Post-Hartree-Fock Atomic Kinetic Energies Data Glossary

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(Dated: revised 23 Nov 2020; original 26 April 2018)

I. BACKGROUND

Very accurate Hartree-Fock (HF) wave functions[1] for the first 86 neutral atoms were used to compute post-SCF kinetic energies for a variety of single-point kinetic energy density functionals (KEDFs). Those HF wave functions are significantly improved over the widely used Clementi & Roetti compilation[2]. Orbital occupancies were obtained from the original dataset and degenerate orbitals were fractionally occupied.

Kinetic energies were obtained by numerical integration using a double exponential radial quadrature[3] with $r_{min} = 10^{-6}\ a_0$, $r_{max} = 50\ a_0$ and 200 points for all atoms. The numerical integration was confirmed to reproduce the first 15 digits of the Kohn-Sham non-interacting kinetic energy obtained by analytical integration over the semi-infinite $[0, \infty)$ interval.

II. NOTATION

Hartree atomic units are used in all formulae. The notation of functions and constants is as follows:

- $n = n(\mathbf{r})$, the electron number density.
- $c_{kf} = \left(3\pi^2\right)^{1/3}$.
- $c_{\text{TF}} = \frac{3}{10} c_{kf}^2$, the Thomas-Fermi constant.
- $s = |\nabla n| / \left(2 c_{kf} n^{4/3}\right)$, the reduced density gradient.
- $p = \nabla^2 n / \left(4 c_{kf}^2 n^{5/3}\right)$, the reduced density Laplacian.
- $\tilde{p} = \frac{\nabla n \cdot \nabla\nabla n \nabla\nabla n \cdot \nabla n}{16(3\pi^2)^{4/3} |\nabla n|^2 n^{10/3}}$. the reduced quadratic density Hessian.
- $x = \frac{5}{27} s^2$.
- $b = 2^{4/3} c_{kf}$, a conversion factor.

In the summary below, analytic expressions for the non-interacting KEDFs $T_s[n]$ are given for the spin-unpolarized case ($n_\uparrow = n_\downarrow$). For spin-polarized electron densities, the corresponding expression $T_s[n_\uparrow, n_\downarrow]$ can be obtained directly by applying the spin-scaling relation[4]

$$T_s[n_\uparrow, n_\downarrow] = \frac{1}{2}\Big(T_s[2n_\uparrow] + T_s[2n_\downarrow]\Big) \tag{1}$$

The general form of a one-point KEDF is

$$T_s[n] = \int d\mathbf{r}\ t_{\text{TF}} F_s\big(n, \nabla n, \nabla^2 n, \ldots\big) \tag{2}$$

where t_{TF} is the Thomas-Fermi kinetic energy density per unit volume (defined below), and F_s is the enhancement function.

III. KINETIC ENERGY DENSITY FUNCTIONALS

The header of each entry shows the notation used in the pop-up periodic table.

TF: Thomas-Fermi[5,6]

$$t_{\rm TF} = c_{\rm TF} n^{5/3} \;\; ; \;\; F_s = 1 \tag{3}$$

W: von Weizsäcker[7]

$$F_s^{\rm W}(s) = \tfrac{5}{3} s^2 \tag{4}$$

GEA2: Second-order gradient expansion[8,9]

$$F_s^{\rm GEA2}(s,p) = 1 + \tfrac{5}{27} s^2 + \tfrac{20}{9} p \tag{5}$$

GEA4: Fourth-order gradient expansion[10]

$$F_s^{\rm GEA4}(s,p) = 1 + \tfrac{5}{27} s^2 + \tfrac{20}{9} p + \tfrac{8}{81} p^2 - \tfrac{1}{9} s^2 p + \tfrac{8}{243} s^4 \tag{6}$$

