Meta-GGA approximations for electronic structure

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Outline

The basics of electronic structure theories
Density functional theory and approximations for $E_{xc}$
Exact constraints for nonempirical DFAs
Why GGAs cannot describe atoms, molecules and solids simultaneously?
Meta-GGAs:
  TPSS
  revTPSS
  MGGA_MS family
  SCAN meta-GGA
Applications
Introduction to ground-state DFT

• What is DFT and what can it do?
  • An electronic structure theory
  • in principle, DFT delivers the exact energy and electron density of a many-electron ground state
  • In practice, the density functional for the exchange-correlation energy must be approximated,
  • total energy, electron density, and a set of auxiliary orbitals are generated

• Advantages and limitations of DFT
  • Efficient and reasonably accurate for most applications, including for most applications, including
    • Large systems (defects, biomolecules,…)
    • Ab initio molecular dynamics
    • High throughput materials searches
  • Limitation: band-gap, etc.
    • Most orbital energies are unphysical (only auxiliary)
Systems of many electrons and nuclei

- Hamiltonian:

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,l} \frac{Z_i e^2}{|r_i - R_l|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|} \]

- Born-Oppenheimer Approx.:

\[ \hat{H} = \sum_i -\frac{1}{2} \nabla_i^2 + \sum_{i,l} \frac{Z_i}{|r_i - R_l|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}} \]

\[ \hat{H} \Psi_k (r_1, r_2, ..., r_N) = E_k \Psi_k (r_1, r_2, ..., r_N) \]

- Hartree-Fock Approx.: \( \Psi_0 = \Phi_0 \)
Basic theorems of DFT

• Hohenberg-Kohn theorem:
  • $n(r)$ as a basic variable
  • Variational principle

$$E_v[n(r)] = \int dV_{\text{ext}}(r)n(r) + F[n(r)] \geq E_g$$

• Kohn-Sham ansatz: Many-electron to one-electron problem

$$F[n(r)] = T_s[n(r)] + U[n(r)] + E_{xc}[n(r)]$$

$E_g$ and $n(r)$ Exact in Principle
Exc approximated in practice
Self-consistent calculation for KS-DFT

- Initial guess $n(r)$ or $\Phi(r)$
- Calculate effective potential
  $$v_s(r) = v(r) + \frac{\delta U[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)}$$
- Solve the K-S equation
  $$\left(-\frac{1}{2} \nabla^2 + v_s(r)\phi_\alpha(r, \sigma)\right) = \varepsilon_\alpha \phi_\alpha(r, \sigma)$$
- Calculate electron density
  $$n(r) = \sum_\alpha \theta(\mu - \varepsilon_\alpha) \phi_\alpha^*(r) \phi_\alpha(r)$$
- Generate new $n(r)$

Flowchart:

1. Initial guess $n(r)$ or $\Phi(r)$
2. Calculate effective potential
3. Solve the K-S equation
4. Calculate electron density
5. Self-consistent?
   - Yes: Calculation converged
   - No: Generate new $n(r)$
Approaches for approximating $E_{xc}$

• Non-emprirical
  - Based on the understanding of $E_{xc}$
  - Knowledge of $E_{xc}$ in different limits (exact constraints)
  - Generated outside applications, but for applications

• Empirical
  - Using training sets
    - Experimental data/ high-level theoretical data
  - Minimal satisfaction of exact constraints
  - From applications and for applications
Categories of $E_{xc}$: Jacob’s Ladder of DFT

KS-DFT: $E[n] = T_s[n] + U[n] + E_{xc}[n] + \int d^3rv_{ext}(r)n(r); \quad \left(-\frac{1}{2}V^2 + v_s\right)\psi_{i,\sigma} = \epsilon_{i,\sigma}\psi_{i,\sigma}$

$v_s = v_{ext} + \frac{\delta U[n]}{\delta n} + \frac{\delta E_{xc}[n]}{\delta n}; \quad n = \sum_{i,\sigma}^{\text{occup}} |\psi_{i,\sigma}|^2; \quad \tau = \sum_{i,\sigma}^{\text{occup}} \frac{1}{2} |\nabla\psi_{i,\sigma}|^2$

$E[n]$ and $n$: exact in principle if $E_{xc}$ exact

$E_{xc}[n_{\uparrow}, n_{\downarrow}] = \int d^3rn\epsilon_{xc}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow})$

