).
- Thakkar functional, F_t is a heuristic combination of different GGA and with parameters fitted to the KE of 77 molecules (Phys. Rev. A **46**, 6920 (1992)).
- The Tran and Wesolowski functional (PBE-TW) with parameters fitted to the KE of the He and Xe atoms (Int. J. Quantum Chem. **89**, 441 (2002)).

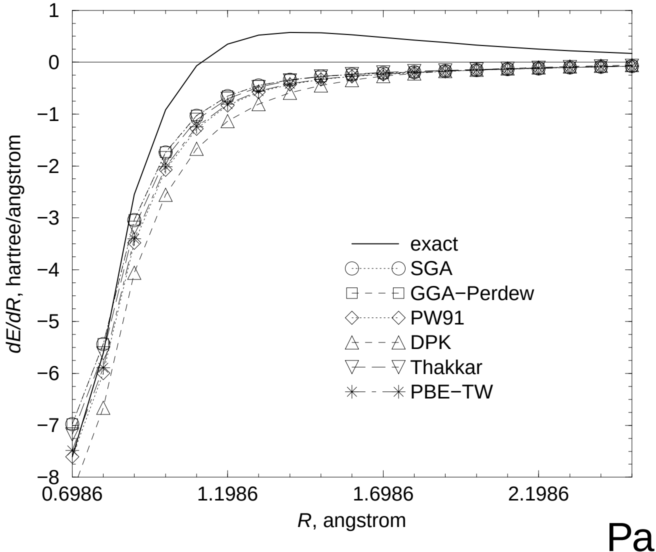
Non-SCF results: F_θ^{GGA} and F_I^{GGA} -

We use Kohn-Sham density as the input to the OF-DFT density functional and calculate corresponding energies and forces. The biggest source of error in these type of calculations is the error due to approximate Pauli functional, T_θ.

- Pauli term enhancement factor F_θ of various GGA KE functionals.

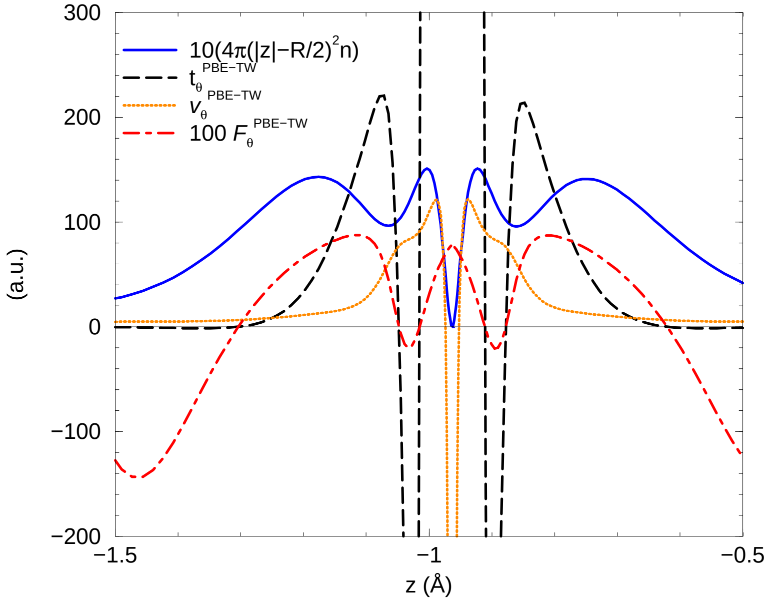


- Gradients of the total energy of the N$_2$ molecule.

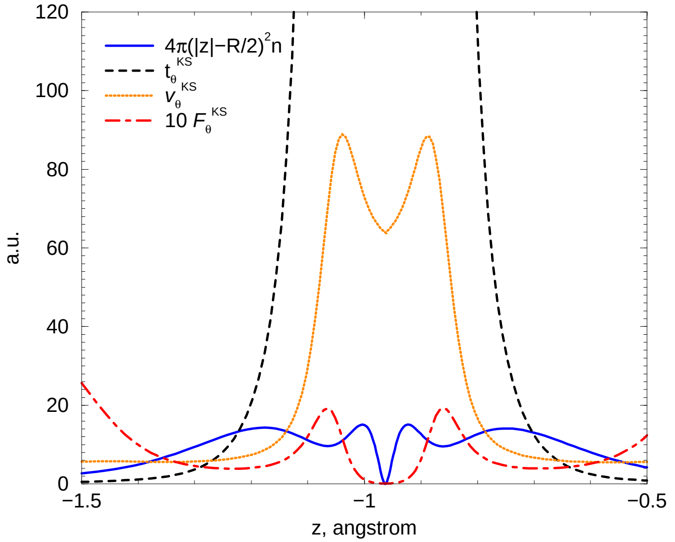


Non-SCF results: F_θ^{GGA} ***and*** F_I^{GGA} ***-***

- GGA (=PBE-TW) Pauli potential (orange line) for the SiO molecule near Si atom. The GGA Pauli potential is negative and singular at the nucleus position.



- “Exact" KS Pauli potential (orange line) for the SiO molecule near Si atom. It is non-negative and finite at nucleus.



OF-DFT: analysis of $v_\theta^{\rm GGA}$ -

SGA Pauli enhancement factor: $F_\theta^{\rm SGA} = 1 + a_2 s^2$, with $a_2 = -40/27$. Near nucleus-cusp behavior defined by Kato's cusp condition: $n(\mathbf{r}) \propto \exp(-2Z|\mathbf{r}|)$, $v_\theta^{\rm GGA}$ becomes:

$$v_\theta^{\rm GGA}(r \to 0) = \frac{3Z}{5r}\frac{\partial F_\theta^{\rm GGA}}{\partial(s^2)} + \text{nonsingular terms.}$$

At small s^2, $F_\theta^{\rm GGA} \approx 1 + as^2$ and we obtain:

$$v_\theta^{\rm GGA}(r \to 0) = \frac{3aZ}{5r} + \text{nonsingular terms.}$$

Important results: the GGA Pauli potential is

(i) Singular at the nuclear position

(ii) The singularity in published GGAs is negative, i.e. it violates the constraint.

Solution:

(i) It is possible to satisfy the non-negativeness constraint by changing the sign of the $\frac{\partial F_\theta^{\rm GGA}}{\partial(s^2)}$ derivative near nuclear positions ($\sim$ at $s^2 \approx 0.14$).

(ii) But positive GGAs have nuclear site divergences ⇒ go beyond GGA.