TFW: Thomas-Fermi plus von Weizsäcker

$$F_s^{\rm TFW}(s) = 1 + \tfrac{5}{3} s^2 \tag{7}$$

TF5W: Thomas-Fermi plus $\frac{1}{5}$ von Weizsäcker

$$F_s^{\rm TF5W}(s) = 1 + \tfrac{1}{3} s^2 \tag{8}$$

P82: Pearson[11]

$$F_s^{\rm P82}(s) = 1 + \frac{5}{27} \frac{s^2}{1 + s^6} \tag{9}$$

DK87: DePristo and Kress[12]

$$F_s^{\rm DK86}(x) = \frac{1 + 0.95x + 14.281111x^2 - 19.57962x^3 + 26.64765x^4}{1 - 0.05x + 9.99802x^2 + 2.96805x^3} \tag{10}$$

LLP: Lee, Lee, and Parr[13]

$$F_s^{\rm LLP}(s) = 1 + \frac{0.0044188 b^2 s^2}{1 + 0.0253 bs \, \sinh^{-1}(bs)} \tag{11}$$

OL1 and **OL2**: Ou-Yang and Levy[14]

$$F_s^{\rm OL1}(s) = 1 + \frac{5}{27} s^2 + 0.01354 \frac{c_{kf}}{c_{\rm TF}} s \tag{12}$$

$$F_s^{\text{OL2}}(s) = 1 + \frac{5}{27}s^2 + \frac{0.1774}{c_{\text{TF}}}\ \frac{c_{kf}s}{1+8c_{kf}s} \tag{13}$$

P92: Perdew[15]

$$F_s^{\text{P92}}(s) = \frac{1 + 88.396s^2 + 16.3683s^4}{1 + 88.2108s^2} \tag{14}$$

T92: Thakkar[16]

$$F_s^{\text{T92}}(s) = 1 + \frac{0.0055b^2s^2}{1 + 0.0253\sinh^{-1}(bs)} - \frac{0.072bs}{1 + 2^{5/3}bs} \tag{15}$$

LC94: Lembarki and Chermette[17]

$$F_s^{\text{LC94}}(s) = \frac{1 + 0.093907s\sinh^{-1}(76.32s) + 0.26608s^2 - 0.0809615s^2e^{-100s^2}}{1 + 0.093907s\sinh^{-1}(76.32s) + 0.000057767s^4} \tag{16}$$

LP97: Liu and Parr[18]

$$F_s^{\text{LP97}}(n) = \frac{3.26422}{c_{\text{TF}}} - \frac{0.02631}{c_{\text{TF}}}\left(\int d\mathbf{r}\ n^{4/3}\right)n^{-1/3} + \frac{0.000498}{c_{\text{TF}}}\left(\int d\mathbf{r}\ n^{11/9}\right)^2 n^{-4/9} \tag{17}$$

VJKS00: Vitos, Johansson, Kollár, and Skriver[19]

$$F_s^{\text{VJK00}}(s) = \frac{1 + 0.8944s^2 - 0.0431s^6}{1 + 0.6511s^2 + 0.0431s^4} \tag{18}$$

E00: Ernzerhof[20]

$$F_s^{\text{E00}}(s) = \frac{135 + 28s^2 + 5s^4}{135 + 3s^2} \tag{19}$$

TW02: Tran and Wesolowski[21]

$$F_s^{\text{TW02}}(s) = 1 + 0.8438 - \frac{0.8438}{1 + 0.27482816s^2} \tag{20}$$

PBE2 and **PBE4**: Karasiev, Trickey, and Harris[22]

$$F_s^{\text{PBE2}}(s) = 1 + 2.0309\frac{s^2}{1 + 0.2942s^2} \tag{21}$$

$$F_s^{\text{PBE4}}(s) = 1 - 7.2333\frac{s^2}{1 + 1.7107s^2} + 61.645\Big(\frac{s^2}{1 + 1.7107s^2}\Big)^2 - 93.683\Big(\frac{s^2}{1 + 1.7107s^2}\Big)^3 \tag{22}$$