- LSDA: $n_{\uparrow}$ and $n_{\downarrow}$
- GGA: adding $\nabla n_{\uparrow}$ and $\nabla n_{\downarrow}$
- MGGA: adding $\tau_{\uparrow}$ and $\tau_{\downarrow}$

- Reasonably accurate
- Computationally efficient
- Bases for nonlocal corrections
- mGGA: potentially most accurate semilocal functional
Introduction of mGGA

Efficient semilocal approximations of $E_{xc}$:

$$E_{xc}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r n \varepsilon_{xc}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow})$$

- LSDA: $n_\sigma = \sum_i^{\text{occ}} |\psi_{i,\sigma}|^2$
- GGA: adding $\nabla n_{\uparrow}$ and $\nabla n_{\downarrow}$
- mGGA: adding $\tau_\sigma = \sum_i^{\text{occ}} \frac{1}{2} |\nabla \psi_{i,\sigma}|^2$
- $\psi_{i,\sigma}$: Kohn–Sham orbitals

Advantages of mGGAS over GGAS: revTPSS metaGGA can simultaneously improve the CO adsorption and surface energies of Pt(111), but GGAs cannot

The role of $\tau$ (spin supressed)

- Limiting forms:
  - Single orbitals systems:
    $$\tau^w = \frac{1}{8} |\nabla n|^2 / n$$
  - Uniform electron gas (UEG):
    $$\tau^{\text{unif}} = \frac{3}{10} (3\pi^2)^{2/3} n^{5/3}$$

Right dimensionless ingredient for mGGA: $\alpha = \frac{\tau - \tau^w}{\tau^{\text{unif}}} (DDSOS)$

<table>
<thead>
<tr>
<th>REGION</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SINGLE ORBITAL (COVALENT)</td>
<td>0</td>
</tr>
<tr>
<td>SLOWLY-VARYING DENSITY (METALLIC)</td>
<td>$\sim 1$</td>
</tr>
<tr>
<td>OVERLAP OF CLOSED SHELLS (NONCOVALENT)</td>
<td>$&gt;&gt; 1$</td>
</tr>
</tbody>
</table>

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J. Sun et al, PRB, 83, 121410 (2011)  
J. Sun et al, PRL, 111, 106401 (2013)
The exact exchange-correlation energy and hole

\[ E_{xc}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r n \varepsilon_{xc}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}) \]

\[ E_{xc} = \frac{1}{2} \int d^3 r \int d^3 r' \ n(\mathbf{r}) \frac{n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \]

The exact exchange-correlation energy is the electrostatic interaction between the electron density at a point and the density of the exchange-correlation hole surrounding an electron at that point.

\[ n_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda n_{xc}^\lambda(\mathbf{r}, \mathbf{r}') : \]

\( \lambda \): coupling constant

The hole is created by three effects:

- self-interaction correction
- Pauli exclusion principle
- Coulomb repulsion


Langreth and Perdew, 1976
Exact constraints

1. $\varepsilon_{xc}(n_\uparrow, n_\downarrow)$ is taken to be the exchange-correlation energy per particle of an electron gas with uniform spin densities

2. scales properly under uniform scaling of the density

3. its exchange term also scales properly under spin scaling

4. its exchange-correlation energies respect the Lieb-Oxford lower bound for all possible densities

5. Its exchange-correlation energy is almost correct for the linear response of a spin-unpolarized uniform electron gas

$E_{xc}$ expansion in powers of the density gradients - GGAs

- The relevance of these expansions to atoms, molecules and solids has recently been established: Perdew, et al. PRL. 97, 223002 (2006).
- For slowly varying densities the $E_{xc}$ and the $n_{xc}$ have expansions in powers of the density gradients.

$$E_{x}^{GE}[n] = \int d^3 r n \varepsilon_x^{unif}(n) \left[ 1 + \mu_{GE} s^2 + ... \right]$$

- LDA is the zero-order term.
- The PW91 GGA starts from the gradient expansions of the $xc$ holes to second order in $\nabla n$, then introduces sharp radial and angular cutoffs of the spurious long-range (large $|r-r'|$) parts to satisfy the sum rules.
Interpretation of the gradient dependence for atoms, molecules and solids

In an atom or small molecule the density is cut off by the small size, leading to a cutoff of the xc hole.