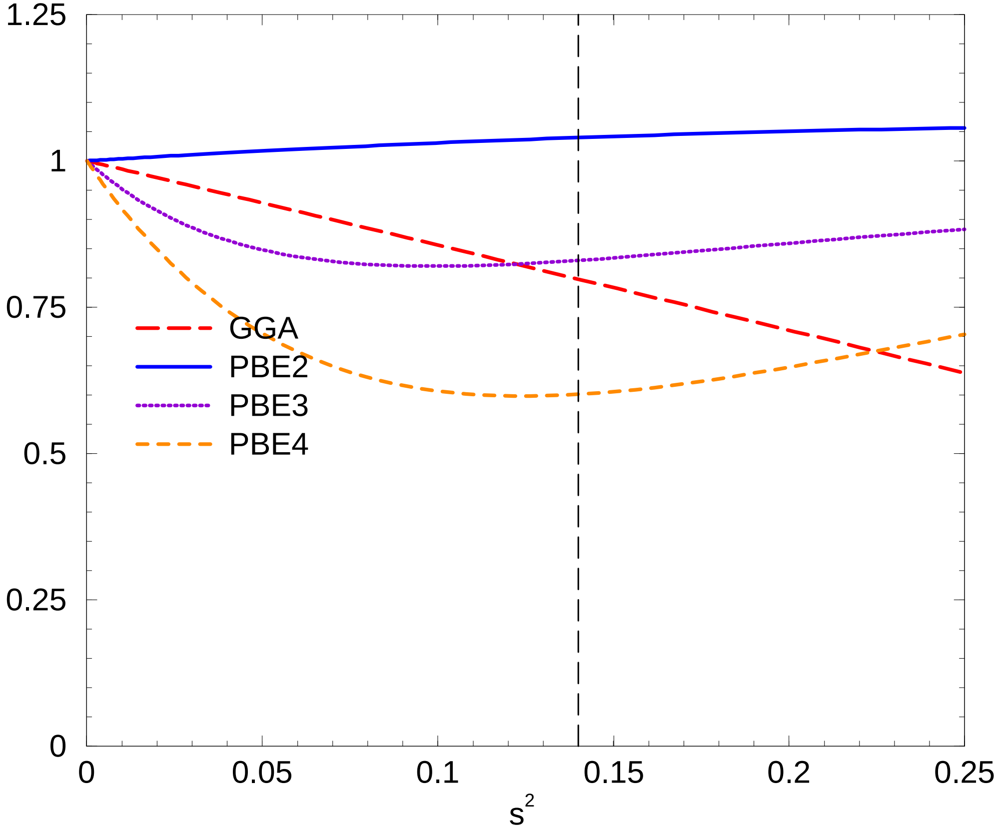
OF-DFT: modified conjoint GGA -

We proposed modified conjoint GGA (mcGGA) KE functionals [J. Comp.-Aided Mater. Des. **13**, 111 (2006)] to remove the negative singularity of the Pauli potential.

- "Conjointness" hypothesis [Lee, Lee, Parr, 1991]: $E_{\mathrm{x}}[n] = C_{\mathrm{x}} \int n^{4/3} F_{\mathrm{x}}(s) d^3r$, $T_{\mathrm{s}}[n] = C_{\mathrm{TF}} \int n^{5/3} F_{\mathrm{t}}(s) d^3r,\ \ F_{\mathrm{t}}(s) \sim F_{\mathrm{x}}(s)$. Useful, not literally correct.
- Parameterization of KE functional using <u>energetic</u> objective function, $\omega_E = \sum_{i=1}^{m} \left| E_i^{\mathrm{KS}} - E_i^{\mathrm{OF\text{-}DFT}} \right|^2$, for a set of nucleai arrangement of same system(s) failed.
- The following ΔE criterion was used: $\omega_{\Delta E} = \sum_{M,i} \left| \Delta E_{M,i}^{\mathrm{KS}} - \Delta E_{M,i}^{\mathrm{OF\text{-}DFT}} \right|^2$ where $\Delta E_{M,i} = E_{M,i} - E_{M,e}$ is the energy difference w.r.t equilibrium nuclear configuration. It is equivalent to parameterization to forces.
- Fitted functionals, modified conjoint GGA, reproduce qualitatively correct total energy gradients ($\Rightarrow$ correct interatomic forces).
- mcGGA Pauli potential is non-negative (satisfies the important constraint).

OF-DFT: modified conjoint GGA

The mcGGA functional enhancement factors (parameterized to forces): $\frac{\partial F_\theta^{\mathrm{mcGGA}}}{\partial (s^2)} > 0$ near nuclear positions (at the nucleus $s \approx 0.38$, $s^2 \approx 0.14$) $\Rightarrow$ The Pauli potential near the nuclei position is positive. $F_{\mathrm{t}}^{\mathrm{PBE}\nu}(s) = 1 + \sum_{i=1}^{\nu-1} C_i \left[\frac{s^2}{1+a_1 s^2}\right]^i, \ \nu = 2, 3, 4.$



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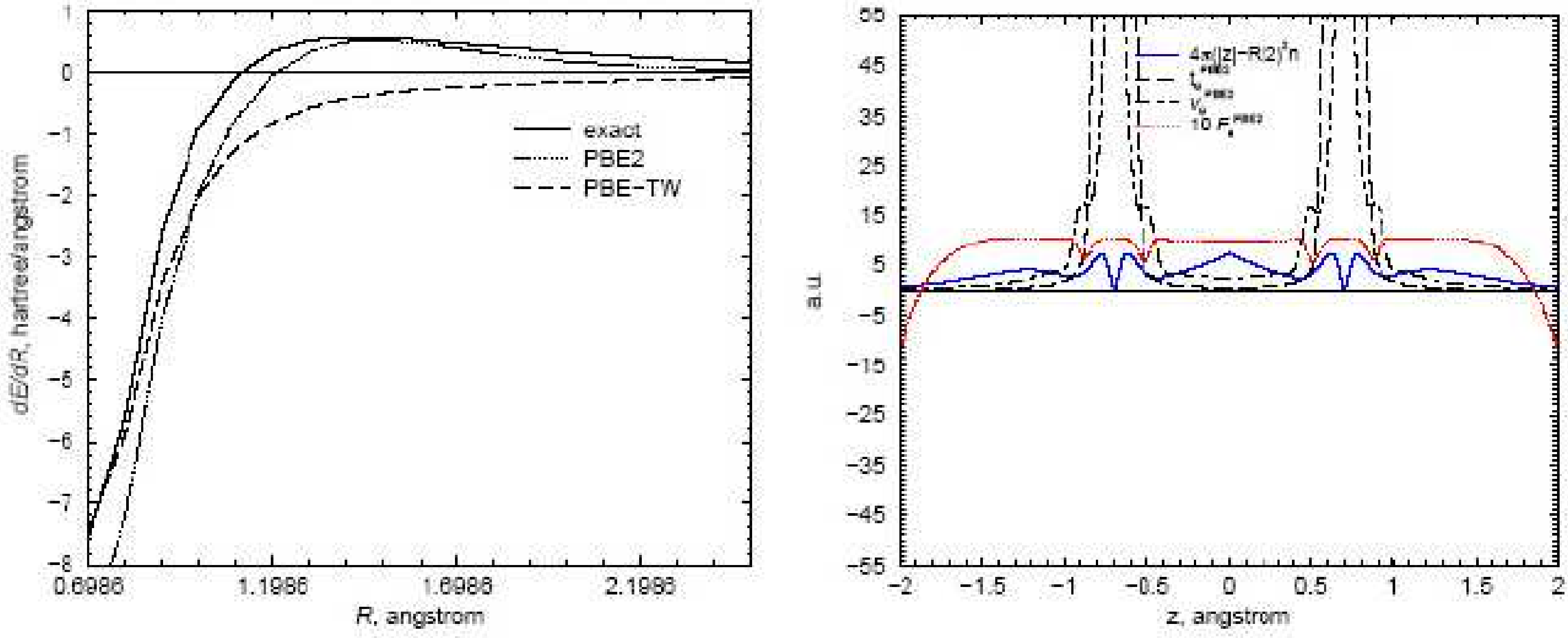
Non-SCF results: mcGGA -



Left panel: Gradients of the total energy of the N_2 molecule for the PBE2 modified conjoint GGA potential, compared with results from the PBE-TW potential and the exact value.
Right panel: Electronic density (scaled by the factor $(4\pi(|z| - R/2)^2$, with R the internuclear distance), Pauli term, Pauli potential, and enhancement factor F_θ.

