Nonempirical Density Functionals that work and Useful Extensions

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- **General idea**
- **MGGA for Exchange**
- **MGGA for Correlation**
- **Useful Extensions**

General idea

- DFT is the most popular method for electronic structure calculations of a many-electron system.

- No other method achieves comparable accuracy at the same cost.

The art of constructing $E_{\mathrm{xc}}[n_\uparrow, n_\downarrow]$ embodies two different philosophies: Empiricism and nonempiricism.

- Empiricism: No hope of writing down the exact universal functional, the best strategy is to make a guess in a parametric form and optimize it by fitting to a set of experiments.

- Nonempiricism: E_{xc} should be developed from first principles by incorporating known exact constraints. If a sufficient number of such constraints is satisfied, properties will come out right by themselves.

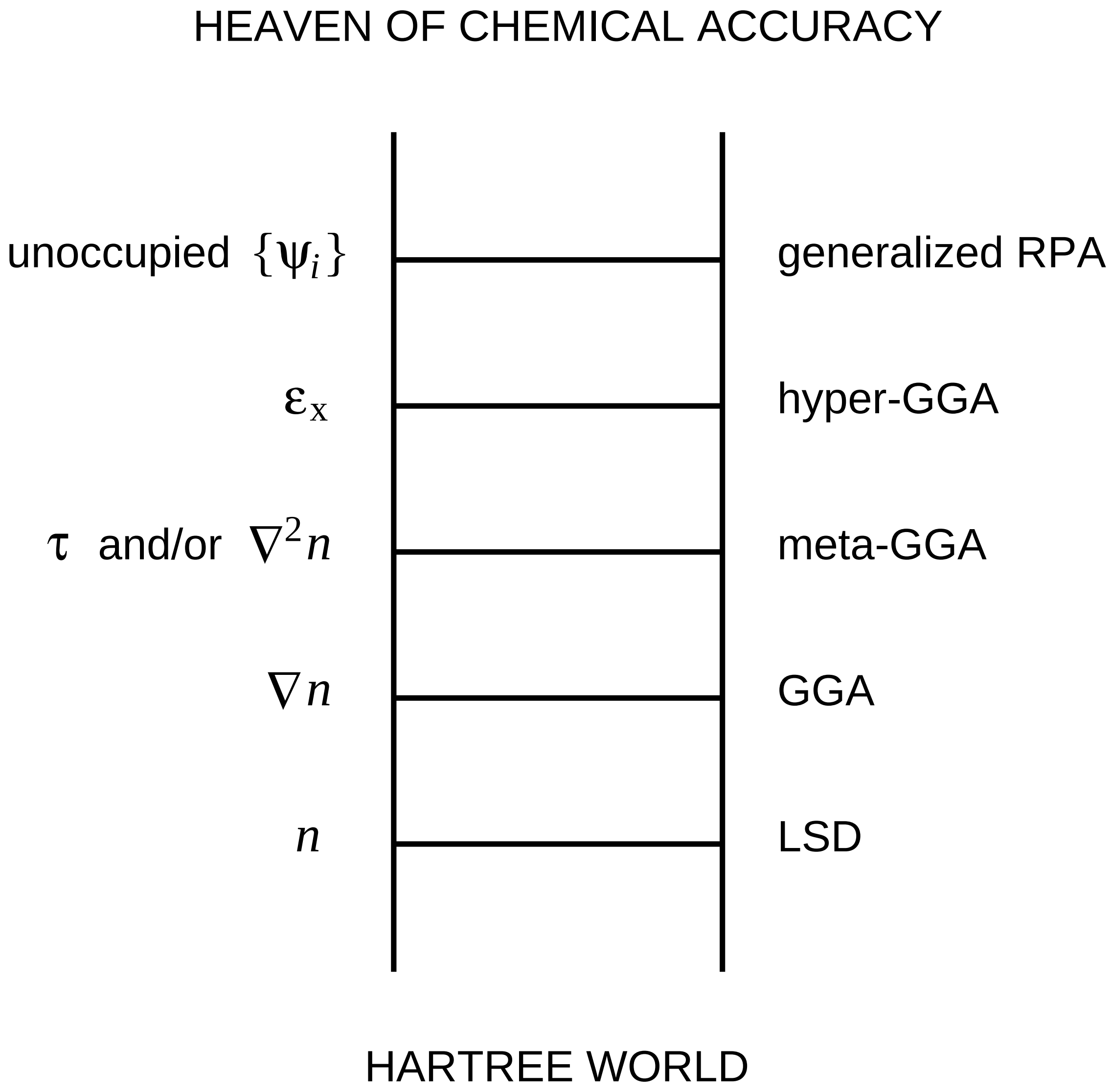

Figure 1: Jacob's ladder of DFT approximations for $E_{\mathrm{xc}}[n_\uparrow, n_\downarrow]$.

PKZB meta-GGA:

- successful in condensed matter physics and thermochemistry such as atomization energies, but PKZB bond lengths are less accurate than those of GGA
- PKZB exchange contains an empirical parameter fitted to atomization energies

Paradigm densities:

- Condensed matter physics: Slowly-varying density (limit A)
- Quantum chemistry: One- and two-electron densities (limit B)

PKZB gives a unbalanced description of the paradigm densities:

- PKZB correlation was designed to be good in these limits.
- PKZB exchange was only designed to be right in limit A.

J. P. Perdew, K. Burke, and M. Ernzerhof, PRL **77**, 3865 (1996);

J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, PRL **82**, 2544 (1999).