In a solid, the xc hole is more diffuse, so a diminished gradient GGA could be more accurate.

Compared to LSDA, PBE gives improvements for atomization energies of molecules, but PBE is unimproved for lattice constants and worse for surface energies because it violates the second-order gradient expansion of the x energy for slowly varying densities.

The PBEsol is designed for solids, delivers accurate results for lattice constants and surface energies, but is less improved for thermochemistry.

There are three $s=0$ (relevant for solids) constraints:

- Gradient expansion for correlation
- Gradient expansion for exchange
- Linear response for the uniform density

These constraints cannot be satisfied simultaneously at the GGA level.
TPSS (2003)—the first nonempirical meta-GGA

\[ E_{x}^{\text{TPSS}}[n] = \int d^3 r n \varepsilon_{x}^{\text{unif}}(n) F_{x}^{\text{TPSS}}(p, z) \]

\[ F_{x}^{\text{TPSS}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{x}{\kappa}} \]

The TPSS chose to retain the form of the PBE enhancement factor, but with \( x = \mu s^2 \) replaced by a Taylor expansion in powers of

\[ s = |\nabla n|/[2(3\pi^2 n)^{1/3} n], \quad p = s^2 \quad \tilde{q}_b = (9/20)(\alpha - 1)/[1 + b\alpha(\alpha - 1)]^{1/2} + 2p/3 \]

\[ x = \left[ \frac{10}{81} + c \frac{z^2}{(1+z^2)^2} \right] p + \frac{146}{2025} \tilde{q}_b^2 - \frac{73}{405} \frac{1}{2} \left( \frac{3}{5} \frac{z}{z} \right)^2 + \frac{1}{2} p^2 + \frac{1}{\kappa} \left( \frac{10}{81} \right) p^2 + 2\sqrt{e} \frac{10}{81} \left( \frac{3}{5} \frac{z}{z} \right)^2 + e\mu p^3 \]

Inhomogeneity parameter \( \tilde{q}_b \) can be constructed form \( p \) and \( z \):

\[ Z = \tau_w / \tau \quad \tau = \sum_{i,\sigma} \frac{\text{ occupp }}{2} |\nabla \psi_{i,\sigma}|^2 \quad \tau_w^{\sigma}(r) = \frac{|\nabla n_{\sigma}|^2}{8n_{\sigma}} \quad \alpha = (\tau - \tau_w)/\tau^{\text{unif}} = (5p/3)(z^{-1} - 1) \geq 0 \]

This expression for \( \tilde{q} \) becomes the reduced Laplacian (as defined above) in the slowly-varying limit, and \(-9/20 + 2p/3\) in the iso-orbital (\( \alpha = 0 \)).

The relevance of \( z \):

**Distinguishes the two paradigms of condensed matter and quantum chemistry:** slowly-varying and iso-orbital limits. The value of \( z \): \( 0 \leq z \leq 1 \).

- for one- and two-electron densities: \( z = 1 \).
- for slowly-varying densities: \( z = \frac{5p}{3} + O(\nabla^4) \to 0 \).

**The large gradient limit**

\[
\lim_{s \to \infty} x \rightarrow \mu s^2, \quad F_x^{\text{TPSS}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}
\]

**Conditions relevant for solids and surfaces**

The TPSS \( F_x \) recovers the good linear response of the LSD for uniform gas.

\[
F_x = 1 + \frac{10}{81} p + \frac{146}{2025} q^2 - \frac{73}{405} qp + Dp^2 + O(\nabla^6)
\]
The TPSS is good enough to describe atoms and molecules, gives good atomization energies at equilibrium and good surface energies.

The main deficiency of the TPSS is that its lattice constants are not accurate. Many solid state properties are very sensitive to the lattice constants.