OF-DFT: reduced derivative approximation -

- Both GGA and mcGGA Pauli potentials are singular at nuclei.
- To remove singularities one must go beyond the GGA.
- Based on 4th order gradient expansion for the KE:

$$t_\theta^{(4)}([n];\mathbf{r}) = t_{\mathrm{TF}}([n];\mathbf{r})\left[\frac{8}{81}\left(p^2 - \frac{9}{8}s^2 p + \frac{1}{3}s^4\right)\right],$$

where $s \equiv \frac{|\nabla n|}{2nk_F}$, $p \equiv \frac{\nabla^2 n}{(2k_F)^2 n}$, we introduce the reduced density derivative (RDD) variable :

$$\kappa_4 = a_4 s^4 + b_2 p^2 + c_{21} s^2 p,$$

For $n \sim \exp(-2Zr)$ the near-nucleus behavior of the 4th order potential is:

$$v_\theta^{(4)}(r) \sim \left[-\frac{16Z^2}{3r^2}\left(5b_2 + 3c_{21}\right) + \frac{32Z^3}{9r}\left(18a_4 + 17b_2 + 18c_{21}\right)\right] + \text{nonsingular terms.}$$

and define coefficients in κ_4 from requirement of cancelation of singular terms

$$\kappa_4 = s^4 + \frac{18}{13}p^2 - \frac{30}{13}s^2 p.$$

OF-DFT: reduced derivative approximation -

- However this cancelation of singularities is not "universal". Only holds for densities with exponential behavior up to 4th term in Taylor series $n(r) \propto 1 - 2Zr + 2Z^2r^2 - (4/3)Z^3r^3$
- **Observation**: $\kappa_4 \sim \mathrm{O}(\nabla^4)$ suggests that the effective or operational order of ∇ in such a candidate variable should be reduced to second order.
- Another RDD variable is defined as $\tilde{\kappa}_4 = \sqrt{a_4 s^4 + b_2 p^2 + c_{21} s^2 p}$
- for density $n(r) \sim 1 + C_1 r + C_2 r^2 + C_3 r^3$, the corresponding Pauli potential is

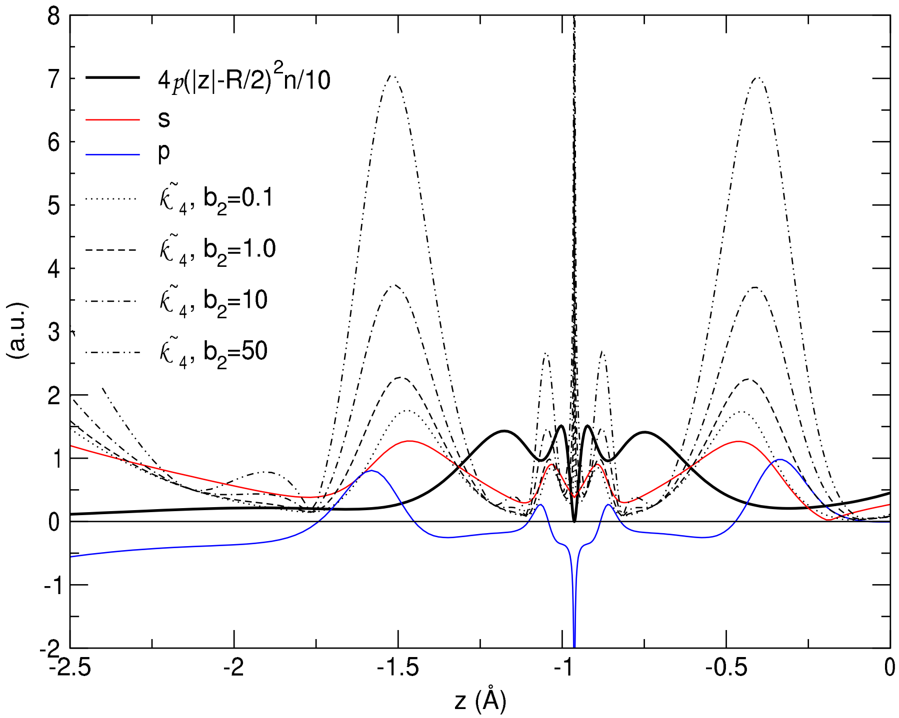
$$v_\theta(r) \sim \frac{c_{21}}{\sqrt{b_2}} \frac{1}{r} + \text{nonsingular terms}\,.$$

With the choice $c_{21} = 0$ the cancelation of singularities would be universal (for arbitrary C_i), hence finally we define the 4th order RDD variable as

$$\tilde{\kappa}_4 = \sqrt{s^4 + b_2 p^2}, \;\; b_2 > 0\,.$$

OF-DFT: reduced derivative approximation -

The fourth order, $\tilde{\kappa}_4$ reduced density derivative for different values of b_2 along the internuclear axis z for the SiO diatomic molecule near the Si atom: Si at $(0, 0, -0.963)$Å, O at $(0, 0, +0.963)$Å. Variables s and p, are shown for comparison.



OF-DFT: reduced derivative approximation -

In parallel with definition of $\tilde{\kappa}_4$ we introduce a 2^d order RDD

$$\kappa_2 = s^2 + b_1 p\,,$$

Thus, we define a class of approx. KE functionals, the reduced derivative approximation (RDA) functionals:

$$T_{\rm s}^{\rm RDA}[n] \equiv T_{\rm W}[n] + \int t_{\rm TF}([n];\mathbf{r}) F_\theta(\kappa_2(\mathbf{r}), \tilde{\kappa}_4(\mathbf{r}))\; d^3\mathbf{r}\,,$$

Parameterization of a RDA functional:

$$F_\theta^{\rm m0}(\{\kappa\}) = A_0 + A_1 \left(\frac{\tilde{\kappa}_{4a}}{1+\beta_1\tilde{\kappa}_{4a}}\right)^2 + A_2 \left(\frac{\tilde{\kappa}_{4b}}{1+\beta_2\tilde{\kappa}_{4b}}\right)^4 + A_3 \left(\frac{\kappa_{2c}}{1+\beta_3\kappa_{2c}}\right)\,.$$

This form has properties: (i) the corresponding v_θ is finite (ii) the divergences of $\tilde{\kappa}_{4a}$, $\tilde{\kappa}_{4b}$ and κ_2 near the nucleus cancel out. We used the usual energy fitting criterion to minimize $\omega_E = \sum_{i=1}^{m} \left| E_i^{\rm KS} - E_i^{\rm OF\text{-}DFT} \right|^2$, for $M = \{{\rm H_6Si_2O_7}, {\rm H_4SiO_4}, {\rm Be}, {\rm Ne}\}$, with a set of six Si–O bond lengths for each molecule.