MGGA: Perdew and Constantin[23]

$$F_s^{\text{MGGA}}(s,p) = F_s^{\text{W}}(s) + z(s,p)f\big(z(s,p)\big) \tag{23}$$

$$z(s,p) = \frac{F_s^{\mathrm{GEA4}}(s,p)}{\sqrt{1+\left(\Delta/(1+F_s^{\mathrm{W}})\right)^2}} - F_s^{\mathrm{W}}(s) \tag{24}$$

$$\Delta = \tfrac{8}{81}p^2 - \tfrac{1}{9}s^2 p + \tfrac{8}{243}s^4 \tag{25}$$

$$f(z) = \begin{cases} 0, & z \leqslant 0.5389 \\ \left[\frac{1+e^{0.5389/(0.5389-z)}}{e^{0.5389/z}+e^{0.5389/(0.5389-z)}}\right]^3, & 0 < z < 0.5389 \\ 1, & z \geqslant 0.5389 \end{cases} \tag{26}$$

GDS08: Ghiringhelli and Delle Site[24]

$$F_s^{\mathrm{GDS08}}(n,s) = \frac{5}{3}s^2 + \frac{0.860}{c_{\mathrm{TF}}n^{2/3}} + \frac{0.224\ln(n)}{c_{\mathrm{TF}}n^{2/3}} \tag{27}$$

RDA: Karasiev, Jones, Trickey, and Harris[25]

$$F_s^{\mathrm{RDA}}(s,p) = \frac{5}{3}s^2 + 0.50616 + 3.04121\Big(\frac{\tilde{\kappa}_{4a}}{1+1.29691\tilde{\kappa}_{4a}}\Big)^2 - 0.34567\Big(\frac{\tilde{\kappa}_{4b}}{1+0.56184\tilde{\kappa}_{4b}}\Big)^4 - 1.89738\frac{\kappa_{2c}}{1+0.21944\kappa_{2c}} \tag{28}$$

$$\tilde{\kappa}_{4a} = \sqrt{s^4 + 46.47662p^2} \tag{29}$$

$$\tilde{\kappa}_{4b} = \sqrt{s^4 + 18.80658p^2} \tag{30}$$

$$\kappa_{2c} = s^2 - 0.90346p \tag{31}$$

APBEK and **revAPBEK**: Constantin, Fabiano, Laricchia, and Della Sala[26]

$$F_s^{\mathrm{APBEK}}(s) = 1 + \frac{0.23889s^2}{1+\frac{0.23889}{0.804}s^2} \tag{32}$$

$$F_s^{\mathrm{REVAPBEK}}(s) = 1 + \frac{0.23889s^2}{1+\frac{0.23889}{1.245}s^2} \tag{33}$$

VT84F: Karasiev, Chakraborty, Shukruto, and Trickey[27]

$$F_s^{\mathrm{VT84F}}(s) = 1 - \frac{\mu s^2 e^{-\alpha s^2}}{1+\mu s^2} + \Big(1-e^{-\alpha s^4}\Big)\Big(s^{-2}-1\Big) + \frac{5}{3}s^2 \tag{34}$$

$$\mu = 2.777028126 \quad ; \quad \alpha = \mu - \tfrac{40}{27} \tag{35}$$

L04 and **L06**: Laricchia, Constantin, Fabiano, and Della Sala[28]

$$F_s^{\mathrm{LK}}(s,p) = 1 + 2\kappa - \Big(\frac{\kappa}{1+x_1/\kappa} + \frac{\kappa}{1+x_2/\kappa}\Big) \tag{36}$$

$$x_1 = x + \Delta + \frac{x^2}{\kappa} \tag{37}$$

$$x_2 = 2\frac{x\Delta}{\kappa} + \frac{x^3}{\kappa^2} \tag{38}$$

$$\Delta = \tfrac{8}{81}p^2 - \tfrac{1}{9}s^2 p + \tfrac{8}{243}s^4 \tag{39}$$

with $\kappa = 0.402$ (L0.4) or $\kappa = 0.6225$ (L0.6)