The earlier PBEsol work suggests that better lattice constants can be found if the exchange functional recovers the second-order gradient expansion over a wide range of densities and not only for the very slowly-varying region where the TPSS is right.
Revised TPSS (2009)


\[
F_x^{TPSS}(s) = 1 + \kappa - \frac{\kappa}{x} = 1 + \frac{10}{81} p + \frac{146}{2025} q^2 - \frac{73}{405} qp
\]

\[
F_x^{PBESol}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}
\]

\[
\mu = \frac{10}{81}
\]

\[
x = \frac{[10/81 + c \frac{z^2}{(1+z^2)^2}] p + \frac{146}{2025} \tilde{q}_b^2 - \frac{73}{405} \tilde{q}_b}{\sqrt{\frac{1}{2} \left( \frac{3}{5} z \right)^2 + \frac{1}{2} p^2 + \frac{1}{\kappa} \left( \frac{10}{81} \right)^2 p^2 + 2 \sqrt{e} \frac{10}{81} \left( \frac{3}{5} z \right)^2 + \epsilon \mu p^3}}
\]

\[
x = \frac{[10/81 + c \frac{z^3}{(1+z^2)^2}] p + \ldots}{\left(1 + \sqrt{e} p \right)^2}
\]

- The term \(c z^2/(1+z^2)^2\) in TPSS has a \(\nabla^6\) contribution.
- The term \(c z^3/(1+z^2)^2\) in the revTPSS contributes in order \(\nabla^8\).

This way a big error of \(\nabla^6\) in the gradient expansion has been shifted to \(\nabla^8\).
The exchange enhancement factor of the revTPSS for $\alpha=1$ (slowly-varying densities) and $\alpha=0$ (one or two-electron densities)
Correlation

\[ E_c^{TPSS} [n_\uparrow, n_\downarrow] = \int n e_c^{revPKZB} \left[ 1 + d e_c^{revPKZB} \left( \frac{\tau}{\tau} \right)^3 \right] d^3 r, \]

\[ \tilde{\varepsilon} = e_c^{GGA} (n_{\sigma}, 0, \nabla n_{\sigma}, 0) \]

\[ e_c^{revPKZB} = e_c^{GGA} (n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \left[ 1 + C(\zeta, \xi) \left( \frac{\tau}{\tau} \right)^2 \right] - \left[ 1 + C(\zeta, \xi) \left( \frac{\tau}{\tau} \right)^2 \right] \sum_{\sigma} n_{\sigma} \tilde{\varepsilon}_c \]

The equation for the correlation were designed to satisfy the conditions:

\[ E_c \leq 0 \]

and

\[ \tau = \tau_w \]

for one or two-electron densities.

The parameter \( C(\zeta = 0) \) is coming from a fitting on the surface correlation energy of PBE. The parameters \( C(\zeta, \xi) \) are coming from a fitting in order to keep the low-density limit of meta-GGA correlation.

Since we change the exchange and correlation in revTPSS, we have to refit these parameters.

\[ C(\zeta, 0) = 0.59 + 0.9269\zeta + 0.6225\zeta^4 + 2.1540\zeta^6 \]
The changes made in revTPSS compared to TPSS and their effects on atomization energies

1. **Exchange, slowly-varying gradient:** \( cz^2p > cz^3p \). This change will raise the energy of a molecule (with more small s regions than an atom) more than it will raise the energy of the atom (with fewer small-s regions). This effect causes a **lowering in the atomization energies**.

2. **Exchange, large gradient limit:** adjust the parameter \( \mu \) of TPSS 2003, which controls the approach to the large-gradient limit, from the PBE value 0.21951 to 0.14 (close to the PBEsol value 0.12346).

3. **Correlation.**
From the change in power of \( z \) and the change of \( \mu \) and the correlation at the same time we get a compensation of the underbinding at the small gradient limit and from the overbinding at large gradient limit.
Meta-GGA made simple (MGGA_MS) (2012)

MGGA_MS is based on the DDSOS, which characterizes the extent of the overlap of orbitals.

\( S = \text{reduced density gradient.} \)

use \( \alpha \) to interpolate between GGA’s for \( \alpha = 1 \) and \( \alpha = 0 \)
and to extrapolate monotonically to \( \alpha \gg 1 \).

\[
F_x(s, \alpha) = F_x(s, 1) + f(\alpha)[F_x(s, 0) - F_x(s, 1)]
\]

\[
F_x(s, 1) = 1 + \kappa - \kappa / [1 + \mu^{GE} s^2 / \kappa]
\]

\[
F_x(s, 0) = 1 + \kappa - \kappa / [1 + (\mu^{GE} s^2 + c) / \kappa]
\]

\[
f(\alpha) = (1 - \alpha^2)^3 / (1 + \alpha^3 + b \alpha^6)
\]

\[
f(0) = 1 \quad f(1) = 0 \quad f(\infty) = -1 / b
\]