Non-SCF results: RDA for molecules

Table 1: KS kinetic energy T_s, and differences ($T_s^{\mathrm{OF-DFT}} - T_s^{\mathrm{KS}}$). All in Hartrees.

	KS	Thakkar	MGGA	RDA
H_2	1.080	−0.022	0.103	0.036
LiH	7.784	0.021	0.296	0.161
H_2O	75.502	−0.285	0.318	−0.188
HF	99.390	−0.353	0.329	−0.171
N_2	108.062	−0.340	0.300	−0.182
LiF	106.183	−0.261	0.566	0.175
CO	111.832	−0.333	0.300	−0.179
BF	123.117	−0.273	0.456	0.080
NaF	260.097	−0.348	1.295	0.711
SiH_4	290.282	0.084	3.112	0.574
SiO	362.441	−0.262	2.825	0.370
H_4SiO	364.672	−0.163	3.338	0.421
H_4SiO_4	587.801	−0.860	4.133	−0.081
$H_6Si_2O_7$	1100.227	−1.408	7.968	0.064
MAE[a]	—	0.358	1.810	0.242

Non-SCF results: RDA for molecules -

Table 2: Energy gradient (Hartree/Å) calculated at extremum point R_m

	R_m, Å	KS	Thakkar	MGGA	RDA
H_2	1.2671	0.164	0.029	0.112	0.017
LiH	2.455	0.046	0.016	0.037	0.028
H_2O(1R)	1.3714	0.216	−0.050	−0.073	0.261
H_2O(2R)	1.3714	0.416	−0.127	−0.163	0.454
HF	1.3334	0.232	−0.071	−0.003	0.192
N_2	1.3986	0.576	−0.349	−0.819	0.212
LiF	2.0405	0.079	−0.019	−0.032	0.041
CO	1.4318	0.474	−0.248	−0.659	0.472
BF	1.6687	0.207	−0.037	−0.118	0.244
NaF	2.4284	0.067	−0.007	1.169	0.157
SiH_4	1.9974	0.447	0.102	0.189	0.088
SiO	1.9261	0.278	−0.098	−0.281	0.125
H_4SiO	2.057	0.162	−0.027	−0.086	0.113
H_4SiO_4	2.037	0.712	−0.278	−0.714	0.600
$H_6Si_2O_7$	2.010	0.194	−0.022	−0.173	0.117

All-electron SCF results: Atoms -

Table 3: OF-DFT self-consistent x-*only* total energies of atoms obtained from various kinetic energy functionals (in Hartrees).

	1/9 vW+TF	1/5 vW+TF	vW+TF	GGA	mcGGA	KS
H	-0.6664	-0.5666	-0.2618	-0.719	-0.321	-0.4065
He	-3.2228	-2.8184	-1.4775	-3.39	-1.53	-2.7236
Li	-8.2515	-7.3227	-4.1054	-8.58	-4.10	-7.1749
Be	-16.1631	-14.4841	-8.4922	-16.69	-8.36	-14.2233
B	-27.2876	-24.6284	-14.9259	-28.05	-14.59	-24.5275
C	-41.9053	-38.0332	-23.6569	-42.94	-22.98	-37.6863
N	-60.2623	-54.9429	-34.9084	-59.53	-34.07	-54.3977
O	-82.5799	-75.5765	-48.8832	-84.26	-47.53	-74.8076
F	-109.0594	-100.13xx	-65.7676	-111.11	-63.76	-99.4072
Ne	-139.8867	-128.8015	-85.7344	-142.34	-82.95	-127.4907