Meta-GGA for Exchange

- Spin-scaling relation

$$E_{\mathrm{x}}[n_\uparrow, n_\downarrow] = \frac{1}{2}E_{\mathrm{x}}[2n_\uparrow] + \frac{1}{2}E_{\mathrm{x}}[2n_\downarrow],$$

- Uniform coordinate scaling property

$$E_{\mathrm{x}}[n_\gamma] = \gamma E_{\mathrm{x}}[n], \qquad n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$$

Assumed form for meta-GGA:

$$\boxed{E_{\mathrm{x}}[n] = \int d^3r\ n\epsilon_{\mathrm{x}}^{unif}(n)F_{\mathrm{x}}(p,z)}$$

where $\epsilon_{\mathrm{x}}^{unif}(n) = -\frac{3}{4\pi}(3\pi^2 n)^{1/3}$, $p = s^2 = \left[\frac{|\nabla n|}{2(3\pi^2)^{1/3}n^{4/3}}\right]^2$, $z = \frac{\tau_W}{\tau}$, $\tau = 2\sum_{i=1}^{\mathrm{occup}} \frac{1}{2}|\nabla\psi_i|^2$, and $\tau_W = \frac{1}{8}\frac{|\nabla n|^2}{n}$.

J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, PRL **91**, 146401 (2003).

Assumed form for enhancement factor F_x:

$$\boxed{F_\mathrm{x} = 1 + \kappa - \tfrac{\kappa}{1+x/\kappa}, \quad x(p,z) \geq 0, \quad \kappa = 0.804}$$

The assumed MGGA recovers the following behaviors:

- In the large gradient ($p \to \infty$) limit,

$$F_\mathrm{x} \to F_\mathrm{x}^\mathrm{PBE},$$

  No new condition for the $p \to \infty$ limit and thus no reason to change from the PBE GGA in this limit.

- In the slowly-varying limit,

$$F_\mathrm{x} \to 1 + \frac{10}{81}p + \frac{146}{2025}q^2 - \frac{73}{146}qp + 0 \cdot p^2 + O(\nabla^6).$$

- Recovery of the exchange energy of the hydrogen density $n_\uparrow = \frac{1}{\pi}e^{-2r}$: $E_\mathrm{x}[n_\uparrow, 0] = -U[n] = -0.3125$ hartree (self-interaction free).

- $\left.\frac{\partial F_\mathrm{x}}{\partial s}\right|_{s\approx 0.4,\ z=1} = 0.$

  This condition ensures that the meta-GGA potential (unlike the GGA exchange potential) has no divergence at the nucleus, where $s \approx 0.4$.