MGGA_MS disentangles \( s \) and \( \alpha \)

\[
\alpha = (\tau - \tau^W) / \tau^{\text{unif}}
\]

dimensionless deviation from the single orbital shape (DDSOS)

\( c \) and \( \kappa \) are fixed by the exchange energy of the hydrogen atom and the 12 electron hydrogenic anion \( 1s^22s^23p^63s^2 \)

\( \kappa = 0.29 \) corresponds to a tighter LO bond than TPSS and revTSS

The main difference between the MGGA_MS family of density functionals and other tested functionals lies in the exchange enhancement factor $F_x(s,\alpha)$, where the weaker $s$-dependence in MGGA_MS is countered by a stronger $\alpha$ dependence. $F_x$ is monotonically decreasing with $\alpha$ in MGGA_MS (but not in revTPSS).

This is the key to a good description of weak bonds. Our recent works has revealed the significance of $\alpha$ for identifying different bonds in molecules and solids.
First step: An artificial order-of limits problem arises in the TPSS and revTPSS meta-GGA’s due to use of BOTH $z$ and $\alpha$

$$z = \tau^W / \tau = 5s^2 /[5s^2 + \alpha]$$

$$\lim_{\alpha \to 0} \lim_{s \to 0} z = 0$$

$$\lim_{s \to 0} \lim_{\alpha \to 0} z = 1$$

For the fix-up of the order-of limits anomaly, see $\text{regTPSS}$:


Our newer meta-GGAs use only alpha, and so avoid this problem.
### Phase transition properties of D-Si and β-tin

<table>
<thead>
<tr>
<th>Properties</th>
<th>TPSS</th>
<th>revTPSS</th>
<th>regTPSS</th>
<th>MGGA_ MS0</th>
<th>MGGA_ MS2</th>
<th>HSE06</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_0$</td>
<td>0.265</td>
<td>0.160</td>
<td>0.285</td>
<td>0.517</td>
<td>0.429</td>
<td>0.398</td>
<td>—</td>
</tr>
<tr>
<td>(eV/atom)</td>
<td>0.266</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.390</td>
<td>0.447</td>
</tr>
<tr>
<td>$\Delta V_0$</td>
<td>5.24</td>
<td>5.25</td>
<td>4.98</td>
<td>5.04</td>
<td>4.98</td>
<td>5.35</td>
<td>—</td>
</tr>
<tr>
<td>(Å³/atom)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_t$ (GPa)</td>
<td>7.3</td>
<td>3.7</td>
<td>8.0</td>
<td>17.3</td>
<td>13.9</td>
<td>13.3</td>
<td>10~14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.4</td>
<td>11~15</td>
</tr>
</tbody>
</table>
Second step: Arguments of the meta-GGA exchange enhancement factor

\[ F_x(s, \gamma) \]

\[ E_x^{MGGA} [n] = \int d^3 r n e_{x}^{\text{unif}} (n) F_x (s, \gamma) \]

\[ s = |\nabla n| / [2(3\pi^2)^{1/3} n^{4/3}] \]

= reduced or dimensionless density gradient

\[ \gamma = z, \; t^{-1} \; \text{or} \; \alpha \]

= reduced variable for the KE density

where

\[ \tau = \sum_{\alpha}^{\text{occup}} \frac{1}{2} |\nabla \psi_{\alpha \sigma}(\vec{r})|^2 \]

\[ z = \tau^W / \tau \]
\[ t^{-1} = \tau / \tau^{\text{unif}} \]
\[ \alpha = (\tau - \tau^W) / \tau^{\text{unif}} \]

where

\[ \tau^W = |\nabla n|^2 / [8n] \]
\[ \tau^{\text{unif}} = \frac{3}{10} (3\pi^2)^{2/3} n^{5/3} \]

Which is the best?
\[
\begin{align*}
\tau &= \tau^W \\
\alpha &= (\tau - \tau^W)/\tau^\text{unif} \\
t^{-1} &= \tau/\tau^\text{unif}
\end{align*}
\]

1) Regions of one- and two-electron density:
\[z = \tau/\tau^W \quad \alpha = (\tau - \tau^W)/\tau^\text{unif} \quad t^{-1} = \tau/\tau^\text{unif}
\]
\[
\begin{array}{c|c|c|c}
\tau = \tau^W & z = 1 & t^{-1} = 5s^2/3 & \alpha = 0 \\
\end{array}
\]
(single bonds)