All-electron SCF results: SiO -

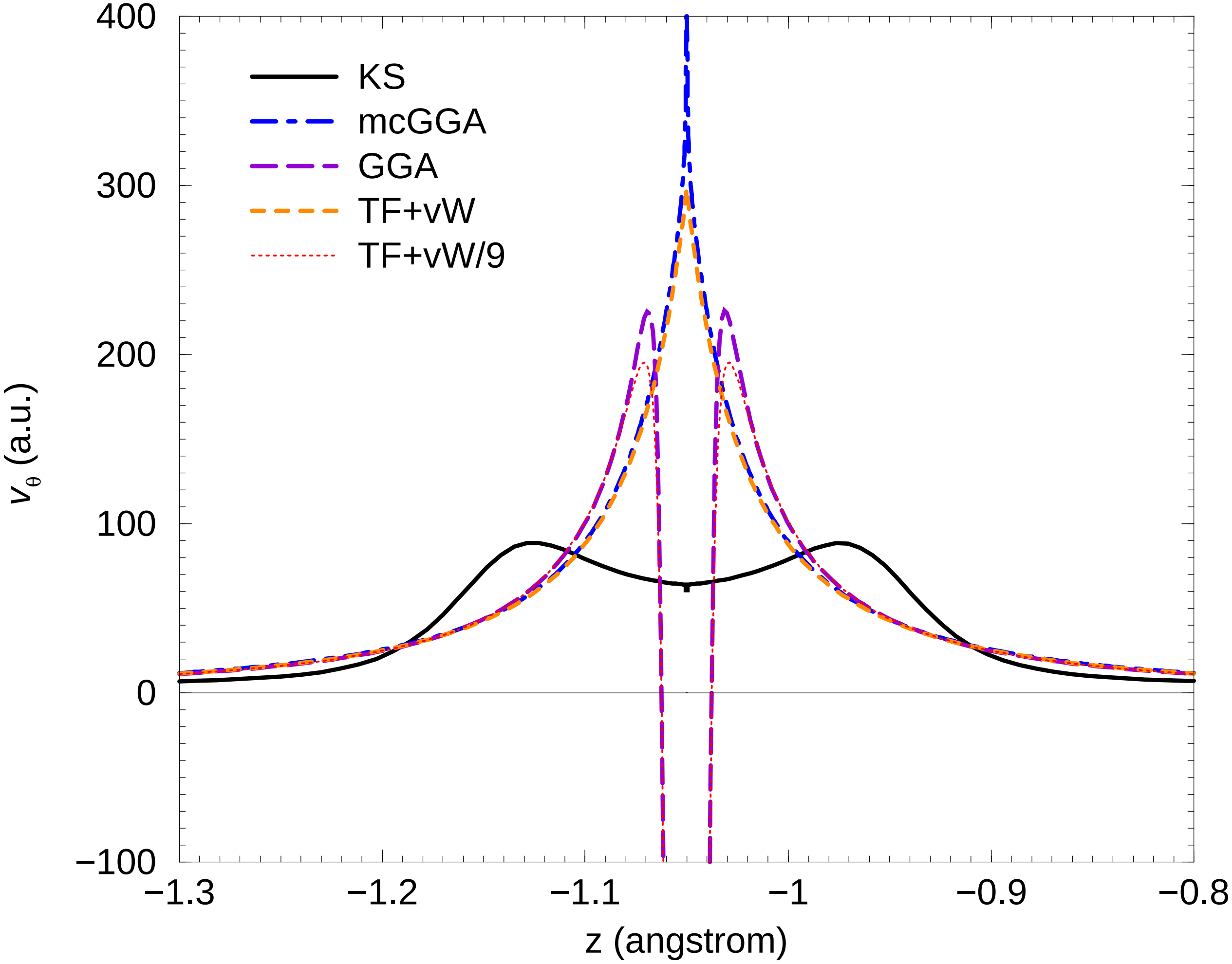


Figure 1: Pauli potential v_θ obtained from self-consistent all-electron Kohn-Sham and OFDFT calculations for SiO with mcGGA (PBE2), GGA(PBETW) and TF kinetic energy functionals.

All-electron SCF results: SiO

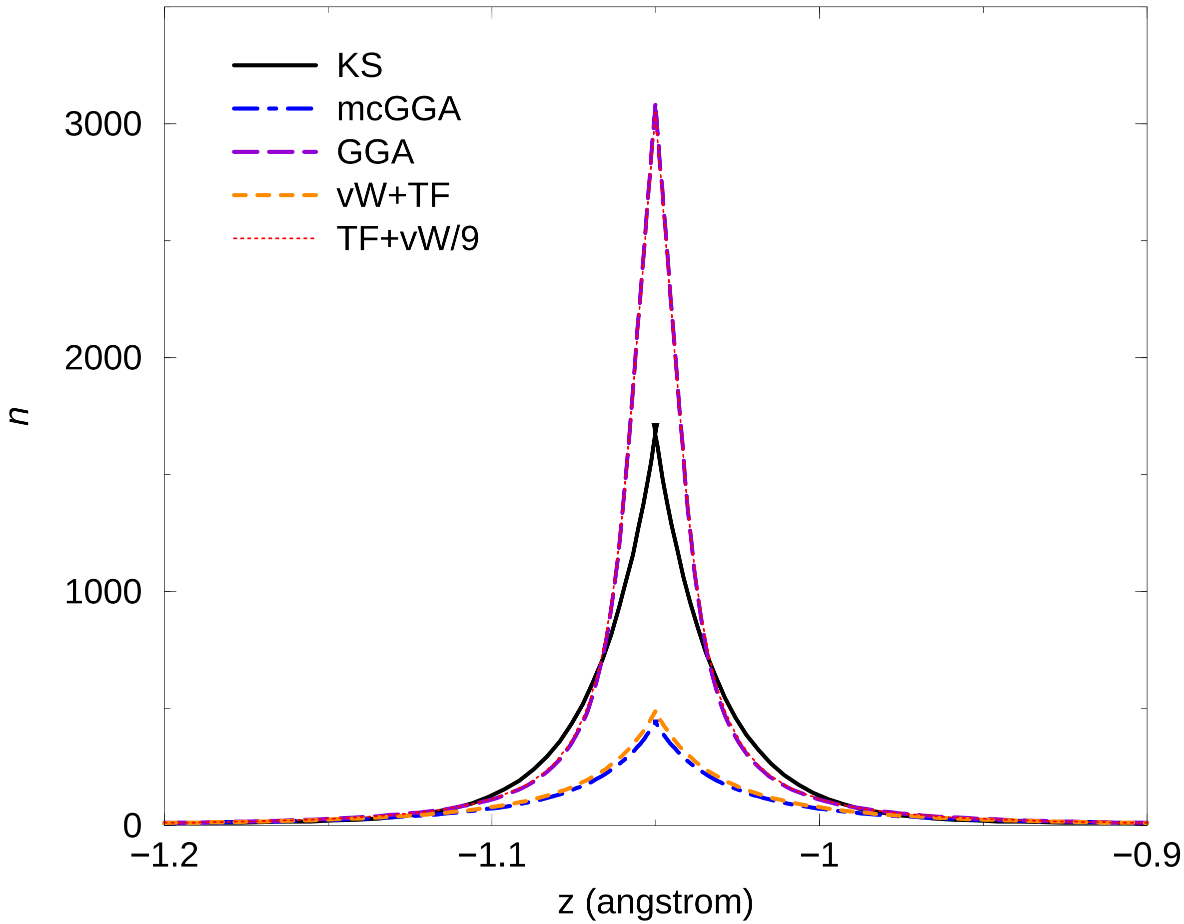


Figure 2: All-electron self-consistent Kohn-Sham and OFDFT electron density profiles calculated for point on the internuclear axis for the SiO molecule; Si at (0,0,-1.05) , O at (0,0,+1.05) .