revMGGA and **revMGGAloc**: Cancio, Stewart, and Kuna[29]; Cancio and Redd[30]
Note (23 Nov. 2020): In Cancio and Redd[30] these are called *mGGArev4* and *mGGAloc4* respectively. There is no explicit equation for *mGGAloc4* there but it can be ascertained by examining their Eq. (37), which gives their "local GEA", including the coefficients listed below. That in combination with their Eqs. (20) and (21) gives the *mGGAloc4* form shown here. It also is described briefly in their section 4.5. (see also Figure 8 and Table 2): "the short-dashed and dot-dashed lines show the mGGAloc with $\alpha = 1$ and $\alpha = 4$, which adhere to the local GEA outside the transition region."

$$F_s^{\text{REVMGGA}}(s,p) = 1 + F_s^{\text{W}}(s) + z_1(s,p) f\big(z_1(s,p)\big) \tag{40}$$

$$F_s^{\text{REVMGGALOC}}(s,p) = 1 + F_s^{\text{W}}(s) + z_2(s,p) f\big(z_2(s,p)\big) \tag{41}$$

$$z_1(s,p) = F_s^{\text{GEA2}}(s,p) - (1 + F_s^{\text{W}}(s)) \tag{42}$$

$$z_2(s,p) = 1 - 0.275s^2 + 2.895p - (1 + F_s^{\text{W}}(s)) \tag{43}$$

$$f(z) = \Big[1 - e^{-1/|z|^4}\big(1 - H(z)\big)\Big]^{1/4} \tag{44}$$

where $H(z)$ is the Heaviside unit step function.

TFLreg: Regularized Thomas-Fermi plus Laplacian[31]

$$F_s^{\text{TFLREG}}(s,p) = \text{Max}\big(1 + \tfrac{20}{9}p\,,\ \tfrac{5}{3}s^2\big) \tag{45}$$

LGAPGE and **LGAP**: Constantin, Fabiano, Śmiga, and Della Sala[32]

$$F_s^{\text{LGAPGE}}(s) = 1 + 0.0131s + 0.18528s^2 + 0.0262s^3 \tag{46}$$

$$F_s^{\text{LGAP}}(s) = 1 + 0.8\Big(1 - e^{-\mu_1 s - \mu_2 s^2 - \mu_3 s^3}\Big) \tag{47}$$

$$\mu_1 = \tfrac{0.0131}{0.8} \tag{48}$$

$$\mu_2 = \tfrac{0.18528}{0.8} + \tfrac{\mu_1^2}{2} \tag{49}$$

$$\mu_3 = \tfrac{0.0262}{0.8} + \mu_1\mu_2 - \tfrac{\mu_1^3}{6} \tag{50}$$

MVT84F: Mejia-Rodriguez and Trickey[33]

$$F_s^{\mathrm{MVT}}[s] = \theta_{\mathrm{MVT}}[n] F_s^{\mathrm{VT84F}}[n] + (1 - \theta_{\mathrm{MVT}}[n])\, F_s^{\mathrm{W}}[n] \tag{51}$$

$$\theta_{\mathrm{MVT}} = \mathrm{Erf}\left[\sqrt{\Theta}\right] \tag{52}$$

with the DORI[34]

$$\Theta := 4\left(1 + \frac{\tilde{p}}{s^4} - 2\frac{p}{s^2}\right) \tag{53}$$

LKT: Luo, Karasiev, and Trickey[35]