2) Regions of uniform density:
\[\tau^W = 0 \quad z = 0 \quad t^{-1} = 1 \quad \alpha = 1
\]
(metallic bonds)

3) Regions of density overlap between closed shells:
\[\tau^W \approx 0 \quad z \approx 0 \quad t^{-1} \to \infty \quad \alpha \to \infty
\]
(weak bonds)
\[
\frac{\tau}{\tau^\text{unif}} \sim n/n^{5/3} \quad \text{as} \quad n \to 0 \quad t^{-1} \to \infty
\]

\(z\) cannot distinguish between regions 2) and 3).
\(t^{-1}\) cannot clearly distinguish between regions 1) and 2).

Only \(\alpha\) can recognize these three regions and treat them differently.

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Plots along the bond axis between two argon atoms separated by 7 Angstroms
Strongly Constrained and Appropriately Normed (SCAN) meta-generalized gradient approximation for exchange and correlation

arXiv:1504.03028
Exchange

\[ E_x^{\text{SCAN}} [n] = \int d^3r n \varepsilon_x^{\text{unif}}(n) F_x^{\text{SCAN}}(s, \alpha) \]

\[ \varepsilon_x^{\text{unif}}(n) = -(3/4\pi)(3\pi^2 n)^{1/3} \]

\[ F_x^{\text{SCAN}}(s, \alpha) = \{ h_x^1(s, \alpha) + f_x(\alpha)[h_x^0 - h_x^1(s, \alpha)]\} g_x(s) \]

**Exact constraints**

1. Tight lower bound for exchange \( F_x^{\text{SCAN}} \leq 1.174 \rightarrow h_x^0 = 1.174 \)

2. 4th-order gradient expansion of slowly varying density limit (\( s \rightarrow 0 \) and \( \alpha \rightarrow 1 \)):

\[ F_x^{\text{GE4}}(s, \alpha) = 1 + \frac{10}{81} s^2 - \frac{1606}{18225} s^4 + \frac{511}{13500} s^2 (1 - \alpha) + \frac{5913}{405000} (1 - \alpha)^2 \]

Resummation of 4th order gradient expansion (RGE):

\[ h_x^1(s, \alpha) = 1 + k_1 - \frac{k_1}{1 + \mu_{AK} s^2 (1 + b_4 s^2 / \mu_{AK}) \exp(-|b_4| s^2 / \mu_{AK})} \left\{ b_1 s^2 + b_2 (1 - \alpha) \exp[-b_3 (1 - \alpha)^2] \right\}^2 \]

\[ \mu_{AK} = 10/81, \ b_1 = 0.156632, \ b_2 = 0.12083, \ b_3 = 0.5, \ b_4 = \frac{\mu_{AK}^2}{k_1} - 0.112654 \]

3. Non-uniform scaling limit: \( \lim_{s \to \infty} F_x^{\text{SCAN}}(s, \alpha) \propto s^{-1/2} \rightarrow g_x(s) = 1 - \exp[-a_1 s^{-1/2}] \)

Interpolation and extrapolation:

\[ f_x(\alpha) = \exp \left[ -\frac{c_{1x}}{1-\alpha} \right] \theta(1-\alpha) - d_x \exp \left[ \frac{c_{2x}}{1-\alpha} \right] \theta(\alpha - 1) \]

\[ \theta(x): \text{step function} \]

Parameters fitted to norms: \( k_1, c_{1x}, c_{2x}, d_x \)

No correction to RGE in any power of \( \nabla n \) at the slowly varying limit
Correlation

\[ E_c^{SCAN}[n] = \int d^3 r n \epsilon_c^{SCAN} \]
\[ \epsilon_c^{SCAN} = \epsilon^1_c + f_c(\alpha)(\epsilon^0_c - \epsilon^1_c) \]

Exact constraints

1. One electron self-correlation free
2. Lower bound of \( E_{xc} \) of 2 electron densities: \( E_{xc}[n] \geq 1.67 E_x^{LDA} \) → nonempirical \( \epsilon^0_c \)
3. 2\textsuperscript{nd}-order gradient expansion of slowly varying density limit → A simplified PBE correlation for \( \epsilon^1_c \)
4. Non – positivity → \( \epsilon^0_c \geq \epsilon^1_c \)