All-electron SCF results: SiO -

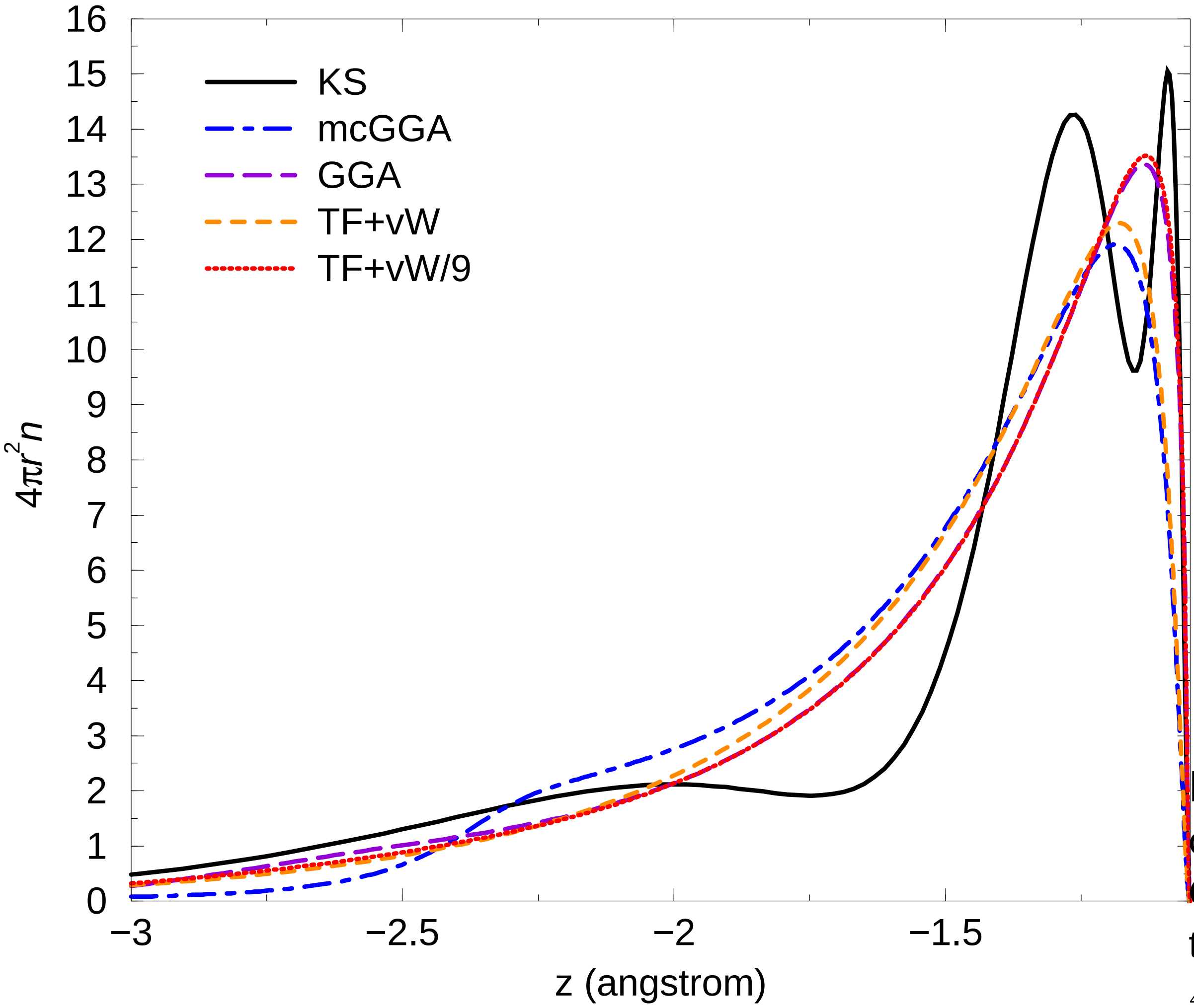


Figure 3: All-electron self-consistent Kohn-Sham and OFDFT electron densities scaled by the factor $4\pi(|z| - R/2)^2$.

All-electron SCF results: SiO -

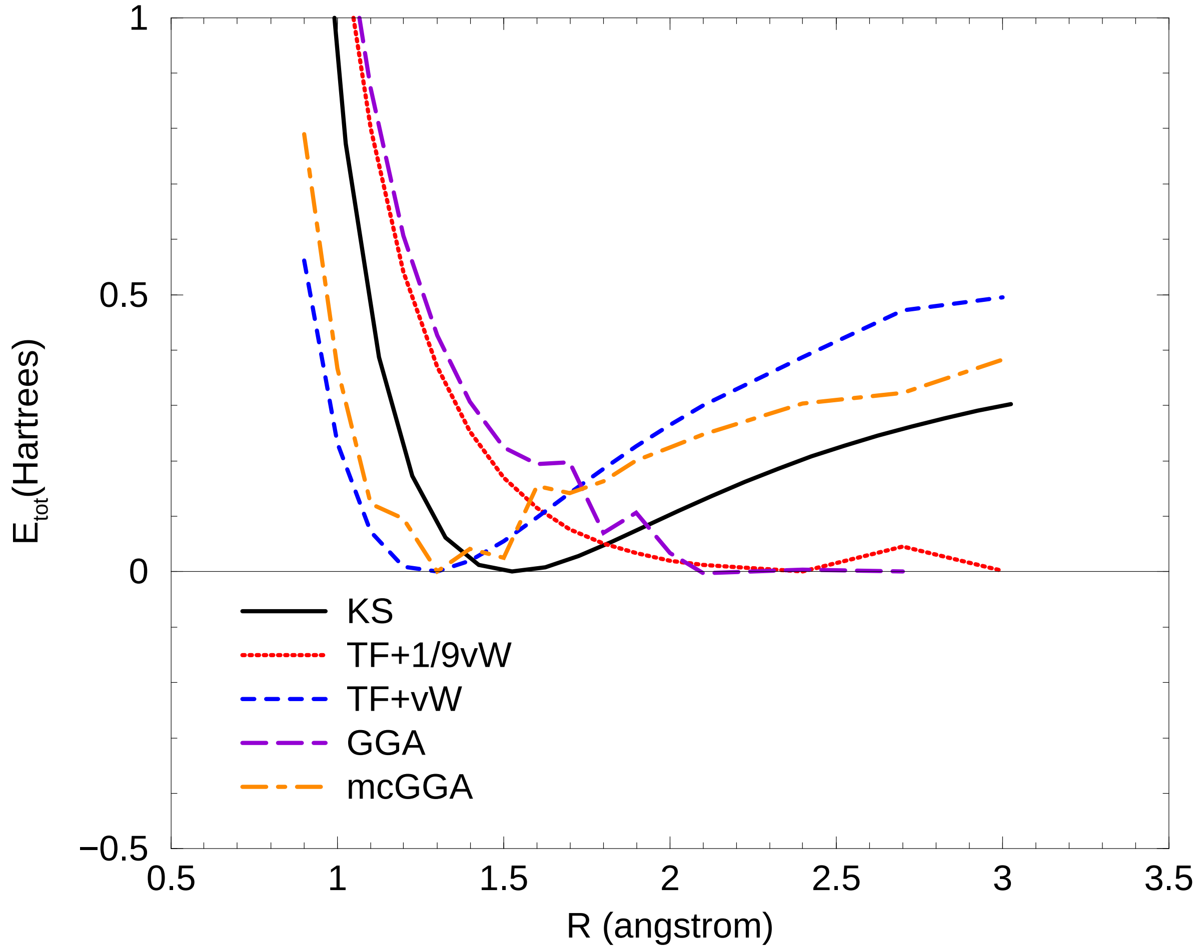


Figure 4: Total energy of the SiO molecule as a function of bond length obtained from self-consistent all-electron Kohn-Sham and OFDFT calculations.