$$F_s^{\mathrm{LKT}}[s] = \frac{1}{\cosh(as)} + F_s^{\mathrm{W}}[n] \tag{54}$$

$$a = 1.3 \tag{55}$$

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1 T. Koga, K. Kanayama, S. Watanabe and A.J. Thakkar, *Int. J. Quantum Chem.* **71**, 491-97 (1999).
2 E. Clementi and C. Roetti, *At. Data and Nucl. Data Tab.* **14**, 177-478 (1974).
3 M. Mitani, *Theor. Chem. Acc.* **130**, 645-69 (2011).
4 G.L. Oliver and J.P. Perdew, *Phys. Rev. A* **20**, 397 (1979).
5 L.H. Thomas, *Proc. Cambridge Philos. Soc.* **23**, 542 (1927)
6 E. Fermi, *Z. Phys.* **48**, 72 (1928).
7 C.F. von Weizsäcker, *Z. Phys.* **96**, 431 (1935).
8 A. Kompaneets and E. Pavlovskii, *Sov. Phys. JETP* **4**, 328 (1957).
9 D.A. Kirzhnits, *Sov. Phys. JETP* **5**, 64 (1957).
10 C.H. Hodges, *Can. J. Phys.* **51**, 1428 (1973).
11 E. Pearson, PhD Thesis, Harvard University, USA (1982).
12 A.E. DePristo and J.D. Kress, *Phys. Rev. A* **35**, 438 (1987).
13 H. Lee, C.T. Lee and R.G. Parr, *Phys. Rev. A* **44**, 768 (1991).
14 H. Ou-Yang and M. Levy, *Int. J. Quantum Chem.* **40**, 379 (1991).
15 J.P. Perdew, *Phys. Lett. A* **165**, 79 (1992).
16 A.J. Thakkar, *Phys. Rev. A* **46**, 6920 (1992).
17 A. Lembarki and H. Chermette, *Phys. Rev. A* **50**, 5328 (1994).
18 S. Liu and R.G. Parr, *Phys. Rev. A* **55**, 1792 (1997).
19 L. Vitos, B. Johansson, J. Kollár and H.L. Skriver, *Phys. Rev. A* **61**, 052511 (2000).
20 M. Ernzerhof, *J. Mol. Struct. (THEOCHEM)* **59**, 201 (2000).
21 F. Tran and T.A. Wesolowski, *Int. J. Quantum Chem.* **89**, 441 (2002).
22 V.V. Karasiev, S.B. Trickey and F.E. Harris, *J. Comput.-Aided Mater. Des.* **13**, 111 (2006).
23 J.P. Perdew and L.A. Constantin, *Phys. Rev. B* **75**, 155109 (2007).
24 L.M. Ghiringhelli and L. Delle Site, *Phys. Rev. B* **77**, 073104 (2008).
25 V.V. Karasiev, R.S. Jones, S.B. Trickey and F.E. Harris, *Phys. Rev. B* **80**, 245120 (2009).
26 L.A. Constantin, E. Fabiano, S. Laricchia and F. Della Sala, *Phys. Rev. Let.* **106**, 186406 (2011).
27 V.V. Karasiev, D. Chakraborty, O.A. Shukruto and S.B. Trickey, *Phys. Rev. B* **88**, 161108 (2013).
28 S. Laricchia, L.A. Constantin, E. Fabiano and F. Della Sala *J. Chem. Theory Comput.* **10**, 164 (2014).
29 A.C. Cancio, D. Stewart and A. Kuna, *J. Chem. Phys.* **144**, 084107 (2016).
30 A.C. Cancio and J.J. Redd, *Mol. Phys.* **115**, 618 (2017).
31 S. Śmiga, E. Fabiano, L.A. Constantin and F. Della Sala, *J. Chem. Phys.* **146**, 064105 (2017).
32 L.A. Constantin, E. Fabiano, S. Śmiga and F. Della Sala, *Phys. Rev. B* **95**, 115153 (2017).
33 D. Mejia-Rodriguez and S.B. Trickey, *Phys. Rev. A* **96**, 052512 (2017).
34 P. de Silva and C. Corminboeuf, *J. Chem. Theory Comput.* **10**, 3745 (2014).
35 K. Luo, V.V. Karasiev, and S.B. Trickey, *Phys. Rev. B* **98**, 041111(R) (2018).