Interpolation and extrapolation:

\[ f_c(\alpha) = \exp \left[ -\frac{c_1 \alpha}{1 - \alpha} \right] \theta (1 - \alpha) - d_c \exp \left[ \frac{c_2 \alpha}{1 - \alpha} \right] \theta (\alpha - 1) \]

Parameters determined by norms: \( c_{1c}, c_{2c}, d_c \)
Appropriate norms: Guiding SCAN from $\alpha = 0$ to $\alpha = 1$, then to $\alpha \to \infty$

- Appropriate norms: systems with localized xc holes
  - Uniform electron gas and H
  - Rare gas atoms
    - Three coefficients of large $-Z$ limit of the exchange and correlation energies of neutral atoms
      \[
      \lim_{Z \to \infty} E_x(Z) = E_x^{LDA} + \gamma x_1 Z + \gamma x_2 Z^{2/3},
      \]
      \[
      \lim_{Z \to \infty} E_c(Z) = E_c^{LDA} + \gamma c_1 Z
      \]
  - $Ar_2$ at compressed bond lengths (1.6, 1.8, and 2.0 Å)
  - Jellium surface

<table>
<thead>
<tr>
<th>$k_1$</th>
<th>$c_{1x}$</th>
<th>$c_{2x}$</th>
<th>$d_x$</th>
<th>$c_{1c}$</th>
<th>$c_{2c}$</th>
<th>$d_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.068</td>
<td>0.688</td>
<td>0.870</td>
<td>1.300</td>
<td>0.627</td>
<td>1.300</td>
<td>0.700</td>
</tr>
</tbody>
</table>

Relative errors (%) in Ex, Ec, and Exc of rare gas atoms

<table>
<thead>
<tr>
<th></th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX</td>
<td>-0.46</td>
<td>-0.26</td>
<td>-0.20</td>
<td>-0.07</td>
</tr>
<tr>
<td>EC</td>
<td>11.85</td>
<td>4.50</td>
<td>5.09</td>
<td>3.38</td>
</tr>
<tr>
<td>EXC</td>
<td>-0.07</td>
<td>-0.15</td>
<td>-0.09</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Relative errors in Ex of $Ar_2$ at different bond lengths where the repulsive energies are about 100~300 kcal/mol

<table>
<thead>
<tr>
<th>R</th>
<th>1.6</th>
<th>1.8</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>REL ERROR (%)</td>
<td>-0.28</td>
<td>-0.26</td>
<td>-0.26</td>
</tr>
</tbody>
</table>

Relative errors of jellium surface exchange-correlation of different densities Note that only $rs=4$ is used for the determination of the parameters

<table>
<thead>
<tr>
<th>rs</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>REL ERROR (%)</td>
<td>-0.2</td>
<td>-0.0</td>
<td>-0.0</td>
<td>4.1</td>
</tr>
</tbody>
</table>
## Results for molecules and solids

<table>
<thead>
<tr>
<th>Method</th>
<th>G3 (kcal/mol)</th>
<th>BH76 (kcal/mol)</th>
<th>S22 (kcal/mol)</th>
<th>LC20 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ME</td>
<td>MAE</td>
<td>ME</td>
<td>MAE</td>
</tr>
<tr>
<td>GGA</td>
<td>ME</td>
<td>MAE</td>
<td>ME</td>
<td>MAE</td>
</tr>
<tr>
<td>BLYP</td>
<td>3.8</td>
<td>9.7</td>
<td>-7.9</td>
<td>7.9</td>
</tr>
<tr>
<td>PBEsol</td>
<td>-58.7</td>
<td>58.8</td>
<td>-11.5</td>
<td>11.5</td>
</tr>
<tr>
<td>PBE</td>
<td>-21.6</td>
<td>22.2</td>
<td>-9.1</td>
<td>9.2</td>
</tr>
<tr>
<td>MGGA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCAN</td>
<td>-4.6</td>
<td>5.7</td>
<td>-7.5</td>
<td>7.7</td>
</tr>
<tr>
<td>TPSS</td>
<td>-6.0</td>
<td>6.5</td>
<td>-8.6</td>
<td>8.7</td>
</tr>
<tr>
<td>M06L</td>
<td>-3.4</td>
<td>5.8</td>
<td>-3.9</td>
<td>4.1</td>
</tr>
</tbody>
</table>