OF-DFT results: GGA and mcGGA F_θ -

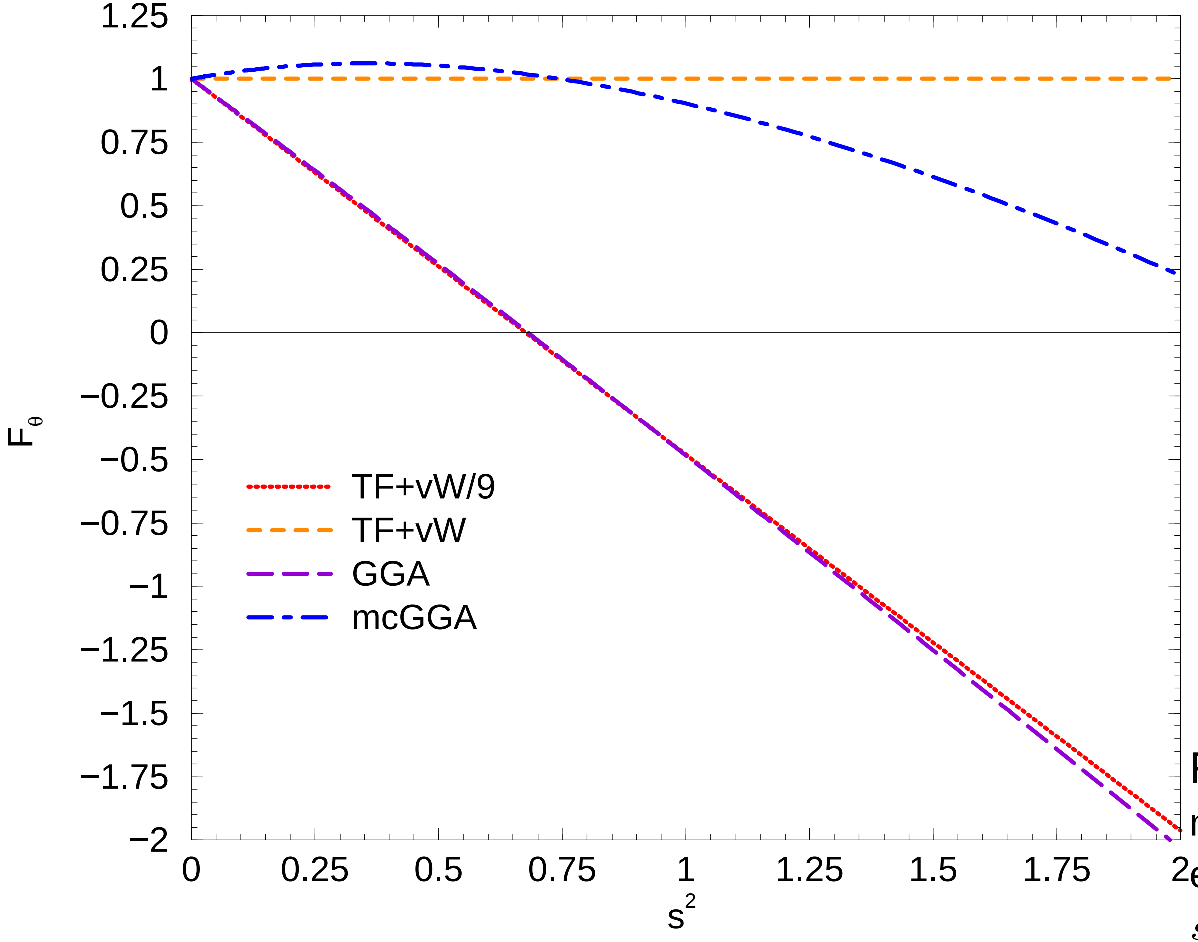


Figure 5: Pauli term enhancement factors F_θ of kinetic energy functionals as a function of s^2.

Local pseudo-potentials for OF-DFT –

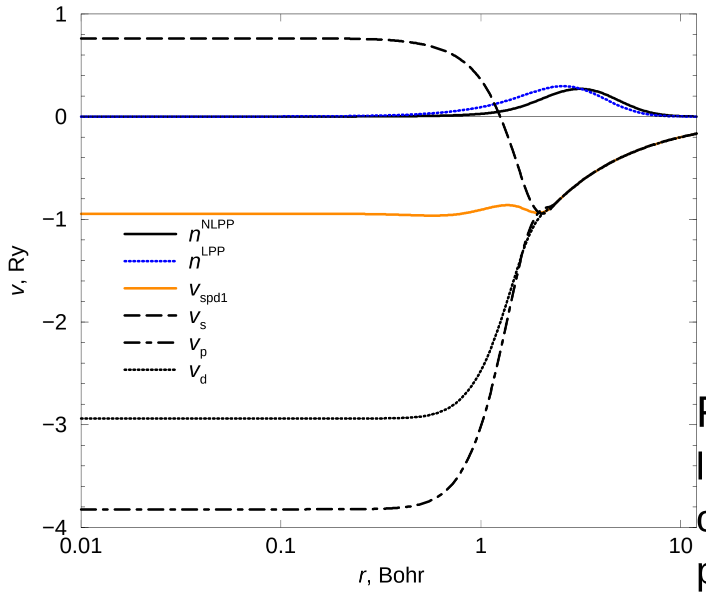


Figure 6: Real space potentials for Li: local v_{spd1}, and different l-components obtained with Troullier-Martins (TM) pseudopotential generation procedure.

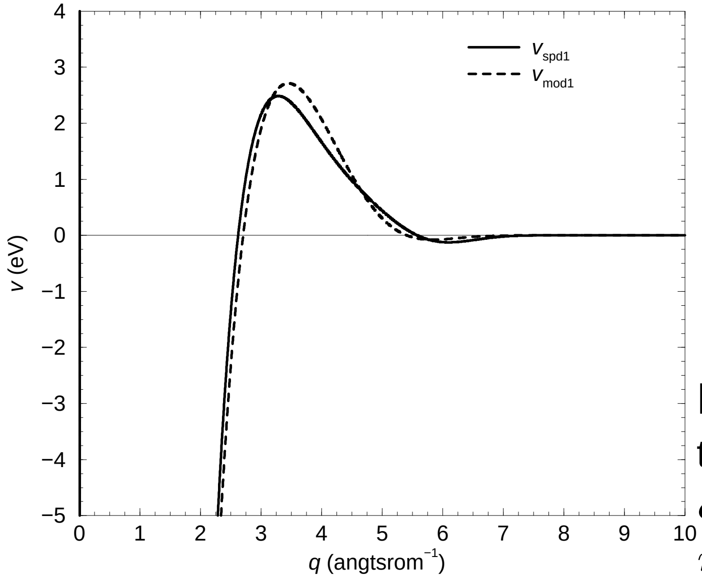


Figure 7: Reciprocal space local potentials for Li: v_{spd1} ($c_0 = 0.69$, $c_1 = 0.24$, $c_2 = 0.1$) and v_{mod1} ($A = 0.45499$, $r_c = 2.2261$, $g_c = 2.86$).

