Implementing meta-GGAs in ONETEP

$$E_{\mathrm{KS}}[\rho] = T_s[\rho] + E_{\mathrm{ext}}[\rho] + E_{\mathrm{Hartree}}[\rho] + E_{\mathrm{xc}}[\rho]$$

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{Hartree}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

$$E_{\mathrm{xc}}^{\mathrm{mGGA}} = \int \mathrm{d}\mathbf{r}\, \epsilon_{\mathrm{xc}}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau(\mathbf{r})]$$

$$T_s[\rho] = \int \mathrm{d}\mathbf{r}\, \tau(\mathbf{r}) \qquad \tau(\mathbf{r}) = \frac{1}{2}\sum_i^{\mathrm{occ}} |\nabla\psi_i(\mathbf{r})|^2$$

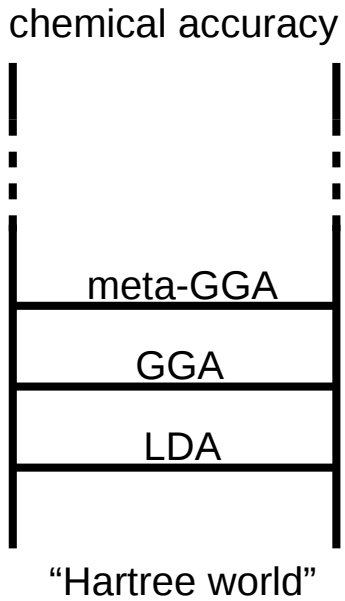

Figure adapted from Perdew, J. P. & Schmidt, K. AIP Conference Proceedings 577, 1 (2001).

Implementing meta-GGAs in ONETEP

meta-GGAs

- $\tau(\mathbf{r})$-dependence based on physical arguments.
- Improved accuracy compared to LDA and GGAs.
- Simple path to self-correlation-free functionals.
  Becke, A. D. J. Chem. Phys. 109, 2092 (1998).

e.g. Minnesota (MXX), TPSS, PKZB etc.

B97M-V functional

- Empirically parameterized local meta-GGA functional.
- Combined with VV10 non-local correlation functional.
- Recently developed, very effective for non-bonded interactions.

MXX: (M11) Peverati, R. & Truhlar, D. G. J. Phys. Chem. Lett. 2, 2810 (2011).

PKZB: Perdew, J. P., Kurth, S., Zupan, A. & Blaha, P. Phys. Rev. Lett. 82, 2544 (1999).

TPSS: Tao, J., Perdew, J. P., Staroverov, V. N. & Scuseria, G. E. Phys. Rev. Lett. 91, 146401 (2003).

VV10: Vydrov, O. A. & Voorhis, T. V. J. Chem. Phys. 133, 244103 (2010).

B97M-V: Mardirossian, N. & Head-Gordon, M. J. Chem. Phys. 142, 074111 (2015).

Implementing meta-GGAs in ONETEP

Functional derivative

Complicated: functional dependence of $\tau[\rho](\mathbf{r})$ on ρ is not known.

$$V_{\mathrm{xc}}^{\mathrm{mGGA}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}^{\mathrm{mGGA}}[\rho]}{\delta \rho(\mathbf{r})} \qquad \frac{\delta \tau(\mathbf{r}')}{\delta \rho(\mathbf{r})} = ?$$

...there are several existing techniques for overcoming this.*

Implementation in ONETEP

The quantities $\tau(\mathbf{r})$, $E_{\mathrm{xc}}^{\mathrm{mGGA}}$ and $V_{\mathrm{xc}}^{\mathrm{mGGA}}$ should be implemented in a way which facilitates linear-scaling with respect to system size, N.

* e.g. Neumann, R., Nobes, R. H. & Handy, N. C. Mol. Phys. 87, 1 (1996); Arbuznikov, A. V. & Kaupp, M. Chem. Phys. Lett. 381, 495 (2003); Zahariev, F., Leang, S. S. & Gordon, M. S. J. Chem. Phys. 138, 244108 (2013).