**G3**: formation energies of 223 molecules (at the order of 100~1000 kcal/mol)

**BH76**: 76 reaction barriers (at the order of 0~50 kcal/mol)

**S22**: 22 molecular complexes bound by weak bond (at the order of 0~20 kcal/mol)

**LC20**: lattice constants of 20 solids including metals, semiconductors, and insulators

**ME**: mean error; **MAE**: mean absolute error
Relative error (%) in lattice constants of tetragonal BaTiO$_3$ and PbTiO$_3$

<table>
<thead>
<tr>
<th></th>
<th>Expt.</th>
<th>PBE</th>
<th>PBEsol</th>
<th>TPSS</th>
<th>SCAN</th>
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</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td></td>
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<tr>
<td>a</td>
<td>3.986</td>
<td>0.5</td>
<td>-0.4</td>
<td>0.6</td>
<td>0.0</td>
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<tr>
<td>c</td>
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<td>0.7</td>
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<td>1.3</td>
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<tr>
<td>c/a</td>
<td>1.010</td>
<td>4.1</td>
<td>1.1</td>
<td>-0.5</td>
<td>1.3</td>
</tr>
<tr>
<td>volume</td>
<td>63.97</td>
<td>5.6</td>
<td>-0.1</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>3.878</td>
<td>-0.9</td>
<td>-0.4</td>
<td>1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>c</td>
<td>4.174</td>
<td>10.5</td>
<td>1.5</td>
<td>-3.6</td>
<td>1.8</td>
</tr>
<tr>
<td>c/a</td>
<td>1.076</td>
<td>11.4</td>
<td>1.9</td>
<td>-5.1</td>
<td>1.8</td>
</tr>
<tr>
<td>volume</td>
<td>62.77</td>
<td>8.6</td>
<td>0.6</td>
<td>-0.6</td>
<td>1.9</td>
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</table>
Phase transition pressure and defect formation energies of Si: The situation before SCAN

Performance of SCAN for solid Si

<table>
<thead>
<tr>
<th></th>
<th>Phase transition</th>
<th>Interstitial defect formation (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta E$(meV)</td>
<td>$p_t$(Gpa)</td>
</tr>
<tr>
<td>PBE</td>
<td>290</td>
<td>8.4</td>
</tr>
<tr>
<td>SCAN</td>
<td>411</td>
<td>14.3</td>
</tr>
<tr>
<td>Ref</td>
<td>480±50</td>
<td>11-15</td>
</tr>
</tbody>
</table>
Energetic ordering of water hexamers (binding energy kcal/mol)

<table>
<thead>
<tr>
<th>method</th>
<th>Prism</th>
<th>Cage</th>
<th>Book</th>
<th>Cyclic</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>332.3</td>
<td>331.9</td>
<td>330.2</td>
<td>324.1</td>
</tr>
<tr>
<td>DMC</td>
<td>331.9</td>
<td>329.5</td>
<td>327.8</td>
<td>320.8</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>347.6</td>
<td>345.5</td>
<td>338.9</td>
<td>332.5</td>
</tr>
<tr>
<td>PBE</td>
<td>336.1</td>
<td>339.4</td>
<td>345.6</td>
<td>344.1</td>
</tr>
<tr>
<td>B3LYP</td>
<td>294.4</td>
<td>297.1</td>
<td>305.1</td>
<td>306.7</td>
</tr>
<tr>
<td>TPSS</td>
<td>303.9</td>
<td>302.8</td>
<td>313.6</td>
<td>316.7</td>
</tr>
<tr>
<td>SCAN</td>
<td>376.8</td>
<td>375.6</td>
<td>370.0</td>
<td>359.7</td>
</tr>
<tr>
<td>PBE+vdW(TS)</td>
<td>369.6</td>
<td>372.6</td>
<td>370.6</td>
<td>360.7</td>
</tr>
</tbody>
</table>

Stabilities of crystal structures

Gerd Ceder found the wrong (alpha) ground-state crystal structure for MnO2, using PBE, PBE+U, and the HSE hybrid.

Haowei Peng tried SCAN, and found the right (beta) ground-state crystal structure for this material, in agreement with experiment.
Summary of SCAN

• A meta-GGA, strongly constrained and appropriately normed
• Computationally efficient and nonempirical
• Systematic improvement over PBE and previous meta-GGAs for a wide range of properties
Thank you