Meta-GGA for Correlation

PKZB correlation:

- PKZB correlation is a nonempirical self-interaction-free functional:

  $E_c[n_\sigma, 0] = 0 \qquad (N = 1)$

- PKZB yields much more accurate low-density limit for a spin-unpolarized density than LSD and PBE do

In the low-density limit, because electrons become classical particles and the repulsions among them are Coulombic, $E_{\mathrm{xc}}[n_\uparrow, n_\downarrow]$ should become independent of relative spin polarization $\zeta = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$.

- LDA is correct

- GGA is correct

- PKZB has an incorrect dependence upon relative spin polarization ζ

TPSS correlation:

Starting from the PBE GGA, TPSS correlation is constructed by

- eliminating the PBE GGA self-correlation energy as the PKZB meta-GGA does
- correcting the wrong dependence of the PKZB meta-GGA upon relative spin polarization, while preserving other correct properties of PKZB

$$\boxed{\begin{aligned} E_{\mathrm{c}}^{\mathrm{TPSS}}[n_\uparrow, n_\downarrow] &= \int d^3r\; n\epsilon_{\mathrm{c}}^{\mathrm{revPKZB}} \\ &\quad \times[1 + d\epsilon_{\mathrm{c}}^{\mathrm{revPKZB}}(\tau^W/\tau)^3], \end{aligned}}$$

where $\epsilon_{\mathrm{c}}^{\mathrm{revPKZB}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow, \tau_\uparrow, \tau_\downarrow)$ is the revised PKZB correlation and $d = 2.8\ \mathrm{hartree}^{-1}$.

J.P. Perdew, J. Tao, V.N. Staroverov, and G.E. Scuseria, JCP **120**, 6898 (2004) for detailed explanation.

Numerical Tests

Table I: Statistical summary of the errors of three density functionals for 13 properties of molecules, solids, and surfaces. 1 kcal/mol = 0.0434 eV = 0.00159 hartree. The errors of H-bond dissociation energy are in kcal/mol.

Property (units)	Test set	Mean value of property	Mean absolute errors LSD	PBE	TPSS
Atomiz. energy (kcal/mol)	G3/99 (223 mols.)	714	121.9	22.2	5.8
Ioniz. potential (eV)	G3/99 (86 species)	10.9	0.23	0.24	0.24
Electron affinity (eV)	G3/99 (58 species)	1.41	0.24	0.12	0.14
Proton affinity (eV)	G3/99 (8 mols.)	6.9	5.9	1.6	1.8
Bond length R_e (Å)	96 molecules	1.56	0.013	0.016	0.014
Harm. freq. ω_e (cm^{-1})	82 diatomics	1430	48.9	42.0	30.4
H-bond dissoc. energy	10 complexes	13.4	5.8	1.0	0.6
H-bond length R_e (Å)	11 H-bonds	2.06	0.147	0.043	0.021
H-bond angle (deg)	13 angles	111	4.0	2.6	2.0
Lattice constant (Å)	18 solids	4.46	0.058	0.064	0.050
Bulk modulus (GPa)	18 solids	116	15.1	7.6	8.2
$\epsilon_0^{\mathrm{cohesive}}$ (eV/atom)	8 solids	4.68	0.70	0.11	0.17
σ_{xc} (erg/cm^2)	$r_s = 2$–6	1276	25	59	14
m.a.r.e. (%)	640 data above	...	16.2	5.2	4.8

(1) All calculations were performed self-consistently by the G03 code except the surface exchange-correlation energy of the jellium. (2) V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P. Perdew, JCP **119**, 12129 (2003); PRB **69**, 075102 (2004).

Conclusions: The overall order of accuracy is: $\mathrm{LSD} < \mathrm{PKZB} < \mathrm{PBE} < \mathrm{TPSS}$.