Pseudo-potential OF-DFT results -

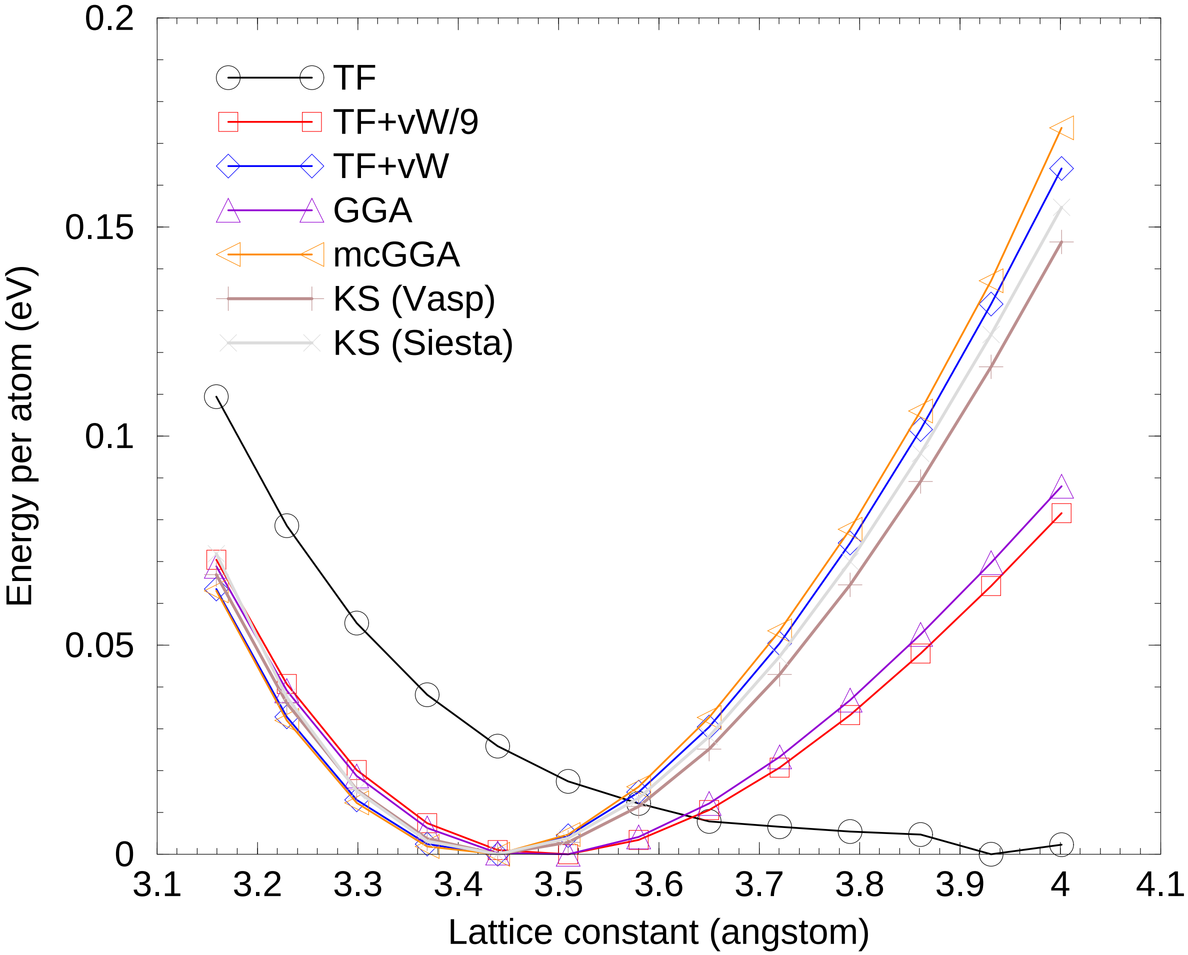


Figure 8: Energy per atom vs. lattice constant for bulk bcc-Li.

Pseudo-potential OF-DFT results -

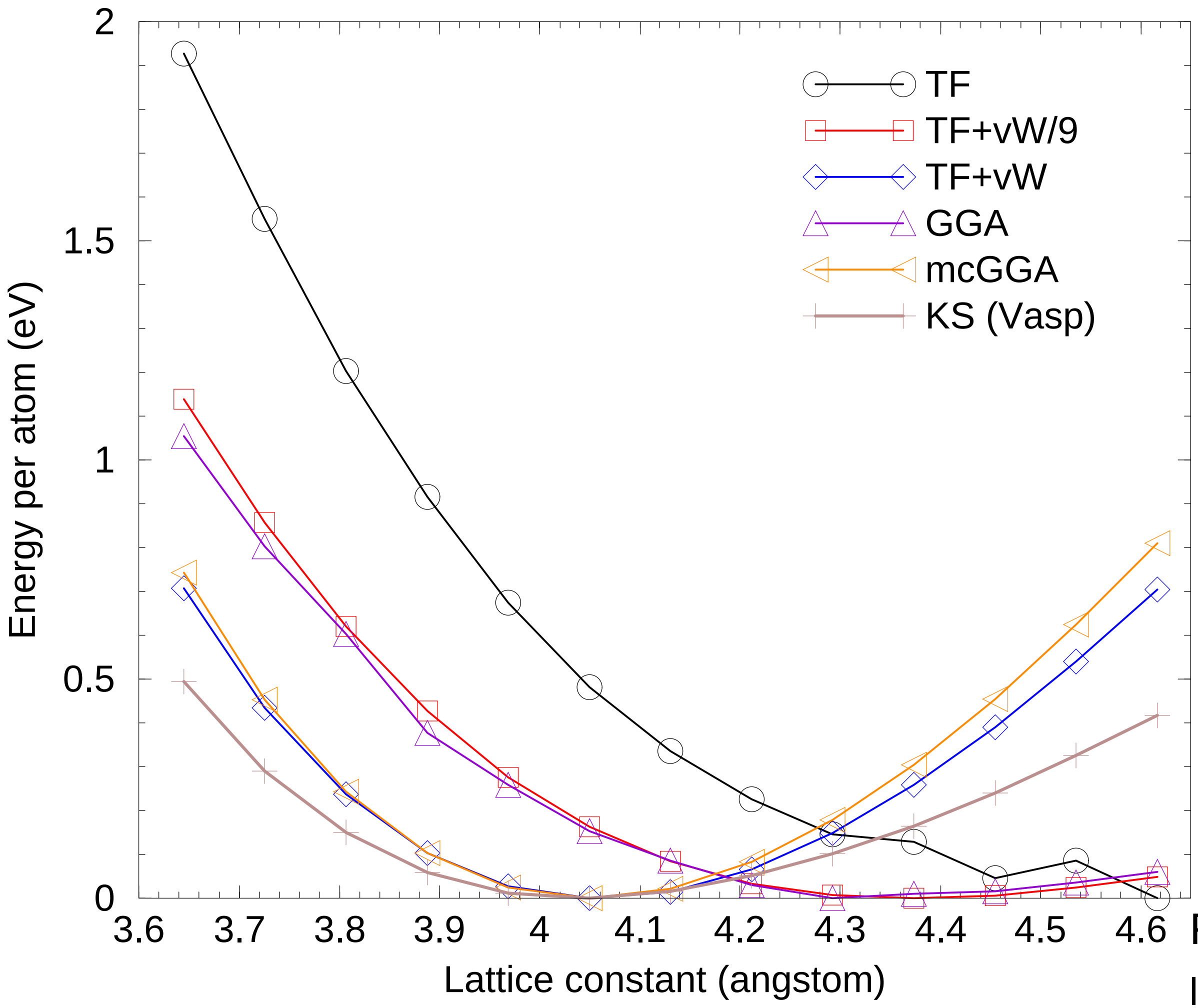


Figure 9: Energy per atom vs. lattice constant for bulk Al.

SUMMARY REMARKS -

- Negative singularity of the GGA Pauli potential is responsible for the poor performance of the GGA KE functionals (no attraction predicted).
- mcGGA Pauli potential is positive. The functional gives better results (attraction region), but it still is singular at nucleus ⇒ kinetic energy is overestimated.
- To eliminate the singularity of the Pauli potential at nucleus requires going beyond the GGA.
- New variable, reduced density derivative (RDD) provides regular behavior of the Pauli potential at nuclear positions.
- RDA is a promising approximation for development functionals capable to predict correctly both, energy and energy gradients (forces).
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