Extension to systems with orbital currents

Density functionals have a common limitation:

- It cannot properly describe systems in the presence of a magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$ which induces an orbital current of electrons. Such currents can be present even for external vector potential $\mathbf{A} = 0$, as in open-shell atoms.

- Example: B (2p^1: 2p$_{-1}$, 2p$_0$, 2p$_1$). Electrons in such an atom can occupy different (degenerate) orbitals with the same total energy.

  Since $E_{\rm xc}[n_\uparrow, n_\downarrow]$ fail to reproduce correct degeneracy, they avoid these currents for $\mathbf{A} = 0$ by using real (not complex) orbitals.

- Solution: Vignale and Rasolt (VR) have extended the Kohn-Sham theorems:

$$\psi_{k\sigma}(\mathbf{r}) = \psi_{k\sigma}([n_\sigma, \mathbf{j}_{p\sigma}]; \mathbf{r}); \quad E_{\rm xc} = E_{\rm xc}[n_\sigma, \mathbf{j}_{p\sigma}].$$

For slowly-varying densities and slowly-varying currents, VR presented an additive correction:

$$\boxed{E_{\rm xc}[n, \mathbf{j}_p] = E_{\rm xc}[n, \mathbf{j}_p = 0] + \Delta E_{\rm xc}^{\rm VR}[n, \boldsymbol{\nu}],}$$

G. Vignale and M. Rasolt, PRL **59**, 2360 (1987); PRB **37**, 10685 (1988); G. Vignale, M. Rasolt, and D.J.W. Geldart, Adv. Quantum Chem. **21**, 235 (1990).

where

$$\Delta E_{\mathrm{xc}}^{\mathrm{VR}}[n,\boldsymbol{\nu}] \quad = \quad \int d^3r \; n\epsilon_{\mathrm{x}}^{\mathrm{unif}} \frac{m}{18\pi n e^2}\left(1-\frac{\chi_{\mathrm{L}}}{\chi_{\mathrm{L}}^{0}}\right)|\boldsymbol{\nu}|^2,$$

$\boldsymbol{\nu}(\mathbf{r}) = \nabla \times [\mathbf{j}_p(\mathbf{r})/n(\mathbf{r})]$ – gauge-invariant vorticity.

$\mathbf{j}_{p\sigma}(\mathbf{r}) = \frac{\hbar}{2mi}\sum_{k=1}^{\mathrm{occup}} [\psi_{k\sigma}^{*}\nabla\psi_{k\sigma} - \psi_{k\sigma}\nabla\psi_{k\sigma}^{*}]$–paramagnetic current density.

Question: How can we construct $\tau([n,0];\mathbf{r})$ for use in $E_{\mathrm{xc}}[n,\mathbf{j}_p = 0]$ from the orbital kinetic energy density $\tau([n,\mathbf{j}_p];\mathbf{r})$?

Under the gauge transformation,

$$\boxed{\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} - \nabla\chi(\mathbf{r}),}$$

the orbitals ψ_k and $\psi_k^{'}$ corresponding to $\mathbf{A}$ and $\mathbf{A}'$ differ only by a phase factor,

$$\boxed{\psi_k \rightarrow \psi_k^{'} = \psi_k \exp\left[(ie/\hbar c)\chi\right]}$$

and thus describe the same physical states.

Consider an interacting uniform electron gas (UEG) in the presence of a weak uniform magnetic field $\mathbf{B}$. By perturbation theory,

$$\boxed{\begin{aligned}\epsilon(n,B) &= \epsilon(n,0) - \tfrac{1}{2n}\chi_{\mathrm{L}}B^2 \ \text{(interacting UEG)},\\ \epsilon^0(n,B) &= \epsilon^0(n,0) - \frac{1}{2n}\chi_{\mathrm{L}}^0B^2 \ \text{(noninteracting)}.\end{aligned}}$$

The Vignale-Rasolt second-order energy shift is

$$\boxed{\epsilon_{\mathrm{xc}}^{\mathrm{VR}} = \epsilon_{\mathrm{xc}}(n,B) - \epsilon_{\mathrm{xc}}(n,0) = -\tfrac{1}{2n}(\chi_{\mathrm{L}} - \chi_{\mathrm{L}}^0)B^2.}$$

For a given vector potential $\mathbf{A}(\mathbf{r})$, the physical current density $\mathbf{j}$ is found by

$$\boxed{\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r}) + (e/mc)n(\mathbf{r})\mathbf{A}(\mathbf{r}).}$$

For the UEG, $\mathbf{j}$ vanishes, so we have

$$\boxed{\mathbf{A}(\mathbf{r}) = -\tfrac{mc}{e}\tfrac{\mathbf{j}_p(\mathbf{r})}{n}, \quad \mathbf{B} = \nabla\times\mathbf{A} = -\tfrac{mc}{e}\boldsymbol{\nu}.}$$

Next we shall construct $\tau([n,\mathbf{j}_p=0];\mathbf{r})$ from the orbitals $\psi_k([n,\mathbf{j}_p];\mathbf{r})$ that yield $\tau([n,\mathbf{j}_p];\mathbf{r})$.

For a noninteracting UEG, all of the energy per electron is noninteracting kinetic energy, so

$$\boxed{\tau^{\mathrm{phys}}(n,B)=\tau^{\mathrm{phys}}(n,0)-\tfrac{1}{2}\chi_{\mathrm{L}}^{0}(n)B^{2},}$$

where $\tau^{\mathrm{phys}}(n,B)=\sum_{k}^{\mathrm{occup}}\frac{1}{2m}\psi_k^*(\frac{\hbar}{i}\nabla+\frac{e}{c}\mathbf{A})^2\psi_k$.

Performing integration by parts on $\tau^{\mathrm{phys}}(n,B)$ yields

$$\tau^{\mathrm{phys}}(n,B)=\tau(n,[\mathbf{A}];\mathbf{r})-m\frac{|\mathbf{j}_p|^2}{2n}.$$

where $\tau(n,[\mathbf{A}];\mathbf{r})=\sum_{k}^{\mathrm{occup}}\frac{\hbar^2}{2m}|\nabla\psi_k|^2$. In the absence of a vector potential, $\tau^{\mathrm{phys}}(n,B=0)=\tau(n,[\mathbf{A}=0])$, so

$$\boxed{\tau(n,[\mathbf{A}=0])=\tau(n,[\mathbf{A}];\mathbf{r})-m\frac{|\mathbf{j}_p|^2}{2n}-\frac{mk_{\mathrm{F}}(n)}{24\pi^2}|\boldsymbol{\nu}|^2.}$$

Generalization to an inhomogeneous but slowly-varying density is

$$\boxed{\tau([n,\mathbf{j}_p=0];\mathbf{r})=\tau([n,\mathbf{j}_p];\mathbf{r})-\frac{m|\mathbf{j}_p|^2}{2n}-\frac{mk_{\mathrm{F}}}{24\pi^2}|\boldsymbol{\nu}|^2.}$$

J. Tao, PRB **71**, 205107 (2005); J. Tao and J.P. Perdew, PRL (to appear).

Numerical Test

$\Delta E_{\mathrm{tot}} = E(M_L = \pm 1) - E(M_L = 0)$ in kcal/mol for open-shell atoms. Since the Vignale-Rasolt correction is essentially a second-order gradient term, LSD has been left uncorrected. (1 kcal/mol = 0.0434 eV.)

	LSD	GGA	C-GGA	MGGA	C-MGGA
B	0.50	2.20	1.19	5.84	2.51
C	-0.13	1.95	1.26	4.77	2.26
O	0.31	4.58	1.82	10.60	3.89
F	-0.88	3.77	2.38	7.91	3.77
Al	0.06	1.13	0.06	2.82	0.69
Si	-0.75	0.44	0.19	2.01	0.82
S	-1.13	1.19	-0.13	3.26	0.38
Cl	-1.13	1.32	0.88	3.26	1.78
mean	-0.39	2.07	0.96	5.06	2.01
m.a.e.	0.61	2.07	0.99	5.06	2.01

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